ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ANAEROBIC PROCESSING OF AND NUTRIENT RECOVERY FROM SOURCE SEPARATED HUMAN URINE

M.Sc. THESIS

Mustafa TAHER

Department of Environmental Engineering

Environmental Science, Engineering and Management Programme

JUNE 2019

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ANAEROBIC PROCESSING OF AND NUTRIENT RECOVERY FROM SOURCE SEPARATED HUMAN URINE

M.Sc. THESIS

Mustafa TAHER
(501151728)

Department of Environmental Engineering

Environmental Science, Engineering and Management Programme

Thesis Advisor: Prof. Dr. Bilsen BELER BAYKAL

JUNE 2019

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KAYNAKTA AYRILMIŞ İDRARIN ANAEROBİK YOLLARLA İŞLENMESİ VE NUTRİENT GERİ KAZANIMI YOLU İLE DEĞERLENDİRİLMESİ

YÜKSEK LİSANS TEZİ

Mustafa TAHER
(501151728)

Çevre Mühendisliği Anabilim Dalı

Çevre Bilimleri Mühendisliği ve Yönetim Programı

Tez Danışmanı: Prof. Dr. Bilsen BELER BAYKAL

HAZİRAN 2019

Mustafa TAHER, a M.Sc. student of İTU Graduate School of Science Engineering and Technology student ID 501151728, successfully defended the thesis/dissertation entitled "ANAEROBIC PROCESSING OF AND NUTRIENT RECOVERY FROM SOURCE SEPARATED HUMAN URINE", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Bilsen BELER BAYKAL** Istanbul Technical University	.....
Jury Members :	**Assoc. Prof. Dr. Mahmut ALTINBAŞ** Istanbul Technical University	.....
	Prof. Dr. Nilgün BALKAYA Istanbul University - Cerrahpaşa	.....

Date of Submission : 03 May 2019
Date of Defense : 12 June 2019

To my beloved family,

FOREWORD

Through this research I learn a lot form people whom were around me not just helping me to fulfill this research but those who always showed unconditioned and unlimited love, support and understanding.

I would like to take the opportunity to thank my parents, my wife and my sister for everything they did that without them I couldn't be the person that I am today and without them I couldn't make any achievement in my life. The love, support they showed toward me through this period was greater than just describing it by words and there is nothing that I can do to show how I am grateful to have those angels beside me who always guided me through good and bad times and their love was always and forever the shield that I depend on it to protect me and illuminate my path in this life. I can't forget the support that I received from my parents in law and my grandparent was they always believed in me and my ability to finish this research in the best way, and they were always asking me if I produced.

Through this research I met a lot of people whom I learned many things on academic and personal level, first of them is my advisor Prof. Dr. Bilsen Beler Baykal, the person that I learned the most from her. Regardless the knowledge that I received from her through the period of this research which is shaping the bases of my future academic life. I learned from her how to be a professional academician through her attitude. On personal level, I would like to thank her for always being a kind and understanding person and as well for her guidance to complete this research and present it in the best form, her effort was so great that only persons who are blind with their hearts can ignore it.

I can't forget Dr. Mahmut Altınbaş who was always there to guide me through my research specially the anaerobic part of it and always showed the required support to help me finish this research. I am grateful for his generosity as he let me enter his laboratory, becoming a part of his team and giving me the freedom to use all the available resources of chemicals, instruments and facilities for my research.

The list is long for those friends who helped me and supported me, so I want to tell them thank you for being there and showing the real meaning of friendship. I am happy that I met such lovely persons whom I shared with moments that will be engraved in my memory for ever. Thanks to all the professors, technicians of the Department of Environmental Engineering of ITU for their help and assistance though the whole master period. I would like to thank Rota Madencilik for supplying this research with all the required amount of clinoptilolite and their quick response for the research need.

Thanks to Bilimsel Araştırma Projeleri-BAP (Scientific Research Projects unit) of Istanbul Technical University for the financial support of this research with the project ID: 40718.

June 2019 Mustafa TAHER

TABLE OF CONTENTS

Page

ABBREVIATIONS

AA	**:** Anaerobic process
COD	**:** Chemical Oxygen Demand
ECOSAN	**:** Ecological Sanitation
EGSB	**:** Expended Granular Sludge Bed
HRT	**:** Hydraulic Retention Time
IE	**:** Ion Exchnage
NRB	**:** Nitrate Reducing Bacteria
OLR	**:** Organic Loading Rate
SRB	**:** Sulfate Reducing Bacteria
TAN	**:** Total Ammonia Nitrogen
TKN	**:** Total K
TP	**:** Total Phosphorus
TSS	**:** Total Suspended Solid
UASB	**:** Upflow Anaerobic Sludge Bed
UDT	**:** Urine Diverting Toilet
VSS	**:** Volatile Suspended Solid
WHO	**:** World Health Organization

LIST OF TABLES

Page

LIST OF FIGURES

Page

ANAEROBIC PROCESSING OF AND NUTRIENT RECOVERY FROM SOURCE SEPARATED HUMAN URINE

SUMMARY

Due to the increase in world population which is around 7.7 billion in early 2019 and it was estimated to increase to 9.0 billion by 2050, the stress on the available resources of water, food, energy, etc. increases as well. This enormous increase in world population will put the mankind under a critical challenge related to resource security. Part of the Millennium Development Goals as well as Sustainable Development Goals are to reduce the degradation and provide a sustainable environment that the current and next generation can live in with an adequate and healthy resources to insure the prosperity of mankind. To meet the increasing needs for resources, the needs for solutions to overcome resource depletion had been increased too, and alternative resources must be found beside those that exists to maintain permanence and sustainability of these resources. It was assessed that the need for food, water and energy will show an increase of 35, 40 and 50% respectively, owning to that increasing demand of the increased number in world population by 2030 which will be 8.3 billion.

Ecological Sanitation or shortly named ECOSAN is a new management concept for domestic wastewater that based on separation at source of generation. According to ECOSAN approach, domestic wastewater can be divided into three streams as grey water (all wastewater generated in household except that one originating from toilets), yellow water (human urine) and brown water (mainly feces and flush water). Human urine is known as a nutrient rich solution, and highly saline with quite considerable amount of organic matter. Human urine consist of 80% nitrogen, over 50% of phosphorus and potassium. Separation of human urine from the rest of the domestic wastewater will enable closing the nutrient loops in domestic wastewater. Several pieces in the literature studied the possibility of recovering nutrient from source separated human urine using different processes. Struvite precipitation, stripping absorption and ion exchange/adsorption are among the available processes studied in the literature. Ion exchange is one of these processes that showed a remarkable recovery of nitrogen, phosphorus and potassium from source separated urine. The studies about the organic matter fate in source separated human urine after employing ion exchange for removal/recovery of nutrients was not reported yet in the literature.

This work is aiming to investigate the removal of organic matter from the liquid residue of ion exchange process using fixed bed clinoptilolite columns by suggesting the use of anaerobic process. Different configurations based on the combination between ion exchange and anaerobic processes was investigated to achieve the best results of concurrent nutrient and energy recovery. Part of the investigation is the adaptation of anaerobic granular sludge that was brought form confectionery wastewater treatment plant to a highly saline solution like urine. Natural fresh and mainly stored urine were used in this work.

This work investigated the possibilities of ammonium release from anaerobic processes and its effect on the selection of the experiment configurations. Fixed bed clinoptilolite column was used for ion exchange process and Expanded Granular Sludge Bed (EGSB) reactor was used for anaerobic process. Human urine was collected from separation system the separates urine from men's toilet at the Department of Environmental Engineering in Istanbul Technical University.

The results revealed that the adaptation of anaerobic granular sludge was successful under very diluted fresh urine solution in the feeding with COD removal efficiency of 75%. While under higher fresh urine concertation in the feeding the COD removal reduced to reach 40% with 65% fresh urine. The release of ammonium was monitored at the adaptation with fresh urine and it was observed that the percent of release was not appreciable with maximum of 6% release only. The poor performance of anaerobic sludge adaptation using fresh urine as its feeding solution was attributed to the increased level of ammonium and salinity. Urine was stored to increase the amount of ammonium as urea in human urine will hydrolyze during storage. The results from urine storage were in line with previous studies specifically in terms of nutrient concentration, pH and electrical conductivity. During this work a considerable reduction of COD concentration was observed through long storage period of about 4 months that counted for almost 65% of COD reduction from its initial state. This observation was not reported by any of the previous studies used natural stored human urine. COD reduction through storage has an important impact on anaerobic processes as the amount of organic matter in the feed is expected to be lower. On the other hand, the reduced COD concentration will be beneficial for protection of the environment.

After hydrolysis was completed, clinoptilolite was used to concentrate nutrients from the stored urine through ion exchange process. The results from this stage was in line with previous studies used ion exchange to remove and recover nutrients from human urine. 80% removal of ammonium from liquid phase was obtained with 99% and 70% of removal for phosphorus and potassium, respectively. It was observed that COD was removed during ion exchange process with a removal efficiency of 25 – 35%. This observation has an influence on the use of anaerobic processing for removing organic matter from the liquid residue of ion exchange process, in which lesser amount of organic matter will be present in the feeding solution.

Stored urine in which nutrients had been removed then was used as a feeding for the EGSB reactor. COD removal efficiency was ranged between 60 – 85%. Under 50% stored urine in the feeding solution COD removal was observed to be the best with 85%. Regarding the use of 100% stored urine in the feeding the removal efficiency was reduced to 60%. Through these stages the salinity level had a major impact on COD removal efficiency. The quality of the EGSB reactors with stored urine as a feeding solution was evaluated for the sack of environmental protection in case the effluent was discharged without further treatment. The results revealed that the effluent of EGSB was still has a considerable amount of nutrients and COD, thus ion exchange employed with stage wise manner and variable initial loadings. The results of the stage wise operation aid to reduce ammonium, phosphorus and COD considerably that the discharge of the effluent to sewer may be possible. About biogas production up on COD removal from human urine, the results were theoretically appreciable and observable with gas counter. Methane was evolved with a range of 0.3 – 0.8 l CH_4/day that corresponds to 0.19 – 0.5 l CH_4/ l of urine.

The effect of salinity on COD removal using anaerobic process was investigated also in this work. Synthetic solution was used to simulate stored urine that was subjected to single stage ion exchange. Synthetic urine was used to create a controlled condition regarding salinity. The results of this experiment indicated that salinity had a considerable negative impact on anaerobic process at high level like 32000 µS/cm. COD removal efficiencies were ranged between 40 – 90% with salinity level between 32000 – 10000 µS/cm. This work suggest that more effort should focus on adjusting the recommended salinity inhibition threshold in the literature.

This work shows that the combination between ion exchange and anaerobic processes is possible and nutrients recovery with organic matter removal is achievable, but factors like adaptation, dilution, storage period, best operational conditions, inhibition from salinity and ammonium must be taken in consideration. This study recommends the combination of ion exchange and anaerobic process in the manner that nutrients will be removed at the first place with single stage ion exchange followed by anaerobic processes, then stage wise operation of ion exchange to improve the effluent quality form environmental protection.

Recovery experiment were conducted under two different contact times, 5 and 300 min in an attempt to mimic two different irrigation type. The results revealed that most of the nitrogen and phosphorus could be recovered from the clinoptilolite surface. The results were in line with previous studies. COD was not recovered from the clinoptilolite surface. Potassium was recovered with a very limited percentage which is in contrast to previous research that reported no potassium recovery at all. Plant experiments conducted to show the effectiveness of nutrient enriched clinoptilolite as a fertilizer using pepper and tomato. The results showed that clinoptilolite had a considerable performance as a n alternative fertilizer compared to synthetic fertilizer that was tested in the same experiment. Plant height, texture and no of fruits that indicate possible fruits in clinoptilolite pots were higher than that one of synthetic fertilizer.

KAYNAKTA AYRILMIŞ İDRARIN ANAEROBİK YOLLARLA İŞLENMESİ VE NUTRİENT GERİ KAZANIMI YOLU İLE DEĞERLENDİRİLMESİ

ÖZET

2019 yılında 7.7 milyar olan ve 2050 yılında 9 milyara yükselmesi beklenen dünya nüfusunun artmasına bağlı olarak su, gıda ve enerji kaynakları üzerindeki baskı da artmaktadır. Dünya nüfusundaki bu büyük artışın bahse konu kaynakların sürdürebilirliği ve güvenilirliği konusunda da tehditler yaratacağı öngörülmektedir. İnsanoğlunun yeterli ve sağlıklı kaynaklara sahip olma gerekliliği, sürdürülebilir çevre kavramı kapsamında Binyıl Gelişme Hedefleri (Millennium Development Goals) ve Sürdürülebilir Gelişme Hedefleri (Sustainable Development Goals) arasında ile yer almakta ve halihazır kuşaklar yanında gelecek kuşaklara da hizmet etme amacı taşımaktadır. Zaman içinde artan kaynak gereksinimlerinin karşılanabilmesi bağlamında kaynakların kontrollu tüketilmesi ile ilgili çözümler önem kazanmakta ve halen kullanılmakta olanlara ek olarak alternatif çözümler gerekmektedir. Bu çerçevede, 2030 yılında 8.3 milyar olacağı tahmin edilen dünya nüfusunun ihtiyaçlarını karşılamak için su, gıda ve enerji kaynaklarında sırasıyla % 35, 40 ve 50 artış olması gerektiği öngörülmektedir.

Kısaca ECOSAN (Ecological Sanitation) olarak anılan ekolojik evsel atıksu yönetimi kavramı, evsel atıksu arıtımında yeni bir yaklaşımdır ve evsel atıksu akımlarının üretildiği noktada ayrılması esasına dayanmaktadır. Bu çerçevede evsel atıksular kaynağında üç ayrı akım halinde toplanmaktadır. Bu akımlar, tuvalet sularını dışta bırakan ve esasen yıkama sularından oluşan gri su, insan idrarından oluşan sarı ve esasen insan dışkısı ile sifon sularından oluşan kahverengi sudur.

İnsan idrarı nütrientler bakımında zengin, tuzluluğu yüksek ve önemli miktarda organik madde içeren bir sıvıdır ve evsel atıksuda yer alan azotun % 80 i ile fosfor ve potasyumun % 50 nin üzerindeki kısmını içermektedir. İnsan idrarının evsel atıksudan ayrılması ile nütrient döngülerinin kapatılması mümkündür.

Literatürde kaynakta ayrılmış insan idrarından farklı yöntemler kullanarak nütrient geri kazanımı olanaklarına odaklanan çeşitli çalışmalar mevcuttur. Struvit çöktürmesi, sıyırma/absorpsiyon ve iyon değişimi/adsorpsiyon bunların başlıcaları arasında yer almaktadır. Bu yöntemlerden iyon değişimi/adsorpsiyon ile önemli miktarda azot, fosfor ve potasyum geri kazanılabilmektedir. Buna karşın literatürde nütrient geri kazanımı sırasında organik maddenin akıbeti ile ilgili çalışmaya rastlanmamıştır.

Bu çalışmada klinoptilolite sabit yataklı reaktörde iyon değişimi sonunda ortaya çıkan kalıntı sıvı fazdaki organik maddenin anaerobik yollarla gideriminin incelenmesi hedeflenmiştir. Çalışma kapsamında, çeşitli düzenek kombinasyonlarının denenmesi yolu nütrient giderimi ve enerji geri kazanımını en etkin şekilde gerçekleştirecek iyon değişimi ve anaerobik arıtma düzeni irdelenmiştir. Bu çerçevede çalışmada şekerleme endüstrisinden alınan anaerobik granüler çamurun yüksek tuzluluk seviyesindeki sıvı

faza adaptasyonu yapılmıştır. Deneylerde sıvı faz olarak hem taze hem de depolanmış gerçek insan idrarı ile çalışılmıştır. Çalışma kapsamında ayrıca anaerobic reaktörde amonyum açığa çıkışı olup olmadığı ve bu durumun önerilecek kombinasyonlar üzerindeki olası etkileri de irdelenmiştir. Deneylerde iyon değişimi için sabit yataklı kolanlar, anaerobik atıtma için ise genleşmiş garnüler çamur yataklı reaktörler (EGSB - Expanded Granular Sludge Bed) kullanılmıştır. Deneyde kullanılan idrar, Istanbul Teknik Üniversitesi Çevre Mühendisliği Bölümü erkekler tuvaletinden toplanmıştır.

Sonuçlar, anaerobik granüler çamurun adaptasyon sürecinde KOI giderim veriminin düşük seyreltideki taze idrar ile %75 lere kadar çıkabildiğini göstermektedir. İdrar konsantrasyonun % 65 seviyesine çıkarıldığında KOI giderim veriminin % 40 lara düştüğü izlemiştir. Bunun nedeninin ise idrar yüzdesinin artması ile tuzluluk ve amonyum konsantrasyonlarının da artarak inhibisyon değerlerine yaklaşması olarak görülmektedir. Bu süreçte amonyum salımı olup olmadığı takip edilmiş ve en yüksek değer olarak ancak % 6 seviyesine ulaşabildiği belirlenerek bu çerçevede önemli bir amonyum salımı olmadığı sonucuna varılmıştır.

Çalışmada iyon değiştirme yoluyla nütrient giderimi için idrar depolanarak hidrolize tabi tutulmuş ve içerdiği ürenin azotun amonyum formuna dönüşmesi sağlamıştır. Bu süreçte nütrient konsantrasyonları, pH ve elektriksel iletkenlik parametreleri izlenmiş ve bu parametrelerin önceki çalışmalarla uyumlu olduğu gözlenmiştir. Önceki çalışmalara ek olarak bu çalışmada depolama süresince KOI izlemesi yapılmış ve zaman içinde KOI de belirgin bir azalma olduğu tespit edilmiştir. Benzer sistemler için literatürdeki diğer çalışmalarda mevcut olmayan KOI irdelemesi sonucunda bahse konu azalmanın dört ayda % 65 düzeylerinde gerçekleştiği görülmüştür. Bu tespit çalışmanın önerdiği anaerobik arıtmada nispeten yüksek organik madde konsantrasyonlarının tercih edilmesi açısından önem taşımaktadır. Öte yandan çevre kirliliğinin kontrolü açısından bu azalma yararlı olabilecektir.

Hidrolizin tamamlanmasını takiben klinoptilolit kullanılarak iyon değişimi yoluyla depolanmış idrardaki nütrientlerin sıvı fazdan ayrılarak katı fazda konsantre edilmesi sağlanmıştır. Bu aşamada da sonuçlar literatür değerleri ile uyumlu bulunmuş, amonyum % 80, fosfor % 99, potasyum ise % 70 oranında sıvı fazdan ayrılmıştır. Ek olarak klinoptilolitle muamele aşamasında KOI'nin de % 25-35 oranında giderildiği gözlenmiştir. Bu durum depolama aşamasında da belirtildiği üzere, sıvı fazda organik madde miktarının azalması ile anaerobik arıtmanın etkinliği arasındaki ilişkiye dikkat çekmektedir.

Bir sonraki aşamada depolanmış idrardan nutrientlerin alınması sonucunda geriye kalan sıvı faz EGSB reaktöründe anaerobik arıtmaya tabi tutulmuş ve KOI gideriminin % 60 – 85 arasında değiştiği belirlenmiştir. İdrarın %50 oranında yer aldığı numune ile en iyi sonuçlar alınmış, %85 giderime ulaşılmış, seyreltilmemiş % 100 lük idrar ile giderim verimi % 60 a inmiştir. Elde edilen sonuçlar tuzluluğun KOI giderimi üzerinde önemli etkisi olduğuna işaret etmektedir.

Çalışmada çevre kirliliğini önlenmesi ve deşarjlar bağlamında EGSB reaktör çıkış suyu kalitesi de değerlendirilmiştir. Bu çerçevede EGSB çıkışında deşarj için hala önemli miktarda nütrient ve organik madde bulunduğu görülmektedir. Çıkış suyu kalitesinin iyileştirilmesi için EGSB sonrası uygulanan kademeli iyon değiştirme işlemi ile olumlu sonuçlar alınmış, çıkış kalitesinin amonyum, fosfor ve KOI açısından gelişme gösterdiği tespit edilmiştir. Biyogaz üretimi açısından bakıldığında ise KOI giderimine bağlı olarak sonuçlar teorik yönden anlamlı bulunmuş, bu mertebede olmasa da gaz çıkışı gözlenmiştir. Yapılan hesaplar sonunda deney şartlarında 0.3 –

0.8 l CH_4/gün ve eşdeğer olarak 0.19 – 0.5 l CH_4/ l idrar gibi bir üretimin beklenebileceği saptanmıştır.

Çalışma çerçevesinde idrarın anaerobik arıtımı sırsında tuzluluğun KOI giderimine etkisi irdelenmiştir. Bu amaçla ek olarak kontrollu şartları sağlayabilmek için depolanmış idrar özelliklerine sahip sentetik idrar çözeltisi hazırlanmış ve sabit KOI konsantrasyonunda değişken tuzluluk değerlerinda sistem performansı incelenmiştir. Bu aşamada alınan sonuçlar tuzluluğun sistem üzerindeki olumsuz etkileri ortaya konmuş ve tuzluluğun literatürde verilen eşik değerlerin altında olan 32000 µS/cm değerinde verimin % 40 mertebelerine düştüğü görülmüştür. Bu grup deneylerde kullanılan en düşük tuzluluk değeri olan 10000 µS/cm de % 90 KOI verimi elde edilmiştir.

Yapılan çalışma sonuçları iyon değişimi ve anaerobik arıtmanın birlikte kullanımı ile insan idrarından nürtrient geri kazanırken organik madde gideriminin de mümkün olduğunu göstermekte ve bu bağlamda adaptasyon, seyrelme oranı, depolama süresi, tuzluluk ve amonyuma bağlı inhibisyon gibi faktörlerin önemine işaret etmektedir. Çalışma sonuçları ayrıca, incelenen çeşitli kombinasyonların içinde iyon değişimi adsorpsiyon ardından yapılacak anaerobik arıtma ve bu ünitenin çıkışında kademeli iyon değişimi sıralamasının gerek nutrient geri kazanımı gerekse çıkış suyu kalitesi açısından en uygun düzenek olduğunu ortaya koymaktadır.

Geri kazanım yönünden bakıldığında, 5 ve 300 dakika temas süresi ile yapılan deneylerde gerek azotun gerekse fosforun klinoptilolit kullanımı ile idrardan ayrılmış olan azot ve fosforun çok büyük bir bölümünün ve hatta tamamına yakınının yüzeyden geri kazanabildiği ve nütrient yüklü klinoptilolitin yavaş salınan bir gübre olarak kullanılabileceği saptanmıştır. Bu bulgular literatür bulguları ile de uyumludur. Potasyumun sınırlı olarak geri kazanılmasına karşın KOI geri kazanımı incelendiğinde ise yüzeyden önemli bir miktarda KOI salınmadığı izlenmektedir.

Gerçekleştirilen bitki deneyleri nütrient yüklü klünoptilolitin biber ve domates için yararlı bir gübre alternatifi olduğunu göstermiş ve sentetik gübreyle kıyaslandığında gerek bitki uzunluğu gerekse ürün adedi açısından daha iyi sonuçlar vermiştir.

1. INTRODUCTION

Due to the increase in world population which is around 7.7 billion in early 2019 and it was estimated to increase to 9.0 billion by 2050 (United nations, 2006), the stress on the available resources of water, food, energy, etc. increases as well. This enormous increase in world population will put the mankind under a critical challenge related to resource security. Part of the Millennium Development Goals as well as sustainable development golas are to reduce the degradation and provide a sustainable environment that the current and next generation can live in with an adequate and healthy resources to insure the prosperity of mankind. To meet the increasing needs for resources, the needs for solutions to overcome resource depletion had been increased too, and alternative resources must be found beside those that exists to maintain permanence and sustainability of these resources. It is assessed that the need for food, water and energy will show an increase of 35, 40 and 50% respectively, owning to that increasing demand of the increased number in world population by 2030 which will be 8.3 billion (National Intelligence Council, 2013).

One of the suggested solutions to mitigate the resource depletion problem is to recycle, reuse and recover from wastewater streams. Due to the fact that wastewater streams contain valuable materials that possibly can be reused again, recovering those valuable material is becoming more popular and in the academic community the interest in this research field is increasing considerably. Domestic wastewater is generated in households, schools, universities and commercial establishments which originates from human activities either from households activities or metabolic wastes from toilets (urine, feces and flushing water). Domestic wastewater seems to be an important candidate for this task. This wastewater stream is collected and treated as one single stream. In an aim to recover and reuse the valuable materials in domestic wastewater like water and nutrients, domestic wastewater must be segregated into two or three wastewater streams depending on the purpose of the reuse or the valuable material that is required to be recovered.

With the help of new the sanitation concept, Ecological Sanitation or shortly named ECOSAN, domestic wastewater can be divided into three streams as grey water (all wastewater generated in household except that one originating from toilets), yellow water (human urine) and brown water (mainly feces and flush water). Each one of these streams has its own benefit after applying suitable physicochemical or biological processes.

One of those segregated streams is yellow water, which is mainly source separated urine which can be collected with the aid of a special type of toilet like urine diverting toilets (UDT) or urinals.

The main focus of this thesis is the yellow water or source separated human urine. Yellow water is a stream rich in terms of nutrients but highly saline, with considerable organic matter content. The nutrients content of this stream makes it a candidate for natural fertilizer that can be used together with or to replace synthetic fertilizers. Majority of the research conducted on the yellow water was to evaluate and recover nutrients embedded in this stream. Several pieces in the literature revealed promising applications of this stream in terms of nutrients recovery (Beler Baykal et al, 2004; Başakçilardan-Kabakci et al, 2007; Beler Baykal et al, 2011; Etter et al, 2011; Kocaturk and Beler Baykal, 2012; Ishii & Boyer 2015). Research that evaluated its organic content are limited, with no attempt on further treatment for the remnant of the liquid phase after nutrients recovery is done. Ion exchange is one of the methods used besides struvite precipitation and stripping/absorption among others.

Part of these studies used fixed bed clinoptilolite columns to concentrate the nutrient from human urine on the clinoptilolite surface and to be used later as a fertilizer. The studies conducted on human urine using ion exchange with fixed bed clinoptilolite obtained a remarkable result upon removal and recovery of nutrients indicating that almost all the nitrogen, phosphorus and potassium can be concentrated on the clinoptilolite surface (Beler Baykal et al, 2004; Beler Baykal et al, 2011; Kocaturk and Beler Baykal, 2012; Allar, 2015; Allar and Beler Baykal 2015). On the other hand, the remnant of the liquid phase of ion exchange/adsorption process using clinoptilolite is still highly saline and has a considerable amount of organic matter.

Conventionally anaerobic processes fit well with wastewater streams with high organic matter concentration. There are very limited studies in the literature where anaerobic processing is employed to handle organic matter in human urine. Previous studies in the literature used urine only in co-digestion rather than using it by itself to feed an anaerobic reactor. In a study (Kpata-Konan et al, 2013), urine was used as a co-substrate in anaerobic biodigestion of manioc wastewater to improve the biogas productivity. The results of that study revealed that addition of human urine helped to increase the biogas productivity from 14.63 dm3 to 60 – 80 dm^3, to may cap for the laking of nutrients in the feed. In another study (Lavagnolo et al, 2017), where anaerobic treatment of kitchen waste in combination with brown water (mainly source separated human feces), and yellow water, (source separated human urine), was investigated, the results showed that, the addition of yellow water had improved the performance of the batch reactor systems used. This was attributed to the micronutrients present in yellow water. According to the same study the percentage of urine in the reactor was observed to be significant due to ammonia inhibition at higher percentages. With 50% urine with an ammonia concentration around 2000 mg N-NH3/l ammonia inhibition was observed. No publications were encountered in the literature which investigated anaerobic treatment for processing/revaluating urine as its focus.

The main aim of this thesis is to investigate the removal of organic matter from residue of ion exchange using source separated stored human urine as the liquid residue and clinoptilolite as the solid phase. The use of anaerobic processes is suggested for this purpose which will result in removal of organic matter accompanied by biogas production. The success of the suggested combination between ion exchange/adsorption and the anaerobic process will provide an investigation that can be considered as the first of its kind in the literature for a concurrent nutrient and energy recovery from source separated human urine as well as anaerobic processing of source separated human urine.

The scope includes the following which constitute the main frame of the primary aim of this thesis,

- Fresh urine which was collected from a collection system and its strored counter part were monitored and characterized in a long time span. Nitrogen in form of ammonium, phosphorus in form of ortho-phosphate, potassium, pH, salinity as

electrical conductivity and organic matter presented by chemical oxygen demand (COD) were monitored.

- Although fresh urine was also investigated to a lesser degree, anaerobic processing was employed to remove organic matter from mainly stored human urine by using Expended Granular Sludge Bed reactor (EGSB). As the granular sludge was taken from confectionery wastewater treatment plant, a considrable part of this work is devoted to the adaptation of this sludge.
- During the adaptation study organic matter removal from fresh urine was investigated using stepwise increments of concentration increase acompaneyd by increasing salinity.
- The stored urine (liquid phase) was treated with ion exchange/adsorption process using a fixed bed of clinoptilolite to transfer and concentrate the nutrients in stored urine on clinoptilolite surface (solid phase).
- The remnant with high salinity and COD from single stage ion exchange/adsorption was subjected to anaerobic processing using EGSB reactor aiming to remove COD. Stored urine concentration in feeding solution was performed in an ascending manner till 100% stored urine was achieved in the feeding.
- The effluent of the anaerobic process from the EGSB reactor was treated further using multiple stages of ion exchange/adsorption processes with fixed bed clinoptilolite columns using different initial loadings.
- The nutrient enriched clinoptilolite from the first stage ion exchange was used for nutrient recovery through desorption by using tap water.
- In an attempt to understand the effect of salinity coming from source separated human urine on the removal of organic matter, an experiment was performed using a synthetic solution which simulates stored urine in which nutrients had been removed with ion exchange. Different salinity levels were tested with constant COD during this experiment to observe the impact of salinity.

2. STREAM SEGREGATION AND YELLOW WATER

2.1. Stream Segregation and Ecological Sanitation (ECOSAN)

Before emphasizing the concepts and requirements of Ecological Sanitation, a brief historical review of the sanitation systems through the human history is required in order to stand on the points that lead to a need of such a new innovative sanitation concept. Most of the early settlements in human history were established nearby water bodies like rivers and lakes. The domestic wastewater at those early times was conveyed directly into those water bodies, and hanse dilution and dissipation were the only means of treatment. Collection and disposal of domestic wastewater had been practiced since the beginning of early civilizations. As examples Mesopotamia, Indus and Ancient Egypt civilizations, the earliest known collection systems were recognized. Ancient cities like Athens in which storm water and wastewater from toilets were collected together in a basin near the city and then used later for irrigation. In Rome, the appearance of more complex wastewater collection systems from houses were observed. It can be considered that the modern sanitation reborn in the middle of the 19th century, and at the 20th century most of the cities in developed countries started to use either separate or combined systems for collection for domestic wastewater and storm water (De Feo et al., 2014). Figure 2.1 and 2.2 show both systems that are used in most of the modern cities at the present time.

In most parts of the world, domestic wastewater is collected using either separate or combined sewer systems. In conventional sanitation systems, domestic wastewater is collected as one single stream that uses a water of drinking water quality for all purposes and then treated in a conventional municipal wastewater treatment plants. The conventional treatment technologies in the municipal wastewater tretment plants is revolved on the indication that the domestic wastewater is a waste that is only suitable for disposal after being treated (Esrey et al., 2001), such a treatment ignores the valuable material embedded in the domestic wastewater like nutrients.

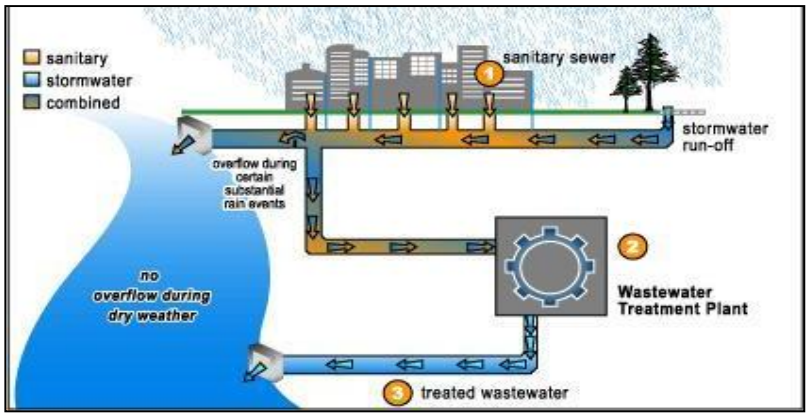

Figure 2.1 : Combined sewer system for domestic wastewater and storm water collection (URL1).

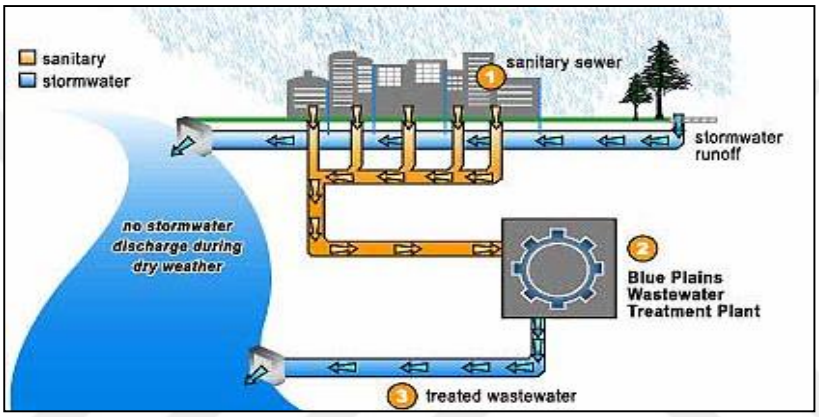

Figure 2.2 : Separated sewer system for collection of domestic wastewater and storm water (URL2).

Facilities used for domestic wastewater treatment impose a financial load on the authorities responsible for constructing, operating and providing the necessary maintenance to these treatment facilities. Figure 2.3 shows the collection of domestic wastewater from different sources in one single stream and treatment in a conventional wastewater treatment plant.

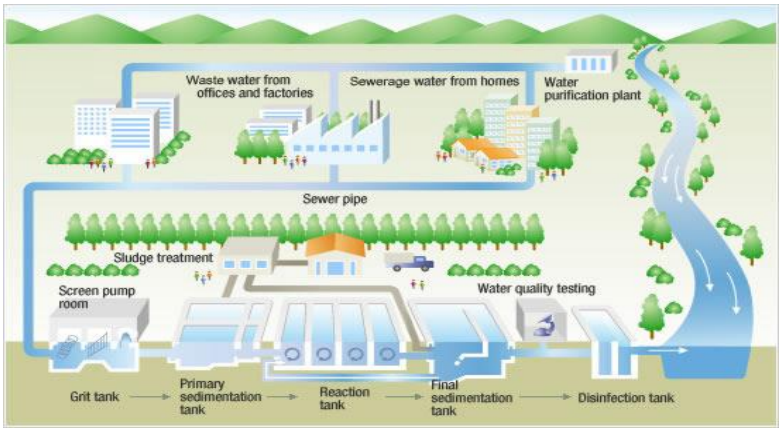

Figure 2.3 : Conventional collection and treatment of domestic wastewater (URL2).

Segregation of domestic wastewater into two components as grey water (washing/cleaning activities) and black water (human urine, feces with or without flushing water) or to three components as grey water, yellow water and brown water in a new sanitation concept known as Ecological Sanitation (ECOSAN) helps closing the material loops through reuse and recovery of water, nutrients and possible energy from the new segregated streams. ECOSAN claims that domestic wastewater is not a waste to be discarded but a source of valuable materials which csn to be revaluated. ECOSAN concept provides a new approach for the management of domestic wastewater taking sustainability principals as its basis. According to the ECOSAN concept the segregation into three streams should be done at the source of generation (Beler Baykal, 2015). Grey water refers to the domestic wastewater stream originating from washing activities, except any wastewater generated from toilets. Those washing/cleaning activities include kitchen sinks, hand washing basins, bath tubs, dish washing and washing machines. For yellow water which refers to source separated human urine, usually the separation is achieved by using special type of toilets, Urine Diverting Toilets (UDT)s or by urinals. Brown water is the stream that includes feces with or without flushing water.

By taking a closer look at the domestic wastewater fraction in Figure 2.4, it can be observed that feces and urine constitute only 0.1 and 1.0 % of the domestic wastewater and 23.9% of the domestic wastewater is a flush water of drinking water quality that is used only to flush and convey the human metabolic wastes. 75% of the domestic wastewater is grey water that could be reused as an irrigational water, for municipal uses like firefighting or street cleaning, but the most significant reuse of grey water is as flushing water replacing the drinking water that used for this purpose.

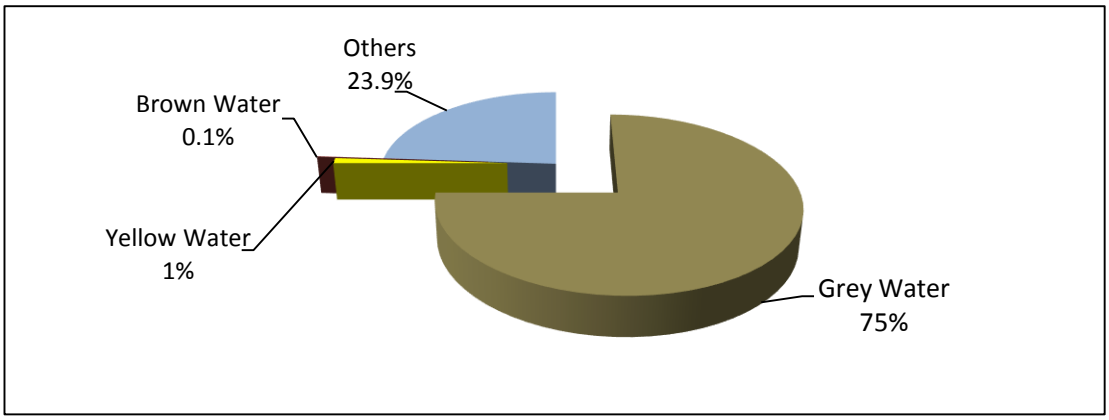

Figure 2.4 : Volume fractions of domestic wastewater (Beler Baykal, 2015).

The characteristics of ECOSAN streams are shown in Figure 2.5. It may be observed that segregation helps to concentrate most of the nutrients in yellow water in which 87% of nitrogen, 50% of phosphorus and 54% of potassium is embedded in 1% as volume of domestic wastewater. In the same manner the majority of the pathogens will be concentrated in brown water which makes 0.1% of the domestic wastewater volume. In terms of organic matter, the smaller fractions, yellow water and brown water, receiving 12 and 47% of the organic matter by mass in domestic wastewater respectively. On the other hand, grey water which is the largest fraction by volume receives 41% of the organic matter diluted in 75% volume of the domestic wastewater.

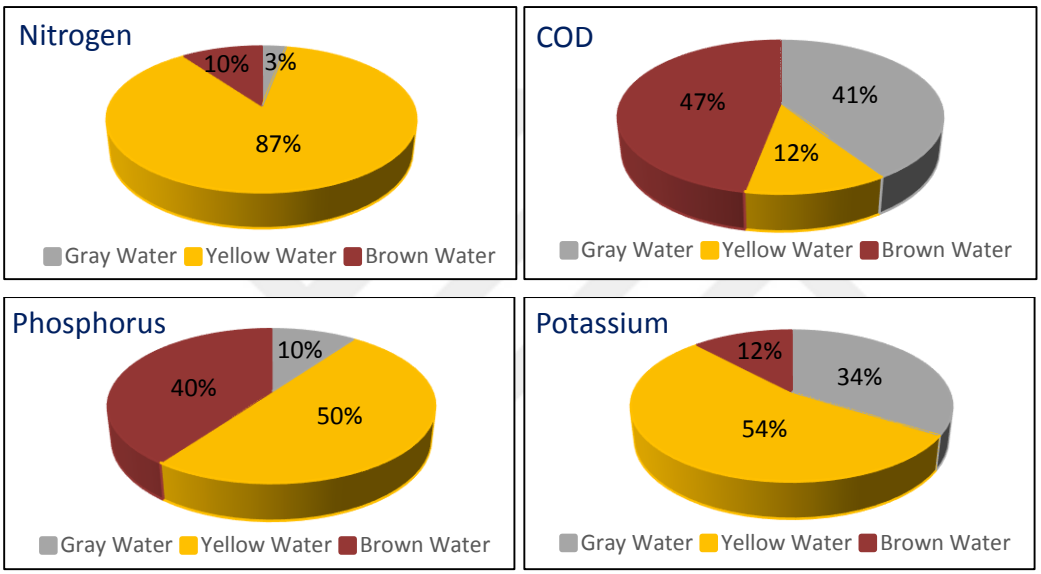

Figure 2.5 : Nutrients and Organic matter fractions in ECOSAN Streams (Otterpohl et al, 2003; Beler Baykal, 2015).

According to Beler Baykal (2015), if ECOSAN segregation concept is applied successfully on domestic wastewater, the separation to three streams will help to produce 75% of mildly polluted stream which is grey water. It is assumed that annually for one person 80550 l of domestic wastewater, 50 l of feces and 500 l of urine will be generated. Urine and feces thus produced is sweeped away with 20000 l of drinking water for toilet flushing. This will further be dissipated in 60000 l of grey water in which almost no nutrients and much lesser pathogens exist. This implies that smaller fractions of domestic wastewater pollute larger fractions. The successful implementation of the ECOSAN concept on domestic wastewater will aid in an easy handling of smaller polluted streams with simple treatment and enhance the concept "fit for purpose" for the three separated streams. Some conventional treatment technologies like nitrogen removal nitrification/denitrification will not be necessary

and phosphorus problem will be partially eliminated by concentrating those two nutrients in yellow water. Likewise, pathogens that will be concentrated in brown water.

Each one of these three streams has its own beneficial final use that can contribute to closing material loops and support sustainability of resources. Figure 2.6 depicts and summarizes source, possible treatment and final beneficial use of the three segregated streams. It can be observed from Figure 2.6 that each stream can be reused based on its content for different application. The grey water is a possible candidate for non-potable uses of water including flushing toilets, irrigation, municipal uses and groundwater recharge. Yellow water is suitable as a natural fertilizer due to the high content of nitrogen, phosphorus and potassium that makes the major ingredients of fertilizers. The availability of nutrients for plants in yellow water makes it a significant candidate of Urine Based Fertilizer (UBF) that can be used as an alternative for the synthetic ones. The use of UBF in agriculture has a considerable contribution to the food security (Jönsson et al., 2004; Beler Baykal, 2015). Regarding brown water, the final use of this stream may be as a soil conditioner after composting or as a source of energy through biogas production by anaerobic processes.

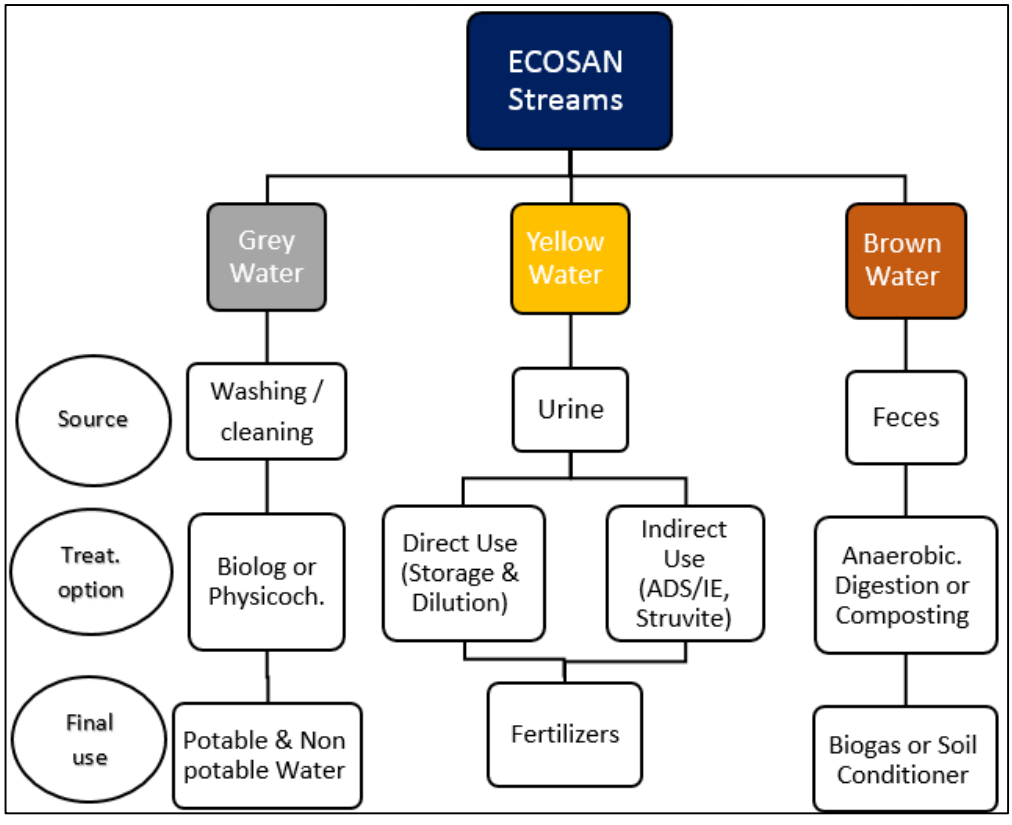

Figure 2.6 : ECOSAN streams and their final uses (Beler Baykal, 2015).

According to Werner et al., (2003) and GTZ (2002), the advantages of ECOSAN approach for domestic wastewater management can be summarized as:

- reduction of health related problems caused by improper and inadequate sanitation,
- prevention of water resource pollution and conservation of water resources
- prevention of soil fertility degradation and introduction of alternative fertilizer that can contribute to minimize the use of synthetic chemical fertilizer,
- maximizing benefits of water and nutrients from domestic wastewater,
- significant contribution to food security and improvement of agricultural productivity,
- reduction in energy consumption for synthetic fertilizer production and treatment technologies used in conventional treatment plants,
- providing sanitation solutions for both developing and developed areas, as the ECOSAN approach may be implemented in both urban and rural areas.

2.2. Yellow Water - Source Separated Human Urine

Applying ECOSAN approach on domestic wastewater will close the material loops and part of these materials are nutrients present as nitrogen, phosphorus and potassium in human urine. The separation of human urine that makes 1% of domestic wastewater by volume is the first step in ensuring that nutrient cycles in domestic wastewater are closed and the fertilizer value can be used for agricultural purposes. According to Otterpohl et al., (2003), yellow water or source separated human urine contains 80% nitrogen and more than 50% of phosphorus and potassium. In another study, Heinonen –Taski & Van Wijk-Sijbesma (2005), the nitrogen content in human urine could go up to 90%, while phosphorus and potassium could be up to 65% and 80% respectively.

The amount of urine excreted by an adult range from 0.6 – 2.6 l/day depending on the personal liquid uptake in a day within an average of 1.4 l/day (Rose et al., 2015). The amount of urine excreted is different from an adult to a child, the previously mentioned amount per an adult person per day may be reduced to a half in case of urine excreted from a child (Rose et al., 2015). Using the assumption that 1.5 l/person/day of urine will be excreted (Beler Baykal, 2015), annually from one person 3.8 kg nitrogen, 0.3 kg phosphorus and 1.1 kg potassium can be recovered, based on the average concentrations from Table 2.1(Allar, 2015).

Table 2.1: Average concentrations and fertilizer value for N, P and K in human urine (Allar, 2015).

Fertilizer componemnt from urine	Average concentration (mg/l)	Mass annually produced (kg/year)
Nitrogen	7000	3.8
Phosphorus	500	0.3
Potassium	2000	1.1

These calculations show the significant role of human urine as a source of fertilizer and it could possibly be used as alternative fertilizers. According to Allar Emek et al, (2016), the contribution of human excreta to global fertilizer need is 35% and the largest contribution in this percentage comes from human urine. Yet in another study (Beal et al., 2007), it was illustrated that the mass of nutrients in urine excreted daily is enough to produce one loaf of bread which almost corresponds to an annual wheat production of 200 kg. Table 2.2 shows the available amount of N, P and K in urine compared to the required amount of nutrients to produce 200 kg of wheat.

Table 2.2 : Nutrients in Urine required to produce 200 kg of wheat (Beal et al., 2007).

Nutrient component	Nutreint in urine (kg/cap.year)	Nutrients required for 200 kg wheat
N	4.4	4.5
P	0.4	0.6
K	1.0	1.0

Hence the contribution of human urine or yellow water is significant toward sustainability in terms of food security, which in parallel will lead successfully to close the nutrient loops between domestic wastewater and agriculture, as shown in Figure 2.7.

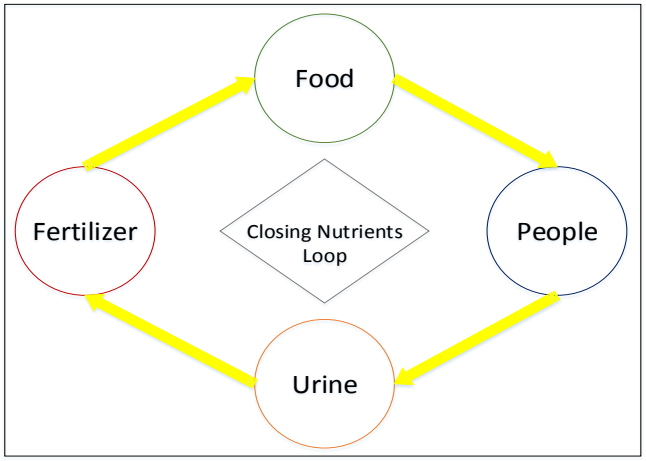

Figure 2.7 : Closing the nutrients loop in domestic wastewater.

2.2.1. Urine diverting toilets

In order to separate human urine from domestic wastewater, a change to the conventional infrastructures must be applied. ECOSAN approach requires a separation of streams at the source of generation, in case of urine that means a separation must be done in the toilets. For this purpose, a special type of toilet is used replacing the conventional ones. Urine Diverting toilets (UDTs) as shown in Figure 2.8 and urinals are used to accomplish the separation of urine from the fecal matter.

Figure 2.8 : Urine diverting toilets (GTZ 2005; Beal et al., 2007).

UDTs have two compartments for separation of urine and feces and may operate with or without flushing water. UDT has an opening that urine can flow through to a collection tank and in some types of UDTs the opening cannot be open unless the user sits on the toilet. UDTs offer similar comfort as conventional toilets, and it can be used both in rural and urban areas. Table 2.3 shows a number of locations in which UDTs are installed, and it can be observed that UDT is suitable for both developing and developed countries. However, it is reported that around 2.8 million persons use UDT around the world (GTZ, 2012).

Table 2.3 : Number of UDT installation in different parts of the world (Savenije & Hoekstra, 2009; Simha & Ganesapillai, 2017).

Location	Number of UDT installation
South Africa	75000
Bolivia	900
Kenya, Burkina Faso, Uganda	1000
Mozambique	575
Chad	800
Zimbabwe	7000
Sweden	300000

The cost of UDTs varies according to the design and the degree of comfort, but still the simpler type of UDT can be provided with a very low budget. According to Savenije & Hoekstra (2009), the cost of UDT in Sweden is USD 360 and the total installation cost that includes a urine collection tank of 1000 l, seat riser, transport container, fan and a processing vault is in a range of USD 650 – 750. In Zimbabwe the cost of UDT is much cheaper with USD 10 for the UDT and the whole installation is USD 70. Table 2.4 includes cost examples for UDT and the whole installation system.

Table 2.4 : Cost of UDT and Separation system (Savenije & Hoekstra, 2009; Lamichhane & Babcock, 2012).

Location	Cost of UDT only (USD)	Cost of Separation system (USD)
Zimbabwe	10	70
Sweden	360	650 – 750
USA	600	1500 – 4600*

* The cost for separation system depends on number of UDT and the size of the collection tank (2000 – 5700 l).

The advantages for using UDT can be summarized as; using UDTs allow nutrient recovery and closing nutrient loops by urine separation, water consumed for flushing can be reduced if a UDT of 0.15 l to flush urine is used instead of conventional toilets that use 3.0 l for flushing urine (Lienert & Larsen, 2006). The use of UDTs helps to separate hormones and pharmaceuticals from the other segregated domestic wastewater streams. The use of UDT leads to an energy reduction in terms of energy used to treat nutrients by nitrification/denitrification or even reduction in energy used for manufacturing synthetic fertilizers. UDT helps to protect the groundwater from nutrients infiltration from septic tanks (Lamichhane & Babcock, 2012).

With all the benefits that UDTs bring, without a proper maintenance, a failure in the separation system could be observed. The use of UDT could cause blockage to the pipes due to the precipitation of struvite and calcium phosphate that occurs as a result of the increased pH due to the urea hydrolysis and its conversion to ammonia. Proper maintenance will eliminate such problems, it is suggested by Kvarnstrom et al., (2006) that a solution of caustic soda with a ratio of 2:1 (water: soda) or acetic acid of concentration >24% will help remove the blockage problems. The selection of materials is very important, metals should be avoided in any part of the urine separation systems and plastic materials or concrete should be used for this purpose.

2.2.2. Characterization of source separated human urine

In literature, human urine is usually differentiated as fresh and stored urine depending on weather urine received storage or not. The main reason for storage of human urine is for pathogenic inactivation. Another reason is to increase the potential recoverable ammonium through hydrolysis of urea. Human urine contains pathogens may cause a serious threat to the environment, nature and humans. Human urine compared to brown water can be considered to have less amounts of pathogens (Giresunlu and Beler Baykal, 2014; Beler Baykal, 2015). Pathogens like Leptospira interrogans, Salmonella typhi, Mycobacterium tuberculosis may be observed in human urine. Beside pathogens viruses, protozoa, and helminth eggs may be incorporated in human urine (Hogland 2001, Heinonen –Taski & Van Wijk-Sijbesma, 2005). Cross contamination with fecal matter in source separated human urine is mainly due to a failure in the collection system. According Schönning et al. (2002) 9.1 mg of feces per one litter of urine is the average contamination. During the storage period and as the ammonia concentration increases due to the hydrolysis of urea, a deactivation of the pathogens and microorganisms in source separated human urine possibly occur. A threshold of 40mM of ammonia and a temperature above 20°C is recommended by (Vinneras et al., 2008), to insure an inactivation of all pathogens. It is reported that for safe use of human urine as a fertilizer for food crops, 6 months is recommended for viruses and protozoa inactivation (WHO, 2006). The 6 months' period of urine storage could possibly have shortened in case the threshold recommended value above is met.

Table 2.5 illustrates the characterization and the differences between fresh and stored urine. pH of fresh urine can be considered neutral, almost in all research conducted on fresh urine it was shown that the pH will fall in a range of 6.0 to 7.3. The ammonium nitrogen content in fresh urine is low if it is compared to its stored form. The major nitrogen component in fresh urine (over 80%) is in the form of organic nitrogen or urea, which during storage time will be converted to ammonium through hydrolysis. The urea hydrolysis is due to the presence of a ureases which is an enzyme existing in human urine, the urease enzyme hydrolyzes urea to ammonia and bicarbonate, the equation below shows the chemical reaction of urea hydrolysis by urease enzyme and the conversion to NH_3 (Udert et al., 2003).

$$NH_2(CO)NH_2 + 2H_2O \longrightarrow NH_3 + NH_4^+ + HCO_3^-$$

Table 2.5 : Characterization of natural fresh and stored urine.

		Fresh urine							Store urine						
Parameter	Unit	1	2	3	4	5	6	7	8	9	10	11	12	13	14
pH	-	6.2	6.2-6.4	7.2	5.93-7.32	6.4	5.78-6.39	6.0	8.9-9.1	9.2	9.1	9.2-9.6	9.2-9.8	9.3	9.0
Electrical Conductivity	mS/cm	-	14.6-17.3	-	-	-	13.0-22.5	14.0	-	-	36.7	53.0-57.0	36.0-48.0	38.7-38.9	45.24
NH_4^+	mg/l	160	330- 340	245	510-1160	627	195 -603	344	1690-8100	8570	6340	6200-8400	3660-7600	7250-8000	5037
TKN	mg/l	9760	6600-6900	-	6180 - 8500	7150	9220	5700	-	-	-	6350-8600	6000-8000	5666-6322	-
COD	mg/l	12000	7800	8150	8120-8700	8187	1534-2604	7120	1650-10000	-	-	-	4300-7275	4498-4666	-
P	mg/l	960	530- 540	367	420-640	350	-	415	200-540	700	-	240-350	260-340	250-319	344
K	mg/l	2160	1760-1900	2170	-		-	1200	770-3284	2000	1213	1750-2015	1550-2175	-	1081

1 Larsen and Gujer (1996)
2 Fittschen and Hahn (1998)
3 Udert et al,. (2003)
4 Kabdaşlı et al,. (2006)
5 Tunay et al,. (2009)
6 Beler Baykal et al,. (2011)
7 Kocaturk & Beler Baykal (2012)
8 Maurer et al,. (2006)
9 Pradhan et al,. (2009)
10 Beler Baykal et al,. (2009)
11 Allar & Beler Baykal (2013)
12 Allar, (2015)
13Allar & Beler Baykal (2015)
14 Jagtap & Boyer. (2018)

The pH of urine increases during the urea hydrolysis due to the release of ammonia and bicarbonate in this reaction (Udert et al., 2003). It can be observed from Table 2.5, that the pH of stored urine is in the range of 8.9 – 9.8 after urea hydrolysis is completed.

Urine storage is a beneficial practice in terms of nutrient recovery which later will be used as a fertilizer. According to Allar (2015) the conversion of urea to ammonium in one-month storage period can reach at least 90%, which will accomplish more nitrogen recovery in form of ammonium. In another study (Kocaturk & Beler Baykal, 2012) almost all the of the urea was converted to ammonium showing a 16-fold increase of ammonium concentration compared to its initial concentration. The electrical conductivity during storage will change to a level over 50 mS/cm starting from an initial value of 13.0 mS/cm showing an increase of almost 4 folds.

Phosphorus in human urine is in dissolved form of phosphate and its percentage of dissolved form corresponds to 95 – 100% of the total phosphorus therein (Udert et al., 2006). Phosphorus content of fresh urine is higher than stored urine due to the spontaneously precipitation occurring in urine collection systems and storage tanks. Calcium phosphate and struvite is the common precipitate in collection tanks, and within this precipitation up to 35 – 40 % of the phosphate can be eliminated (Udert et al., 2003; Kocaturk, 2010), even though after such precipitation the phosphorus concentration is in a range of 250 – 350 mg/l. Regarding potassium which is one of the main components of fertilizers, its concentration seems unchanged during the storage period (Kocaturk and Beler Baykal, 2012; Allar, 2015).

From Table 2.5 it may also be observed that the human urine is rich in terms of organic concentration, even though after separation human urine receives only 12% of the COD in domestic wastewater by mass this is because very small volume of urine which is 1%. The COD concentration in source separated human urine falls in a range of 1650 mg/l (Maurer et al,.2006) to 12000 mg/l (Larsen and Gujer. 1996) depending on personal diets. The high organic concentrations of human urine impose a threat on the environment in case of discharge into water bodies. Human urine also contains hormones and pharmaceuticals that upon there accumulation can cause a serious threat to the environment, nature and eventually to humans.

2.2.3. Nutrient removal and recovery from source separated human urine

Source separated human urine can be applied as a fertilizer for agricultural purposes by direct or indirect methods. The direct application method of human urine must comply with storage requirements for pathogenic inactivation reported by World Health Organization (WHO, 2006) and use other studies recommendations about the suitable conditions to ensure a safe use of human urine that do not impose a threat upon human health and environment (Höglund, 2001; Vinneras et al 2008).

Usually the direct application of source separated human urine requires dilution due to the high salinity that can bring harm to the soil as well as to the plants that are supposed to be fertilized with urine. Due to the presence of pathogens, pharmaceuticals, hormones and salinity in human urine, some barriers limit the direct application for agricultural purposes (Beler Baykal, 2015; Rose et al., 2015).

According to Maurer et al, (2006), urine treatment can be divided into 7 categories each one of these categories has a different purpose or handle a different pollutant group in urine. According to the same study the wide range of treatment for urine can be attributed to the unique nature of this stream. Table 2.6 shows the 7 treatment categories for urine with the technologies used for each category. Not all of the treatment technologies in Table 2.6 are used for nutrient recovery, like biological nutrient removal, which is applied for improving the water quality from pollution caused by nutrient which eventually leads to eutrophication. Some of these technologies partially or indirectly serve nutrient recovery from human urine like stabilization, hygienisation, which prevent loss of nutrient and aid in pathogenic inactivation. Many studies engaged with investigating different methods to replace the direct use of human urine with indirect application that will recover the nutrients and possibly eliminate the imposed risks of pathogens and other harmful ingredients in human urine. Physicochemical processes such as struvite precipitation, stripping/absorption and adsorption/ion exchange are suggested by researches to produce a urine based fertilizer from source separated human urine (Lind et al., 2000; Beler Baykal et al., 2004; Basakcilardan-Kabakci et al., 2007; Ganrot et al, 2008; Kocaturk Beler Baykal, 2012; Beler Baykal et al., 2011; Ishii & Boyer 2015).

Table 2.6: Treatment categories and used technologies for human urine (Maurer et al, 2006).

Treatment category	Used Technologies	Aim of the category
Volume reduction	Evaporation Freeze and thaw Reverse osmose	Concentrating nutrients for storage and transportation purposes
Stabilization	Acidification Partial nitrification	Prevention of organic matter degradation, loss of ammonia, and precipitation process
Hygienisation	Storage	Pathogenic content reduction
Phosphorus recovery Nitrogen recovery	Struvite Ion exchange Ammonia Stripping Isobutylaldehyd e-diurea (IBDU)	Phosphorus and nitrogen recovery from urine as a source of fertilizer
Micro pollutant removal	Electrodialysis Nano filtration Ozonation and advanced oxidation	Elimination of Pharmaceuticals and hormones in urine
Biological nutrient removal	Anammox process	Nutrients removal for improvement of water quality

Struvite precipitation is used to produce phosphorus fertilizers in form of magnesium ammonium phosphorus shortly named MAP or in another form as potassium struvite (Wilsenach et al. 2007; Etter et al. 2011; Ishii & Boyer, 2015; O'Neal, & Boyer**,** 2015; Beler Baykal & Dogan, 2016), while to produce nitrogen fertilizer stripping/absorption processes can be used (Basakcilardan-Kabakci, et al., 2007; Beler Baykal & Dogan, 2016). Ion exchange/adsorption processes is employed to produce nitrogen, phosphorus and potassium fertilizers (Lind, et al., 2000; Beler Baykal, et al., 2004, 2009, 2011; Kocaturk & Beler Baykal, 2012; O'Neal & Boyer, 2013, 2015).

It is reported in the literature that all the investigated methods show high efficiency for recovery of nitrogen and phosphorus, which makes the choice among these processes based on the required nutrient to be recovered. Table 2.7 shows a number of research in literature that focuses on nutrient removal and recovery from source separated human urine.

In stripping/absorption nitrogen is recovered from source separated human urine in the form of ammonia and then an acid solution is used to capture ammonia as frequently used example is sulfuric acid as an acid and ammonium sulfate as the fertilizer product. In this method almost all the ammonia can be recovered, up to 98% (Tetterborn et al. 2007), but in stripping/absorption phosphorus cannot be recovered from source separated human urine. Basakcilardan-Kabakci et al., 2007 in their study regarding nitrogen recovery using stripping/absorption, urine was collected from individuals and diluted 1:4 and stored for hydrolysis to be completed. For the stripping stage with air at high pH levels of 11 – 13, 1 l reactor used for ammonia separation from urine, then the gaseous form of ammonia was carried through a connection tube to an absorber in which the ammonia is absorbed in a sulfuric acid solution (0.5M H_2SO_4). The product of this experiment was ammonium sulfate which is a form of fertilizer that potentially can be used for agricultural purposes. This experiment gave a prove regarding the efficiency of this method to recover nitrogen from human urine with 93%.

Recovery of phosphorus can be achieved by using struvite precipitation method. The precipitation of struvite can occur naturally due to the presence of the main ingredients that form the struvite, magnesium, phosphorus and ammonium. Both phosphorus and ammonium are sufficiently available in urine, while magnesium is much lesser in comparison to them, and that will make magnesium the limiting reactant of struvite precipitation. Different pieces of studies in literature investigated the struvite precipitation in urine with the best fit condition of this process, in Tettenborn et al. (2007) it was found that the addition of magnesium with a ratio 1.5: 1 as Mg:P will result in a 98% recovery of phosphorus.

Table 2.7: Research on removal and recovery of nutrients from human urine.

Process Used	Type of Urine	Collection method	Results achieved	Reference
Struvite precipitation & adsorption/ion exchange	Synthetic human urine and natural fresh urine.	Fresh urine collected from Individual donors	100% recovery of P and K with 65-80% recovery of NH_4^+	Lind et al., 2000
Adsorption/ Ion exchange	Natural fresh and composite urine	Individual donors	Nearly 100% removal of NH_4^+ from liquid phase with 63% recovery from solid phase	Beler Baykal et al., 2004
Stripping/Absorption	Natural stored urine	Individual donors	97 to 99% recovery efficiency can be achieved	Başakçilardan-Kabakci et al., 2007
Ion exchange using clinoptilolite	Natural stored urine	Individual donors	NH_4^+ recovery 56-97% and K^+ 91-99%	Beler Baykal et al., 2009
Ion exchange using clinoptilolite	Natural fresh and stored urine	Individual donors	Removal from liquid phase, NH_4^+ 90%, P 97% and K^+ 89% Recovery from solid phase, NH_4^+ 96% and P 99%	Kocaturk, 2010; Kocaturk Beler Baykal, 2012
Ion exchange using clinoptilolite	Natural fresh and stored urine	Individual donors	97% NH_4^+ removal from liquid phase with different initial loading and 88% recovery from solid phase	Beler Baykal et al., 2011
Ion exchange using clinoptilolite	Natural stored urine	Individual donors	Up to 95-99% P removal from liquid phase with different initial loading and 88- 99% recovery from solid phase	Allar & Beler Baykal 2013
Struvite Precipitation	Natural stored urine	Collection system from university community	90% recovery of P and N	Ishii & Boyer 2015
Struvite precipitation	Natural stored urine	Households using urine diverting toilet - dry model	50 – 91% P recovery with sedimentation reactor and external filter bag respectively, and	Etter et al., 2011
Ion exchange using anion exchange and	Synthetic fresh and stored urine		Over 90% removal of P	O'Neal & Boyer 2013; 2015
Ion exchange using anion exchange followed by struvite precipitation	Synthetic fresh and stored urine		Almost 100% recovery of P from ion exchange and struvite precipitation combination	O'Neal & Boyer 2013; 2015

Another study showed that one of the parameters that effect the struvite formation is pH and it was found that with addition of 1.5:1 times magnesium to phosphorus under pH of 9.4 – 9.7, the phosphorus precipitation as struvite will be 99% (Harada et al. 2006). In Etter et al., (2011) in which the experiment was performed over pilot scale in a village in Nepal, over 90% of the phosphorus could be recovered in form of struvite with a magnesium dosage as 1.1 mol Mg for each mol of P with a very low capital cost that does not exceed 60€ for a reactor with of volume of 50l. Tilley et al. (2008) investigated the struvite precipitation from natural urine spontaneously and by magnesium addition. In this study spontaneous precipitation contributed to about 23% of the phosphorus recovery, while magnesium addition at a ratio of 1.7:1 Mg:P contributed to an additional 70% of phosphorus recovery.

During struvite formation, not only phosphorus can be recovered but nitrogen in form of ammonium as well (Sweet, 2006; Kabdasli et al., 2006 a and b). In Sweet (2006) and under pH values of 7.5, 8.5, 9.5, not only 99% of phosphorus recovery achieved but also up to 23% of ammonia could be recovered. However, Kabdasli et al. (2006 a, b), showed that with a ratio of 1:1:1 Mg:P:N and at pH range of 8.0-9.5 a 95% of nitrogen removal was observed, and at pH 7 in the experiment 90% of nitrogen removal was observed. However this theoretically is possible but practically is misleading as addition of Mg and more importantly P is required in order to precipitate more N.

Ion exchange process may also be employed to remove and recover nutrients in source separated human urine. Ion exchange/adsorption processes is part of adsorption in which the pollutant or the desired item to be removed from a liquid phase (adsorbate) is concentrated on the solid phase (adsorbent). Many studies investigated the use of adsorption/ion exchange in nutrient removal and recovery by contacting human urine with clinoptilolite which is a natural zeolite, also used as a soil conditioner, to concentrate nutrient on its surface then by contacting it with water nutrients will be released from the surface. Beler Baykal et al. (2004), illustrated the removal of ammonium from human urine collected from individual donors using ion exchange process with clinoptilolite. In this research, the results showed about 100% of the ammonium could be removed from urine and 63% could be recovered by desorption with tap water.

Implementation of the previous research was applied in Beler Baykal et al. 2009, in which both ammonium and potassium were removed and recovered from human urine. The recovery percentages were 56-97% and 91-99% for ammonium and potassium respectively due to different initial loadings used. In the same study, it was found that 1716 – 268 g/day nutrients enriched clinoptilolite that is loaded with 5.1-18.7 mg NH_4^+/g clinoptilolite respectively can be produced. It is indicated that the removal of ammonium from human urine was related to the initial loading, the lower the initial loading the higher the removal efficiency and more potentially recovered nitrogen in form of ammonium (Beler Baykal et al., 2009). In another study, in which phosphorus removal from human urine with different initial loadings ranging between 0.26 – 1.35 mg PO_4/g clinoptilolite was investigated, it seems that initial loading did not impose any noticeable effect on the removal efficiency, with initial loading ranging 0.26 – 1.35 mg P/g clinoptilolite the removal efficiency ranged from 95 – 99% (Allar & Beler-Baykal, 2013). All in all, initial loadings were more effective in terms of ammonium removal than phosphorus.

Kocaturk, (2010); Kocaturk and Beler Baykal, (2012) found that nutrient recovery from stored urine is much beneficial than nutrient recovery from fresh urine. The hydrolysis of urea will help to increase the ammonium concentration by converting 95% of the organic nitrogen to ammonium. In this study, dilution at different rates was applied to investigate the effect of dilution on nutrient recovery from human urine and it was found that using undiluted human urine will give a better result in terms of removing nutrients from liquid phase. In this study, 10 mg NH_4^+/g clinoptilolite initial loading was used and the removal percentages were up to 93% for ammonium, 98% for phosphorus and 95% for potassium for 100% urine. The recovery experiment was performed using tap water and both ammonium and phosphorus were released with 96% and 99% for ammonium and phosphorus respectively. This research did not report any potassium release from the clinoptilolite used in the removal experiment due to the high potassium content in the tap water used for recovery experiments.

Allar, & Beler Baykal, (2015) conducted an experiment of nutrient removal in a way that will not lead only to nutrient removal from human urine, but will also improve the quality of the ion exchange columns for environmental protection. In this study, stage wise operation was employed with four stages.

The experiments were performed in two different loading modes, constant and variable. Constant loading performed with stage at initial loading of 20 mg NH_4^+/g clinoptilolite, while variable loadings were performed at initial loadings of 20, 10, 5 and 5 mg NH_4^+/g clinoptilolite. The results revealed that variable loading mode gave better removal efficiency than constant loadings. In variable loadings the initial ammonium concentration of 7000 mg NH_4^+/l decreased to 24 mg NH_4^+/l at the end of the fourth stage, it indicates that almost 100% removal of ammonium could be achieved in case variable loadings were applied. First two stages were sufficient for recovery however the last two were necessary for higher effluent quality. Regarding phosphorus, Allar, & Beler Baykal, (2015) indicated that 95-97% of phosphorus was removed during the first stage and the following stages did not have an appreciable amount of phosphorus removal. Therefore, the stage wise application using ion exchange columns is more effective in terms of ammonium removal than phosphorus. As mentioned before in this part, removal of nutrients using ion exchange via clinoptilolite can done by contacting the clinoptilolite with human urine either in a continuous or batch mode (Allar, 2015; Allar and Beler Baykal, 2017).

Nutrients recovery from human urine was achieved not only using one single method but also by applying a combination of those methods as well, researchers tried different combinations of struvite, ion exchange and stripping/absorption processes. Lind et al. (2000) applied both struvite precipitation and adsorption/ion exchange to achieve both phosphorus and nitrogen recovery from urine. Clinoptilolite and wollastonite were used for ammonium removal. The result of the combination of struvite and clinoptilolite or wollastonite revealed that most of potassium and phosphorus can be removed during struvite precipitation while up to 80% of ammonium can be removed by applying adsorption/ ion exchange. In another research that used the combination of struvite and ion exchange, it was found that the addition of 0.5 MgO and 15 g of zeolite to one letter of urine will result in 88 and 99% removal of nitrogen and phosphorus respectively (Ban and Dave 2004).

Antonini et al. (2011) performed an experiment using struvite precipitation for phosphorus recovery followed by stripping absorption for nitrogen recovery. The study used stored urine that was collected from students' dormitory. First struvite precipitation was conducted in a pilot plant and it resulted in 98% recovery of phosphorus, sequentially the stripping/absorption experiment was conducted and the

results revealed that 90% of nitrogen could be recovered in the form of ammonium sulfate. The same study observed that 100% of nitrogen can be achieved if 100% recycle stripping processed is applied.

Dogan (2015) is one of the researches who investigated the combination of struvite precipitation, stripping/absorption and adsorption/ion exchange in different configurations. The research included a single stage of nutrient recovery using struvite precipitation, stripping/absorption and adsorption/ion exchange and combinations between removal methods were performed to improve nutrient recovery as well as the effluent. The combinations experiment included the following configurations:

- Two stage ion exchange/adsorption
- Struvite precipitation followed by stripping/absorption
- Struvite precipitation followed by ion exchange/adsorption
- Stripping/absorption followed by struvite precipitation

The results of this research showed the removal efficiencies of single stage operation were, 99% and 10% of phosphorus and nitrogen by struvite precipitation, 99% nitrogen removal by stripping/absorption with no phosphorus removal and over 80% removal of nitrogen and nearly 100% removal of phosphorus by ion exchange. The combinations between two methods were successful in terms of improving the nutrient recovery. The combination between struvite and ion exchange or struvite and stripping/absorption helped to recover both phosphorus and nitrogen in a subsequent stage.

According to the literature review of the three nutrient recovery methods, Table 2.8 can be built up to summarize the nutrients that can be recovered with each method or methods combinations based on the previously mentioned references. Struvite precipitation seems to be very effective in phosphorus recovery in contrast to nitrogen which is removed to a very low level. Stripping/absorption is effective in removing the nitrogen while the remnant of the stripping stage will still have an abundant amount of phosphorus. Upon that a combination of these two methods will be more successful in case nitrogen and phosphorus recovery is required. Adsorption/ion exchange provides a method for recovery of nitrogen, phosphorus and potassium even if it used alone without combination with struvite precipitation and stripping/absorption. Multiple stages of ion exchange process will help a lot in terms of removal and recovery of more

nutrients to be used as a fertilizer beside improving the quality of the remaining liquid phase after ion exchange process.

Table 2.8 : N, P and K recovery by single stage process or process combination.

Process/Process combination	Nutrients recovered			Chemical addition
	N	P	K	
Struvite precipitation		✓		✓
Stripping/absorption	✓			✓
Adsorption/ion exchange	✓	✓	✓	
Struvite + Stripping/absorption	✓	✓		✓
Struvite + Ion exchange	✓	✓	✓	✓
Multiple stages ion exchange	✓	✓	✓	

It is good to mention that the research using human urine for nutrient removal and recovery put a great effort in this specific subject, but ignored whether organic matter was removed or not during these processes. The remnant of nutrient removal process from human urine is still a highly saline and contain a considerable amount of organic matter. More effort should be concentrating on the possibilities of removing organic matter during recovery using the mentioned processes. The investigation upon the organic matter in the remnant after nutrients had been removed is a sensitive matter due to the threat that such a remnant with high salinity and organic matter imposes on the environment if it is disposed without treatment.

3. AN OVERVEIW OF MAIN FUNDAMENTALS OF PROCESSES INVOLVED

3.1. Ion Exchange

3.1.1. Fundamentals of ion exchange

Ion exchange is a type of an adsorption process in which ions retained through electrostatic forces to fixed charged groups on the surface of a solid matter are exchanged for ions in solution. The exchange process is conducted between two phases in which ions of similar charges will be exchanged. Ion exchange is used for water treatment mainly for removing hardness ions calcium and magnesium in water supply systems as well being used for ground water treatment to remove both manganese and iron. Ion exchange in wastewater treatment is recognized as well for treating different industrial wastewater streams that may contain valuable materials. Ion exchange may be used as well in nuclear reactor, hospitals and laboratories (Weber, 1972). The resent application of ion exchange process is in domestic wastewater to remove/recover nutrients from wastewater.

The reaction below shows a typical cation exchange reaction between liquid and solid phase. In this reaction R- presents the functional group on the surface solid phase, while A^{n+} and B^{+} are cations. During ion exchange process, B^{n+} will be moving from liquid phase to solid phase while A^{+} will move in the other way until equilibrium is reached between the two phases.

$$B^{n+} + n(R^{-})A^{+} \leftrightarrow nA^{+} + (R^{-})nB^{n+}$$

(liquid phase) (solid phase/resin) (solution) (solid phase/resin)

The ion exchange reaction usually is a reversible reaction, that means the exchanged ions can be put in back to the liquid phase by changing reaction conditions. Usually the ion exchange process will continue in the direction between solid and liquid phase in which the ion concentration is smaller.

Resins used in ion exchange processes can be classified as anionic and cationic. The resin is a non-soluble material that will carry either exchangeable anions or cations. Figure 3.1 shows the resin used for cation removal contains fixed anions on its surface

on to which exchangeable cations are attached. The ion exchange reaction starts once the liquid phase comes in to contact with the resin and continues till it reaches equilibrium.

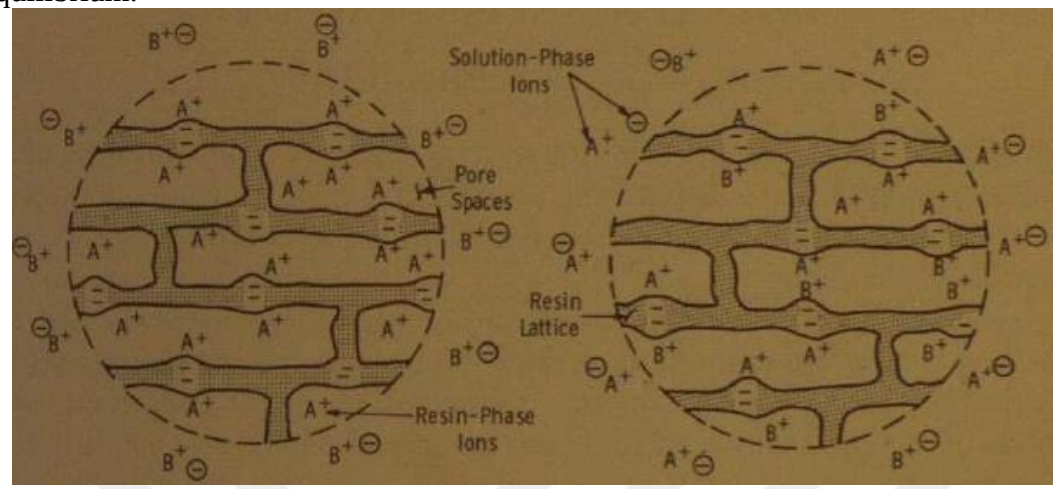

Figure 3.1 : Exchange of cations during cation exchnage process (Weber, 1972).

Resins used in ion exchange processes can be classified as anionic and cationic. The resin is a non-soluble material that will carry either exchangeable anions or cations. Figure 3.1 shows the resin used for cation removal contains fixed anions on its surface on to which exchangeable cations are attached. The ion exchange reaction starts once the liquid phase comes in to contact with the resin and continues till it reaches equilibrium.

Ion selectivity can be defined as the preference of the resin towards a specific ion as compared to another. Each resin has a selectivity that makes the exchanging ability with an ion more preferable than another one. Ions of the same charge present in a solution in the same concentration can be removed from the solution according to the ion selectivity of that resin. The selectivity of resin depends on a number of factors, ions' charge, size, interaction of ions with resin and exclusion of ions by screening or sieving action (Weber, 1972). The ion exchange process is strongly dependent on the following steps:

1- Transport of exchangeable ions from liquid phase to the external surface of resin;
2- Film layer transport of ions from liquid phase to resin;
3- Pore diffuse of exchangeable ions from liquid phase toward active charge sites in the resin;
4- Real exchange reaction;

5- Pore diffuse of the exchanged ions from resin toward liquid phase;
6- Film layer transport of ions from resin;
7- Transport of exchanged ions from resin's external surface to liquid phase;

Two of the previous seven steps are controlling the ion exchange process, both of them are in terms of diffusion. The ion diffusion through the film of liquid around the resin's particle and the diffusion of ions through resin's pores (Weber, 1972).

3.1.2. Factors affecting adsorption/ion exchange

The factors affecting the adsorption/ion exchange process can be listed as, the structure of the adsorbent, the structure of the adsorbate, temperature, pH, the presence of other adsorbates (Weber, 1972).

As adsorption is a surface phenomenon, the adsorption/ion exchange capacity is proportional to the specific surface area of the adsorbent. The specific surface area is the total surface area where adsorption reaction occurs. The smaller the particle size of the adsorbent the more the number of pores, thus increased surface area. In the case of large pores, the surface of the adsorbent is used by the large size adsorbate, whereas in the case of small pores, the retention of large molecular size adsorbates increases. Adsorption shows differences according to adsorbate nature. There is an inverse ratio between the solubility of the adsorbate in solution and the amount of adsorption. As the solubility of the adsorbate increases, the adsorption decreases. The molecular size of the adsorbate also affects the adsorption. The distribution of the adsorbate in the adsorbent differs according to the size distribution of the adsorbate according to the molecular size. A large molecule size adsorbate is less adsorbed in an adsorbent with smaller pores. Regarding the pH, the hydrogen and hydroxyl ions present in the medium affect the adsorption. Adsorption/ion exchange process is an exothermic process and it is a process affected by temperature. The activity of the adsorption process increases when the temperature decreases (Weber, 1972).

Considering the ion exchange/ adsorption process for nutrient removal/recovery from source separated human urine using clinoptilolite as adsorbent or ion exchanger, the pH of the liquid phase affects the process in terms of exchanging for specific ion. In case of removing nitrogen from human urine in form of ammonium, the clinoptilolite is known for its affinity for exchanging for ammonium. In case the pH of urine is lower than 8.5 the ammonium percent will be higher compared to ammonia, thus more potentials for removing nitrogen in form of ammonium.

Water and wastewater treated in environmental engineering are generally mixtures containing different substances for this reason the adsorption/ ion exchange process used for treatment of water and wastewater is effected by the presence of this mixture of substances. When adsorption is performed in pure solutions, adsorption activity of the adsorbents is high because surfaces available for adsorption are used by only one substance. In the presence of other substances in solution, different substances or adsorbates will compete to be adsorbed on the surface. In this case a portion of the adsorption capacity is used by these substances and the capacities in the pure solution cannot be reached. For this reason, targeted capacities cannot be obtained through pure solution results for the desired pollutant when the liquid phase is a mixture.

Regarding using adsorption ion exchange for removal/recovery of nutrients from human urine, it was reported by Beler Baykal et al. (2009) that the removal of plant nutrients from human urine using clinoptilolite as ion exchanger during adsorption/ion exchange process was effected by initial loading. In the same study different initial loadings were used to investigate its effect on the removal of ammonium and potassium. Initial loadings of 5 – 30 mg NH_4/g clinoptilolite and 1 – 8 mg K/g clinoptilolite were used. It was observed that up to an initial loading of 10 mg NH_4^+/g clinoptilolite, removal of ammonium and potassium was unaffected and removal efficiencies of 94% for ammonium and 99% for potassium were obtained and both plant nutrients remaining in liquid phase solution were low. Up to 15mg NH_4/g clinoptilolite loading, removal efficiencies were at an acceptable level with 84% and 91% for ammonium and potassium, respectively. Increases in the initial loading higher than 15mg NH_4/g clinoptilolite led to higher surface concentrations on the zeolite but resulted in significant reductions in the removal efficiencies, leaving considerable amounts of ammonium and potassium in the liquid phase.

In another study, in which phosphorus removal from human urine with different initial loadings ranged 0.26 – 1.35 mg PO_4/g clinoptilolite was investigated, it seems that initial loading did not impose any noticeable effect on the removal efficiency, with initial loading ranging 0.26 – 1.35 mg PO_4/g clinoptilolite the removal efficiency ranged from 95 – 99% (Allar & Beler-Baykal, 2013).

3.1.3. Zeolite and clinoptilolite

Zeolite is natural material which was discovered first in 1756 by A. F. Cronstedt, a Swiss mineralogist. During the 20th century, experiments were conducted on its separation properties and possible uses for field application. Natural zeolite is formed in volcanic regions and sedimentary rocks, the diversity of zeolite structure is related to the structure and composition of the original rocks, pressure, temperature, and water content. Around 40 types of natural zeolites exist today. Beside natural ones, zeolites had been synthesized and produced on an industrial basis, today there are 150 types of synthetic zeolites (Sadeghbeigi, R.; 2012).

Clinoptilolite, mordenite, phillipsite, chabazite are types of natural zeolite. Faujasite, zeolite A, and ZSM-5 are types of synthetic zeolite. (Sadeghbeigi, R. 2012; Dogan G. 2015). The world reserve of natural zeolite is not well determined ,however (Polat et al., 2004) reported that during 2001, 3.5 million tons of zeolite was used worldwide, with 18% of this consumption coming from natural zeolite. Natural zeolite mining dramatically increased in 2010 with an estimate of 5.5 million tons (Ozaydin et al., 2006). U.S. Geological Survey, (2011) estimated values for the prduction of zeolite from mines around the world as shown Table 3.1.

Table 3.1 : Estimated zeolite mine productione (U.S. Geological Survey, 2011).

Location	Production (ton/year)
China	2,000,000
Jordon	425,000
Republic of Korea	165,000
Japan	155,000
Turkey	100,000
Slovakia	90,000
United State	59,500

Zeolite is classified based on its content of alumina and silica, the classification is based on the ratio between these two elements. Low, intermediate and high ratio of Si:Al was established with values starting from 1-1.5 for low ratio, 2-5 for intermediate and from 10 up a ratio of thousands for high Si:Al ratio (Tsitsishvili et., 1992). According to another study that used another approach to classify zeolites, zeolites were classified

based on the pore size to small, medium, large and extra-large (Flanigen, 2001), Figure 3.2 shows the classification of zeolites that is available in the literatures.

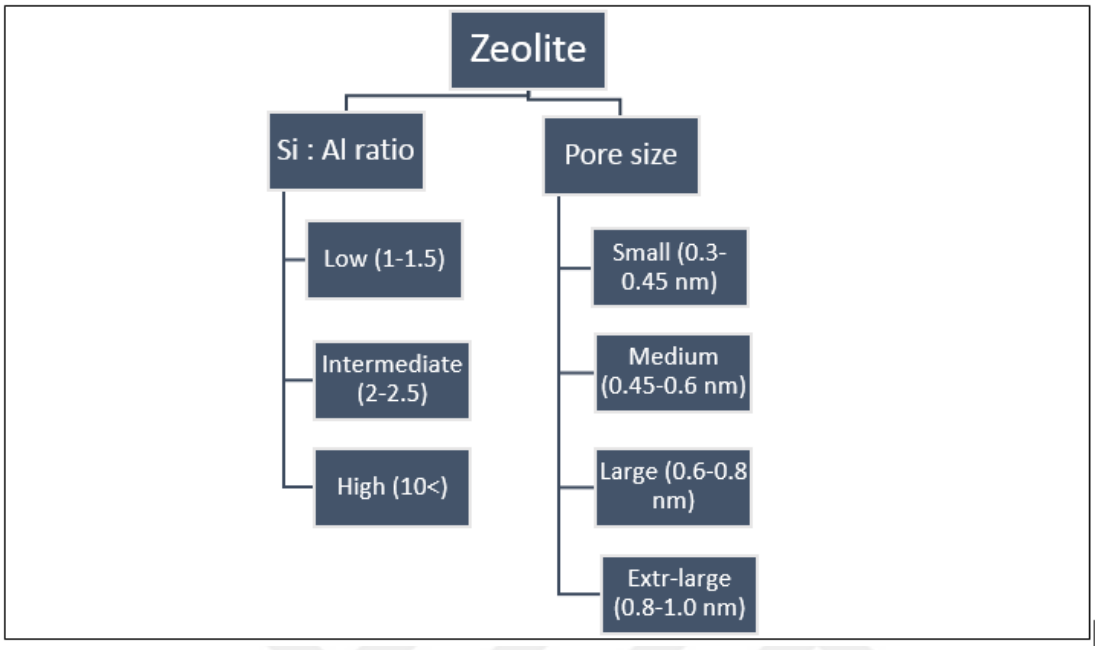

Figure 3.2 : Zeolite classification (Tsitsishvili et., 1992; Flanigen, 2001).

Zeolite is widely used in many industrial applications, due to its availability as a natural or synthetic material. Mainly used as an ion exchanger or adsorbent, application field of zeolite include pollution control, agriculture, energy and mine metallurgy (Yurtoglu, 2007). The use of zeolites in environmental engineering for pollution control includes:

- Nitrogen removal from domestic and industrial wastewater.
- Separation of heavy metals
- Water softening
- Oil spills and cleaning in water bodies
- Remove and recovery of radioactive materials from radioactive waste.
- Carbon dioxide and other pollutants in gaseous for example from oil and coal plants chimneys.

Zeolite can be used as a catalyst for separation of CO_2 and water from gases. Zeolite is used in agricultural application due to properties of cation exchange, selectivity towards ammonium and potassium and high porosity. Zeolites can be used as a soil conditioner because it can gain and lose water without any change in its crystal structure. Many studies showed that zeolite can be used as a carrier and medium for nutrients. The application field of zeolites in agriculture are listed as, organic manure

management, phosphorus and nitrogen management, slow release of nutrients and herbicides, remediation of contaminated soil, soil amendment and improvement of soil physical properties. Zeolite is used with animals' food as a mixture that contribute to weight increment of the animals without adverse health effect (Sangeetha & Baskar, 2016).

Clinoptilolite is a natural zeolite that was discovered late in the 19th century. It contains a microscopic structure of silica and alumina tetrahedral. The typical chemical formula of clinoptilolite shown as $(Na,K)_6Al_6Si_{30}O_{72}.20H_2O$. Beside silica and alumina, clinoptilolite contains cations like, Na, Ca, K, Sr, Mg, and Ba (Breck, 1974). Clinoptilolite is classified as a part of the heulandite group, but the ratio of Si to Al is $4 < Si:Al < 5.2$ which is different than that of heulandite, $Si:Al < 4$ (Mansouriet al., 2013), which makes the clinoptilolite classification in the heulandite family doubtful. The temperature stability of clinoptilolite is another feature that makes clinoptilolite classification under this group is uncertain, clinoptilolite maintains thermal stability under a temperature up to 800°C, while heulandite thermal stability is under a temperature up to 550°C (Mansouriet al., 2013). According to Bozoglu, A. (2010), the majority of the clinoptilolite reserves can be found in the Balkan region and USA.

The application of clinoptilolite is not different from the application of zeolite, clinoptilolite can be used in protection of the environment, mainly due to its ion exchange properties. These applications help in removal of ammonium, hardness ions, heavy metals and radioactive substances. The use of clinoptilolite in agricultural applications is wide spread. Clinoptilolite can be used as carriers of different useful substances like plant nutrients, pesticides, insecticides, growth simulaters and antibacterial agents for implemintation of biological activity and fertility of the soil. Adding clinoptilolite to soil will aid in increasing yield capacity, enhancing the nitrogen balance in snad and light soil. Part of its application is to remove harmful materials from soil like heavy metal or toxic substances. Clinoptilolite can be used as a source of minerals in animals' food, and it is suitable for ammonia removal in fish breeding ponds. Clinoptilolite has a water holding capacity, in which its addition to the soil will provide a control for the moisture content in the soil that eventually provides water to the plant during dry periods (Rehakova et al., 2004). Clinoptilolite is also used in the energy sector in gas separation processes and as a gas adsorbent in gas purification to adsorb CO_2, SO_2 and water (Ozaydin et al., 2006).

3.2. Anaerobic Metabolism / Processes

3.2.1. Developments of anaerobic process

Anaerobic metabolism or process is the biological degradation of organic compounds by microorganisms in the absence of oxygen. It is different than aerobic metabolism in which oxygen is an important element for degradation of organic compounds. In the nature there are locations where oxygen is absent like, swamps, near the bottom of oceans and ponds.

In the 18th century, specifically in 1776, it was discovered by Volta that the anaerobic process helps in degradation of organic compounds and as a result methane will be produced and methane was described as a "combustible air". The 19th century witnessed the first full scale anaerobic system for treating domestic wastewater in France, and by 1897 methane obtained from the anaerobic process was utilized for heating and lighting purposes. With the beginning of the 20th century, the rule of methane as an energy source became more recognizable. In 1923, in Germany methane was collected from septic tanks on a large scale basis and transported to the municipal gas system at Essen-Rellinghausen plant. During 1920s and due to the contributions of A. M. Buswell and his team, the application of anaerobic processes was introduced in industrial wastewater treatment and agricultural remainder. Till mid-20th century, the application of anaerobic processing for wastewater treatment was limited because of the failure to understand the fundamentals of this process. In 1950s and by understanding the sludge retention time (SRT) and hydraulic retention time (HRT) related to anaerobic processing, the application of anaerobic processing became wider and used for industrial wastewater treatment and biogas recovery. Most of the researches used anaerobic processes for wastewater treatment was based on the use of Imhoff tank or septic tank, till 1972 when the first full scale anaerobic biofilm reactor was reported for wheat starch wastewater treatment. It was considered that the most successful anaerobic reactor design that for application was appropriate for both industrial and municipal wastewater treatment was the upflow anaerobic sludge blanket reactor that was described by Lettinga during 1970s (McCarty, 2001; Khanal, 2011).

3.2.2. Mechanism of anaerobic process

Anaerobic degradation of organic compounds leads to the production of biogas that contains a mixture of gases. The most important component of the biogas is methane (CH_4) that can be recovered and transformed to electricity or can be used for heating and cooking purposes. To reach the final end product, there are interconnected steps and stages that organic compounds must undergo. Anaerobic degradation of organic matter in known as a multiple stage process in which the organic matter is reduced to different simpler organic compounds till generation of methane, carbon dioxide and treated effluent. Anaerobic degradation of organic compounds to CH_4 and CO_2 is an exceptionally complex interaction of multiple stage processes of parallel and sequential reactions performed by different groups of microorganisms (Khanal, 2011).

It was understood at the beginning of that anaerobic process mainly consists of two stages. In first stage, anaerobic and facultative bacteria convert complex organic compounds into a smaller and simpler organic compounds. Usually, proteins, carbohydrates, and lipids are converted during this stage to volatile fatty acids, carbon dioxide and hydrogen gases by hydrolysis and fermentation. In the second stage, by the metabolic activity of a methanogens archaea using the acids produced in the first step, hydrogen and organic acids from the first step will be converted to methane and carbon dioxide (De Lemos Chernicharo,2007), as shown in Figure 3.3.

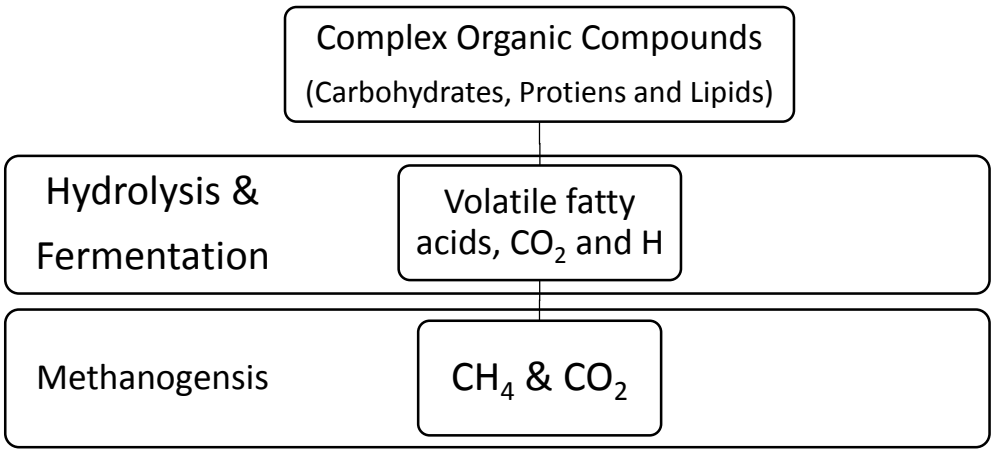

Figure 3.3 : Two stage of anaerobic process (two stage model).

Mainly the anaerobic process consists of four main stages which in turn consist of sub stages that will lead to different products (Van Haandel & Lettinga**,** 1994; Henze et at., 2008**)**, those four main stages are:

- Hydrolysis
- Fermentation (Acidogens)
- Acetogenesis (Anaerobic oxidation)
- Methanogenesis

- Hydrolysis

Bacteria is incapable to utilize organic material in a particulate form; thus hydrolysis step solves this problem by converting the particulate organic compounds to dissolved organics. Protein and carbohydrates are converted to amino acids, while lipids are mainly converted to fatty acids which are in the dissolved stage. The hydrolysis stage is carried out by exoenzymes that are generated by fermentative bacteria. This step is important due to need for the presence of dissolved organic compounds for the formation of methane and carbon dioxide, thus the rate at which gas will be produced depends on the rate at which particulate organic material will be hydrolyzed. According to Gujer and Zehnder (1983) hydrolysis rate depends on a number of factors including particulate matter with large size, and low surface/volume ratio of the particulate which lead to slower hydrolysis. Different organic compounds like, protein, starch and cellulose are hydrolyzed at different rates. Presence of non-degradable materials like wax and lignin will hinder or slow down hydrolysis. Another study listed more factors that are related both to the nature of particulate matter and operational conditions. Temperature, pH, residence time, size and composition of organic particulate matter, and ammonium concentration were among those factors (De Lemos Chernicharo,2007).

- Fermentation (Acidogenesis)

Fermentation or acidogenesis is the second stage of anaerobic processing that is carried out by a number of different fermentative bacteria in which organic matter work both as electron donor and acceptor. The substrate of fermentation stage are sugar and amino acids, that will be converted to biomass, acetate, hydrogen and other products that are considered as intermediary products like propionate, butyrate and lactate.

- Acetogenesis (Anaerobic oxidation)

Acetogenesis or anaerobic oxidation is the third stage that will reduce products from fermentation stage and produce acetate and hydrogen. According to Gujer and Zehnder (1983), this stage will include anaerobic oxidation of fatty acids and intermediary

products from fermentation stage. Anaerobic oxidation of fatty acids will result in production of hydrogen. Anaerobic oxidation of the intermediary products from fermentation stage will produce eventually acetate and hydrogen that will turn at the end to methane.

- Methanogenesis

Methanogenesis is the last stage of the anaerobic process and it is divided to two parts methanogenesis of acetate and methanogenesis of hydrogen, the following reactions illustrate the conversion of acetate and hydrogen to methane

$CH_3COO^- + H2O \longrightarrow CH_4^+ + HCO_3^-$ (acetate to methane)

$CO_2 + 4H_2O \longrightarrow CH_4 + 2H_2O$ (hydrogen to methane)

Acetate conversion to methane makes about 70% of the methane production, for this reason acetate is the major element of methane production, while hydrogen conversion contributes about 30%. (Van Haandel & Lettinga**,** 1994). The rate limiting reaction of the whole anaerobic process is methanogenesis and this is attributed to the sensitivity of the microorganisms involved at this stage to changes in the environment.

More studies were conducted to emphasize the degradation of organic compounds in anaerobic process. In 1983 Gujer and Zehnder described more complicated steps of degradation of organic compounds under anaerobic processing and according to this study anaerobic degradation is a multiple stage process. Figure 3.4 illustrates the stages of an anaerobic process. Organic compounds will undergo the following stages:

- Hydrolysis of protein, lipids and carbohydrates
- Fermentation
- Conversion of long chain fatty acids and alcohol to simpler compounds by anaerobic oxidation
- Anaerobic oxidation of volatile fatty acids
- Acetate conversion to methane
- Hydrogen conversion to methane

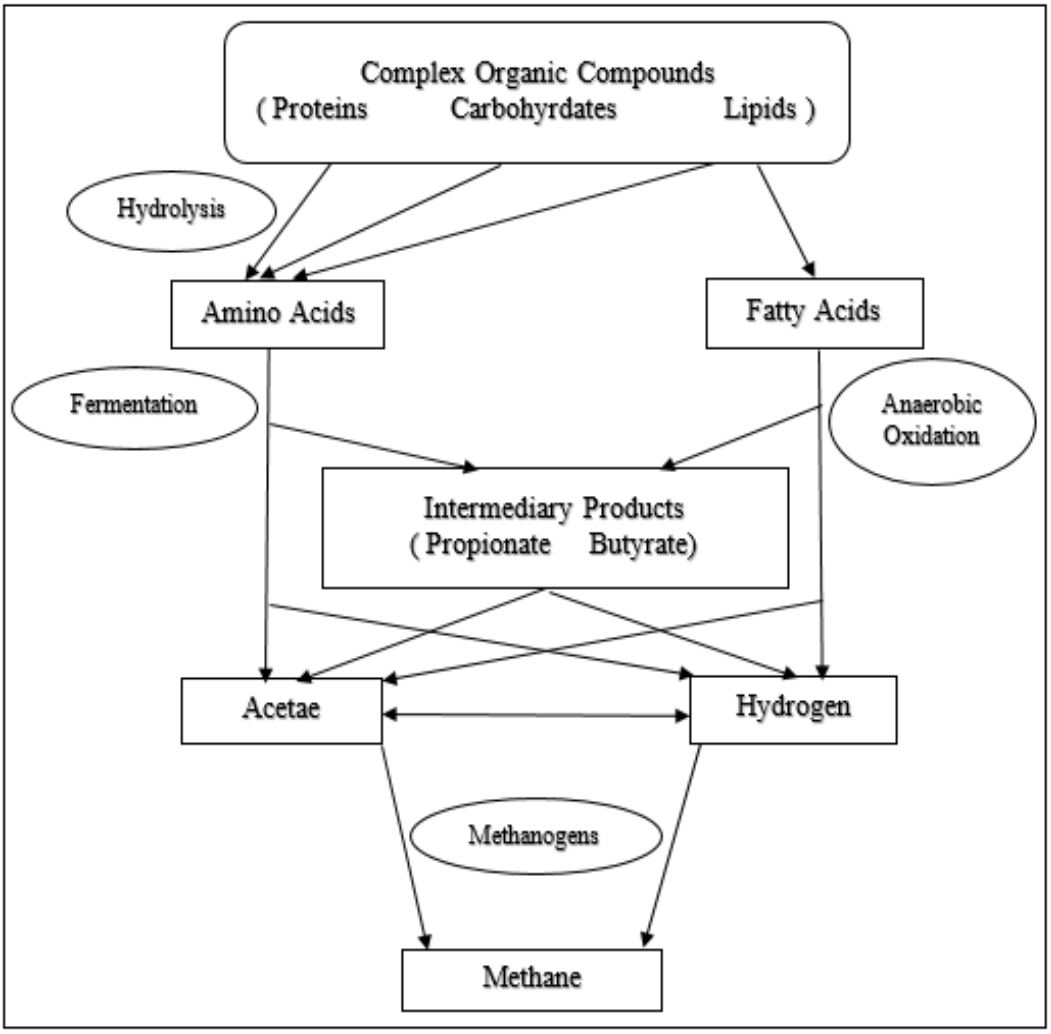

Figure 3.4 : Organic compounds degredation in anaerobic process – mutiple stage model (adopted from Gujer and Zehnder (1983)).

Another study went further in describing more stages and steps in anaerobic processes, Harper & Pohland (1986) and Malina & Pohland (1992) described 9 steps of anaerobic processes that included the action of sulfate reducing bacteria (SRB), nitrate reducing bacteria (NRB) and homoacetogens, those 9 steps are:

- Hydrolysis
- Fermentation
- Rule of OPRA (Obligate Proton Reducing Acetogenic) bacteria in oxidation of butyric and propionic acids and alcohol.
- Acetogenic respiration of bicarbonate
- Rule of NRB and SRB in oxidation of butyric and propionic acids and alcohol.
- Rule NRB and SRB in oxidation of acetic acid

- Rule NRB and SRB in oxidation of hydrogen
- Methane formation from acetate
- Methanogenic respiration of bicarbonate

3.2.3. Microorganisms participating in anaerobic process

Anaerobic process is a complex and multi stage process in which many types of microorganisms are involved to work together to achieve the end product of this process. Studies were conducted to classify the different types of bacteria in anaerobic processes according to the stages that they are involved in. Mainly the classification which is given below as was published by Gujer and Zehnder (1983) and Khanal (2011) was based on five different groups.

- Fermentative bacteria

This bacteria group handles the first and second stages (hydrolysis and acidogenesis). During the hydrolysis process, this group is responsible for production of enzymes that will hydrolase complex organic compounds to smaller molecules that will be transported to the inside part of the bacteria cells and produces different products through fermentation. Carbohydrates are degraded by *Acetovibrio cellulities*, *Bacteroides Clostridium and Staphylococcus*. Proteins are degraded to amino acids by proteolytic bacteria. Other types of fermentative bacteria like *Bacteroides*, *Micrococci* and *Sarcina* facilitate the degradation of neutral fatty acids to fatty acids, aminoacids, sugar and alcohol.

- Hydrogen producing acetogenic bacteria

This group of bacteria is active in the acetogenesis stage and it is usually known as obligate hydrogen producing bacteria or shortly OHPA. The significant role of this group of bacteria for anaerobic process is demonstrated by their metabolic activity that mainly focuses on catabolizing the long carbon chain acids (C3 and higher organic compounds) to acetate, CO_2 and H_2.

- Hydrogen consuming acetogenic bacteria

This group of anaerobic bacteria plays an essential rule in anaerobic processes due to the final product of their metabolism which is acetate. *Hydrogen consuming acetogenic bacteria* or *homoacetogenic* use the available CO_2 and H_2 in producing acetate. This group of bacteria work on the conversion of butyrate and propionate to acetate ad hydrogen.

- Methanogenic bacteria

The microorganisms in this group are rather classified as archaea than bacteria. This group is considered as a rate limiting group in anaerobic processes. Methanogens archaea can be found in organic rich anaerobic environments like ponds, swamps, marine and lake sediments. The methanogens archaea are classified as acetoclastic and carbon dioxide-reducing methanogens. The metabolic activity of this group mainly focuses on converting acetate and carbon dioxide to methane as explained in methanogenesis stage previously. *Methanothrix* and *Methanosarcina* are responsible for utilizing acetate while *Methanobrevibacter*, *Methanospirillium* and *Methanobacterium* are responsible for utilizing hydrogen.

- Sulfate reducing bacteria

The presence of this bacterial group in anaerobic culture is usually in relation with methanogens archaea. Sulfate reducing bacteria produce hydrogen and sulfate, and they compete with methanogens for acetate. It is recognized that in anaerobic environments three types of sulfate reducing bacteria may exist, *Desulfobulbus*, *Desulfotomaculum* and *Desulfovibrio*. In case sulfate exists in wastewater, sulfate reducing bacteria will tend to produce sulfide which is considered toxic for methanogens. The competition between sulfate reducing bacteria and methanogens can inhibit methane formation in high sulfate concentration.

3.2.4. Advantages and disadvantages of anaerobic process

A number of advantages and benefits compared to other treatment concepts like aerobic process are listed below (McCarty, 1964; Malina & Pohland, 1992; McCarty, 2001):

- No need for aeration or oxygen supply
- Low sludge production
- Biogas (methane) production with potential of use for energy recovery that can be used for heating, lighting, and cooking
- High removal efficiency
- Lower nutrition supplement requirement

On another hand the disadvantages that may put limitations for the applications of anaerobic process application can be due to that anaerobic processes requiring long startup periods, no phosphorus and nitrogen removal, sensitivity of anaerobic microorganisms to effect of low temperatures, sensitivity to toxic substances, odor

production, corrosive gases, requirements of further treatment in case it was used for concentrated wastewaters in terms of COD, alkalinity addition may be required and suitability of the anaerobic process is still questionable for dilute wastewater for sufficient methane production (McCarty, 1964; Feilden 1983).

3.2.5. Organic content and wastewater suitability

The applicability of anaerobic process to treat a specific wastewater stream depends on the characteristics of the wastewater. Nature of the wastewater will ensure if anaerobic process is a suitable treatment method or not, and will affect both economic and technical aspects. A number of factors had been listed in literature to test the suitability of wastewater to be treated by anaerobic processes. Malina & Pohland (1992), mentioned factors required for selection of anaerobic process to be appropriate for wastewater treatment. Among these factors, concentration and nature of organic matter, suspended solid concentration, presence of substances which are toxic to anaerobic bacteria, wastewater temperature, required removal efficiency, biogas and sludge production were listed. In the literature and according to these values the following wastewater streams are suitable candidates for anaerobic processing including wastewater from industrial sectors. Wastewater from dairy processing, fruits and vegetables, alcohol distilling, landfill leachate, pulp and paper, sugar processing, seafood processing, manufacturing of chemical products, beverage and breweries, and slaughterhouses, are to make an appropriate applicant for anaerobic processes and methane production.

Organic matter concentration is a key factor for the applicability of anaerobic processes. In general, the presence of high biodegradable COD is taken as an indication that the wastewater is more appropriate for the anaerobic process. It is indicated that the suitable COD range for anaerobic processes is 2000 – 20000 mg/l (Malina & Pohland, 1992; Khanal, 2011). It can be true also that any wastewater with a COD concentration between 1500 – 2000 mg/l will be suitable for anaerobic process as this COD concentration will be sufficient for biogas production (Tchobanoglous et al., 1991, Metcalf and Eddy, 2003). However, studies conducted on wastewater streams in which COD concentrations were out of the mentioned range revealed that anaerobic treatment can still be accomplished. Diluted and concentrated wastewater like municipal wastewater and rum production industry wastewater respectively were treated with anaerobic processes, in which the COD concentration were out of 2000 -

20000 mg COD/l range, and the performance of the anaerobic systems in these studies was reasonably successful (Schellinkhout and Collazos, 1992; Draaijer et al., 1992; Yoochatchaval et al., 2008; Yang et al., 2018).

3.2.6. Factors effecting anaerobic process

Anaerobic processes are severely sensitive to the conditions of surrounding environment, as it demands a simultaneous interaction between all the microbial groups in order to perform a complete anaerobic degradation of organic compounds. Studies were conducted to understand the environmental factors that affect anaerobic processes. Studies have revealed each wastewater stream may impose its effect on anaerobic bacteria but generally the following factors limit the performance of anaerobic bacteria. Temperature, pH, nutrients, alkalinity, volatile fatty acids, sulfide, heavy metals, salinity as presented by the existence of salts are factors that should be maintained in a proper balance to ensure suitable environmental conditions for anaerobic bacteria. Investigation regarding salinity which constitutes a major part of this work is very limited. The excess of one or a group of these factors may be toxic or inhibitory to the activity of one or the whole anaerobic microbial culture.

Temperature

Anaerobic process is a temperature dependent biological process, in which the microbial culture is affected by the temperature changes of the surrounding environment. Methanogens are the microorganism group affected the most by this factor. The range that methane can be produced at is very wide from 0°C to 97°C (De Lemos Chernicharo,2007). However, there are three temperature ranges recognized for methanogens to work in, psychrophilic, mesophilic and thermophilic conditions. Methanogens archaea will give optimum performance at the temperature range 5 – 15°C for psychrophilic, 35 – 40°C for mesophilic and about 55°C for thermophilic conditions with different growth rates as indicated in Figure 3.5 (Cheremisinoff, 1997; Lettinga et al., 2001).

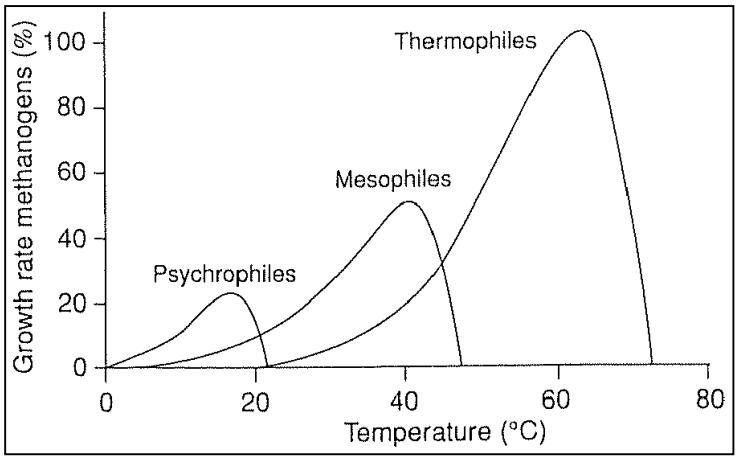

Figure 3.5 : Methanogens growth rate at different temperature rates (Lettinga et al., 2001).

Pohland (1992) indicated that anaerobic degradation of organic compounds will increase with the increase of temperature as high as 60°C. As a rule of thumb the anaerobic activity will increase with each 10°C increment in temperature and 11% decrease in the digestion rate is expected with each 1°C below the optimum temperature range (Khanal, 2011). The temperature changes from optimum condition affects the biogas production, and it could lead to 80% reduction as the case discussed by Speece (1983) when the temperature dropped from 35 to 25°C. In the same study it was indicated that the microbial activity and biogas production will recover immediately as soon as the optimum temperature is maintained again (Speece; 1983).

The majority of the anaerobic reactors are designed to work under mesophilic condition, although thermophilic has some field applications but the results of this practice was not satisfactory. The reasons were attributed to high heating requirement and process instability that will lead to poor effluent quality (De Lemos Chernicharo,2007).

pH

The methanogens group is very sensitive to pH level of the environment; it is reported that the optimum pH level for the anaerobic process to produce methane is between 6.8 – 7.4. In anaerobic microbial culture, bacteria can be grouped according to the sensitivity to pH, acidogens bacteria that works under pH levels of 5.5 – 6.5 and methanogens archaea that works under the pH level of 7.8 – 8.2. The mixed culture of these two groups work under the optimum pH level of anaerobic process (Speece 1983, 1996; Khanal, 2011). Since methanogenesis is the rate limiting step, the pH level should be maintained in a level that allow this step to perform at the best condition as

acidogens has a lower pH sensitivity compared to methanogens. Figure 3.6 shows the relation between pH and the methanogens activity. It clearly illustrates that the methanogenesis step will be inhibited at a pH level higher than 8 mostly due to the ammonia inhibition as the nitrogen in ammonium form will shift to ammonia at pH values over 8. It was reported by Speece (1996), that the methanogens archaea will perform at 25% activity if it was operating under low pH level. The recovery time for methanogens to restore its activity if it was working under low pH values is considerable (Khanal, 2011).

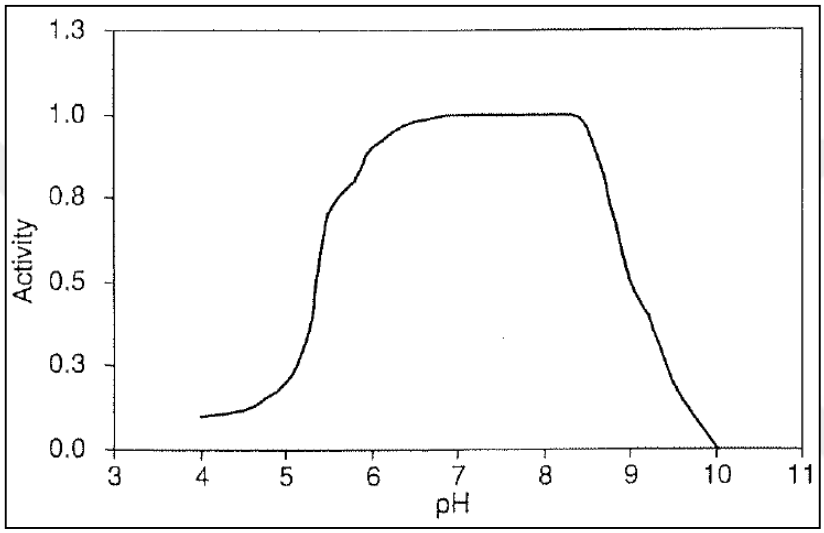

Figure 3.6 : Methanogens activity under different pH levels (Speece, 1996).

Alkalinity and volatile fatty acids

Alkalinity and volatile fatty acids are interconnected factors of anaerobic processes. Their relation is established based on the neutralization ability and pH buffering that alkalinity impose in case of accumulation of volatile fatty acids occur.

Volatile fatty acids and alkalinity both result from the decomposition of organic matter during anaerobic processes. In anaerobic systems, volatile fatty acids are produced due to the degradation of complex organic matter from acidogens stage, while production of alkalinity occurs from degradation of protein substrate that contains organic nitrogen which break down to ammonia. The combination of ammonia resulting from protein degradation and carbonic acid in wastewater will produce ammonium bicarbonate (NH_4HCO_3) that will act as a buffer. The activity of this buffer can be neglected at pH level 6 – 7.5 (De Lemos Chernicharo, 2007). The two following reactions illustrates the degradation of volatile fatty acid like sodium acetate with formation of sodium

bicarbonate and formation of ammonium which is resulted from protein degradation with carbonic acid.

$CH_3COONa + H_2O \rightarrow CH_4 + CO_2 + NaOH \rightarrow CH_4 + NaHCO_3$ (sodium acetate degradation)

$NH_3 + H_2O + CO_2 \rightarrow NH_4 + HCO_3$ (ammonium bicarbonate formation)

The drop in pH of anaerobic systems is usually related to the excessive accumulation of volatile fatty acids and carbon dioxide and acetic acids is known to have a small toxic effect compared to propionic acids that are usually recognized as a main system failure in anaerobic systems. The pH drop will inhibit the methanogenesis stage and then an inhibition of anaerobic process and no methane production will be observed. To overcome this problem, it is recommended to reduce the organic loading rate (OLR) or addition of external alkalinity sources that will buffer the system for the required pH level. Reducing the OLR to the level in which the volatile fatty acids decomposition is faster than its generation will help the anaerobic system to recover from pH drop after excess volatile fatty acids are consumed. In some extreme cases the reduction of OLR must be joined with addition of chemicals for recovery of the system to the desired pH level (Khanal, 2011).

The stability of anaerobic process can be arbitrated by the ratio of volatile fatty acids to alkalinity. A ratio of 0.1 – 0.25 described as the favorable condition for anaerobic systems, while a ratio of 0.3 – 0.4 will rise an alarm for taking a correction or adjustment action. In case a ratio of 0.8 is observed, it will result in a strong drop in pH and an inhibition of methanogenesis stage (Khanal, 2011).

In case supplying alkalinity is required to eliminate the volatile fatty acids action on pH drop, an evaluation of alkalinity addition should be made for applicability and economic prospective (Van Haandel & Lettinga**,** 1994). Different sources of chemicals can be used as a source of alkalinity like, ammonium, potassium or sodium hydroxide, sodium carbonate, sodium bicarbonate, lime, gaseous ammonia. Lime option is preferred mostly due to cost over sodium bicarbonate even though the addition of sodium bicarbonate will increase the pH directly, and has a high solubility. The use of lime does not impose a threat of calcium toxicity in anaerobic systems but create a scaling issue in bioreactors (De Lemos Chernicharo, 2007; Khanal, 2011).

Nutrients

Macronutrients

The microorganisms involved in anaerobic process like any other bacteria that require nutrients for their metabolic activity. Nitrogen and phosphorus are considered as macronutrients that should be supplied at sufficient amounts to support microbial growth. Two C:N:P ratios are used to estimate the amount of nitrogen and phosphorus required for anaerobic processes based on the strength of the wastewater. 350:5:1 ratio is used for high strength wastewater and 1000:7:1 is used for light strength wastewater (Henze and Harremoes 1983; Ammary, 2004; Khanal 2011). Nitrogen is supplied in the form of urea, ammonium chloride, ammonia, while phosphorus is supplied as phosphate salts and phosphoric acid. Table 3.2 illustrates the required amounts of macro nutrients for anaerobic processes. The minimum required amount of nitrogen should be between 40 – 70 mg/l (Lettinga et al, 1996), although it is noted that 50 to 200 mg/l of total ammonia nitrogen will be beneficial for anaerobic systems (McCarty, 1964).

It was reported by Suschka & Grübel, (2014) and Yang et al. (2018) that ammonium release during anaerobic processing may be observed. The ammonium release was attributed most probably to anaerobic hydrolysis of the organic nitrogen in the feed. In Yang et al. (2018), it was reported that the organic nitrogen was completely converted to ammonia form with a change from an average of 8.4 NH_3-N/l in influent to 17.5 - 20.5 mg NH_3-N/l at the effluent in which synthetic wastewater used to simulate domestic wastewater.

Phosphorus seems does not to impose any thereat if it exists in more than what is required but at least a sufficient amount to match the C:N:P ratio should be provided.

Sulfur is another element required for anaerobic processes, methanogen group utilizes sulfur in form of sulfide, even in the presence of inorganic sulfate it will be reduced to sulfide then will be used by the methanogens group. Sulfur is important for the bacterial growth and it is indicated that the required amount of it is similar to that of phosphorus (De Lemos Chernicharo, 2007). It is reported that the required amount of sulfide for optimal conditions of methanogens activity to degrade organic compounds is 1 – 25 mg/l (Speece, 1983).

The anaerobic process requires supplying of other elements like potassium, magnesium, calcium that are important for growth of bacterial cells. Regarding potassium, it is reported that a potassium concentration of 400 mg/l or less will obtain an improvement for the anaerobic process under both mesophilic and thermophilic conditions (Chen et al., 2008). Calcium is important for growth of methanogens, even though the research on the required amount of calcium that benefit the anaerobic bacteria is not common in literature, a concentration of 100 to 200 mg/l will be beneficial for growth and granulation of anaerobic sludge (Yu et al., 2001). Regarding magnesium, it was reported that concentrations below 400 mg/l will not inhibit methanogens and provide a suitable condition for bacterial growth (Schmidt and Ahring, 1993). Table 3.2 provides the required amount of macronutrients that sustain anaerobic bacteria.

Micronutrients

In addition to macronutrients needed, a number of other elements are essential for anaerobic digestion, such elements make about 4% of the bacterial cell dry weight (De Lemos Chernicharo, 2007). It is not easy to state the required amount of these trace elements due to the presence of sulfide in wastewater. Sulfide existence lead to a loss in the concentrations of these micronutrients due to precipitation and leave very small amounts of them in wastewater (Khanal, 2011). Micronutrients include zinc, nickel, cobalt, iron, copper and manganese (Lettinga et al 1996; De Lemos Chernicharo, 2007). Table 3.2 provides the required amount of micronutrients that sustain anaerobic bacteria.

Table 3.2 : Macro and mirco nutrients requiremnt for anaerobic process (Lettinga et al 1996; De Lemos Chernicharo, 2007).

Macronutrients		Micronutrients	
Element	Value (g/kg TSS)	Elemnt	Value (g/kg TSS)
Nitrogen	65	Nickel	100
Phosphorus	15	Cobalt	75
Sulfur	10	Iron	1800
Potassium	10	Zinc	60
Magnisium	3	Manganese	20
Calcium	4	Copper	10

Toxicity and Inhibition

Anaerobic bacteria are sensitive to the changes in conditions of the surrounding environment, and as any biological process it has its own requirements of organic matter, macronutrients and micronutrients. The abundance of these elements may cause inhibition to anaerobic processes and some may be toxic that cease the whole anaerobic system. The ranges that these elements may cause inhibition is different and starts from a few mg/l to thousands mg/l. the inhibitory substances can be in organic or inorganic form.

Ammonia and Ammonium

Inhibition of ammonia and ammonium for anaerobic process was studied, and different concentrations in terms of free ammonia (NH_3), ionized ammonia or ammonium (NH_4^+), and Total Ammonia Nitrogen (TAN) was reported. Ammonia and ammonium usually exists in wastewater and in anaerobic process produced during the degradation of some organic compounds like proteins and amino acids. Both ammonia and ammonium exist in the same wastewater stream and their concentrations are related to the pH level of the wastewater. Ammonium dominates at low and neutral pH levels while higher pH levels will shift the concentration to ammonia as shown in Figure 3.7. The following reaction shows the relation between NH_4 and NH_3 and the relation with pH:

$$NH_4^+ \longleftrightarrow NH_3 + H^+$$

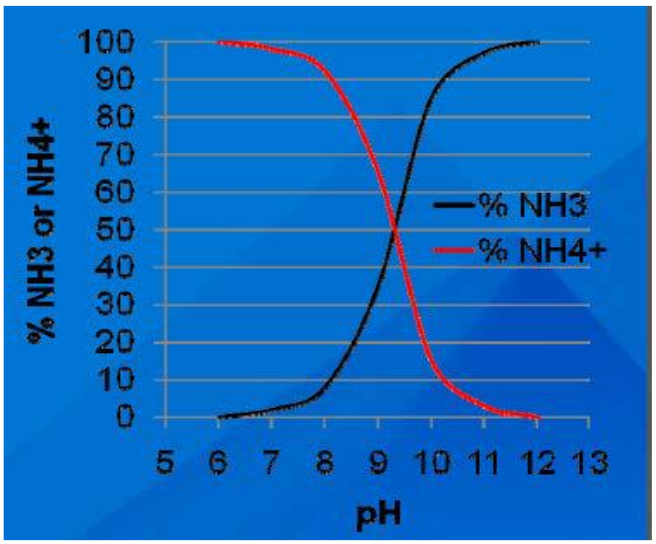

Figure 3.7 : Ammonia nitrogen form vs pH (Wendt, 2011).

Studies were conducted to investigate on which form of ammonia is the toxic for methanogens, and free ammonia (NH_3) had been suggested as the most toxic form (de

Baere et al., 1984). The toxic action of NH_3 was stated as NH_3 penetration through the cell membrane and diffusion causing a proton imbalance in the bacterial cell (Gallert et al., 1998). Most of the studies reported that 150 mg/l of free ammonia will be toxic to anaerobic methanogens (De Lemos Chernicharo, 2007; Khanal, 2011). Ammonium as well is an inhibitor to methanogens, and studies revealed that a concentration of 3000 mg/l will be the threshold for ammonium inhibition (McCarty, 1964; De Lemos Chernicharo, 2007; Khanal, 2011). Other studies reported the inhibition of ammonia in terms of TAN, wide range of concentrations were given in the literature that starts from 1500 mg/l to 7000 mg/l and some others observed a higher value that was up to 14000 mg/l (McCarty and McKinney, 1961; McCarty 1964; Zeeman et al., 1985; Koster and Lettinga, 1988; Gallert and Winter,1997; Bujoczek et al., 2000; Hejnfelt and Angelidaki, 2009). The wide range of ammonia inhibition in terms of TAN was attributed to different types of wastewater, to the required adaptation time and conditions of the environemnt (Hejnfelt and Angelidaki, 2009). Table 3.3 illustatres the different concentration and their effect on anaerobic processes.

Table 3.3 : Effect of ammonia concentration on anaerobic process (McCarty 1964; Khanal, 2011).

TAN (mg N/l)	Observed effect on anaerobic process
50-200	Beneficial
200-1000	No adverse effect
1500-3000	Inhibitory at higher pH values
Above 3000	Toxic

Volatile fatty acids

Volatile fatty acids either existing in wastewaters or it is produced in the acidogenesis stage of the anaerobic process. They are of short chain fatty acids usually C2 – C6. It is reported that the effluent of anaerobic process containing 50 - 250 mg HAc/l is usually considered as low and has no adverse effect on the anaerobic systems. (Sawyer, 2003). The reports about volatile fatty acids concentration that inhibit anaerobic systems was based on the presence of these fatty acids in correlation to other factors like pH, temperature, nutrients. It was reported that a concentration of above 2000 mg HAc/l will cause an inhibition to the methanogens. That was in contrast to some values of 10000 mg/l of acetic and butyric acids that do not impose any inhibition factor under pH value equal to 7, while propionic acids with 6000 mg/l concentration is inhibitory at the same pH value (Grady et al., 2000).

Sulfide

Sulfate in excess amount in wastewater imposes an inhibition act on anaerobic processes due to the competition of SRBs to acetate and hydrogen with methanogens to reduce sulfate to sulfide (Harada et al., 1994) and the indirect inhibition and toxicity of sulfide for different types of bacteria (Colleran et al., 1995).

Sulfide can be classified as soluble and insoluble sulfide, and also as hydrogen sulfide (gaseous form). The insoluble form of sulfide does not impose a harmful effect on the anaerobic microorganisms because it is insoluble and can precipitate out from solution (De Lemos Chernicharo, 2007; Khanal, 2011.). Sulfide in its soluble form is very toxic at concentrations of 100 - 150 mg/l (Speece, 1983; Speece 1996), In contrast to that range, a concentration higher than 200 mg/l is considered to be toxic in later works (Yamaguchi et al. 1999; Chen et al., 2014).

The sulfide inhibition significantly depends on the pH level and ratio of COD/SO_4. Under pH of 6.5 to 7 almost the dominant form of sulfide is H_2S that will exist at 50% of the sulfide form. A ratio of COD/SO_4 greater than 10 will not impose any threat of inhibition to the anaerobic processes, while inhibition starts to be observed at a ratio between $3 < COD/SO_4 < 10$, a ratio of COD/SO_4 smaller than 3 will definitely have an inhibition to the methanogens archaea due to the high competition on substrate between methanogens and SRB bacteria (De Lemos Chernicharo, 2007). Table 3.4 shows the COD/SO_4 ratios of the anaerobic process related to the inhibition level. The inhibition of acetoclastic methanogens by gaseous hydrogen sulfide was found to be more than 40% at a free H_2S level of 50 mg/l, increasing to 100% inhibition at 250 mg/l free H_2S.

Table 3.4 : Inhibition of sulfide for anaerobic process.

Soluble Sulfide (mg/l)	Effect on Anaerobic Treatment
50-100	Tolerable
100-200	Acceptable with acclimation
200 >	Toxic

Heavy metals

Heavy metals exist in wastewater resulting from industrial activities especially from metal industries. If they are found in a soluble form that cause will failure to anaerobic systems. A mixture of different heavy metals, cobalt, zinc lead, nickel, iron, copper can be found in wastewater. However, those heavy metals are required for specific functions for anaerobic microorganisms but at high concentrations could lead to inhibition of the microorganism activity (Khanal, 2011; Chen et al., 2014). The toxicity

of heavy metals to anaerobic bacteria follows the order reported by Khanal, (2011), which is Ni > Cu > Pb > Cr > Zn. The inhibition of heavy metals include the anaerobic bacteria involved in all the stages, acidogens, acetogens, and methanogens (Zayed and Winter, 2000; Karri et al., 2006; Li and Fang, 2007).

Regarding studies conducted on the evaluation of the toxicity of heavy metals, Ahring and Westermann, (1985) reported ranges of 10 – 2000 mg/l of nickel, 70 – 400 mg/l of copper, and 200 – 600 mg/l of zinc that cause toxicity of methanogens bacteria. Studies conducted later showed lower ranges that causes 50% toxicity for methanogens. Zayed and Winter, (2000) reported such concentrations to be 60, 40, and 10 mg/l for nickel, zinc and copper respectively and in the same study the researchers believed that acidogens showed more tolerance to these concentrations than methanogens.

Salinity and effect of cation

Inhibition by salts is possible in anaerobic processes. It is usually related to cations including calcium, potassium, magnesium and sodium. Table 3.5 include inhibitory concentrations of cations mentioned that was reported by McCarty (1964). The studies about the calcium toxicity or inhibition is very limited. Even with the reported values, calcium toxicity on anaerobic bacteria still not very well understood (Chen et al., 2014). A calcium concertation of 2500 – 4500 moderately inhibits the anaerobic process, but strong inhibition occurs with a concentration of 8000 mg/l (McCarty, 1964). On another, hand Jackson-Moss et al. (1989) reported lower concentrations i.e. 700 mg/l causes strong inhibition compared to McCarty (1964). The abundance of calcium in anaerobic systems lead to precipitation of calcium phosphate and calcium carbonate which leads to scaling of anaerobic methanogens and loss of activity, loss of important nutrients and scaling in the anaerobic reactor (van Langerak et al., 1998; Chen et al., 2014).

Potassium is another salt cation that is inhibitory, however its effect is not commonly indicated in the literature. Low concentrations of potassium were noticed to be enhancing the anaerobic process performance under mesophilic and thermophilic conditions, but with high concentrations it was observed that an inhibition in thermophilic conditions and the sensitivity of different anaerobic bacteria groups to potassium concertation is not very well addressed in the literature. (Chen et al., 2014). The observations from Fernandez and Forster, (1994), revealed that the inhibition related with potassium could happen at the acidogens stage.

Regarding the inhibition caused by magnesium to anaerobic processes, the results differ from one study to another. Schmidt and Ahring, (1993) reported that a concentration of 400 mg/l of magnesium will stop the bacteria growth while another study reported that an optimum concentration for different types of methanogens is 720 mg/l (Ahring et al., 1991).

Regarding sodium, a concentration of 100 – 200 mg/l was reported to be essential for growth of anaerobic bacteria (McCarty, 1964). It was reported that anaerobic bacteria under mesophilic conditions are affected less by the sodium concentration than anaerobic bacteria under thermophilic conditions (Soto et al., 1992). McCarty (1964) reported that sodium with a concentration of 3500 – 5500 mg/l will moderately inhibit the activity of anaerobic methanogens, and concentration of 8000 mg/l will inhibit the methanogens strongly. Gourdon et al., (1989), reported that concentration of sodium exceeding 10000 mg/l will strongly inhibit the methanogenesis stage in anaerobic processes, this observation was even higher than what was reported by McCarty, (1964). The adaptation of methanogens to salinity resulting from sodium is a key factor for a better performance. Adaptation under sufficient amount of time will result in tolerance of bacteria to high sodium concentration (Feijoo et al., 1995; Omil et al. 1995; Chen et al., 2003). The results from Chen et al, (2003) showed that a successful acclimation of methanogens is possible when the concertation was elevated from about 4000 mg/l to 12000 mg/l if the acclimation was performed stagewise. A study performed for the adaptation of anaerobic bacteria reported that an adaption to sodium concentration of 17000 mg/l is possible during a period over 700 days (Mende´z et al. 1995).

Table 3.5 : Salts concnetration causing inhibition for anaerobic process reported by **(**McCarty, 1964).

Inhibition	Cations (mg/l)			
	Calcium	Potassium	Magnesium	Sodium
Moderate	2500 – 4500	2500 – 4500	1000 – 1500	3500 – 5500
Strong	8000	12000	3000	8000

Lefebvre et al., (2007) conducted a study to understand the effect of sodium on methangens archea. Sodium level was increased as NaCl was added to the reactors. The increasment in NaCl concenetration started from 0 mg/l and then follwed by 1, 5, 10, 20, 40 and 60 g/l each stage of NaCl concenetration lasted for about two weeks. Methane production till 10g/l of NaCl was not affected by the increased level of NaCl.

However, the observations showed that the concenetrations above 10 g NaCl/l reduced methane production by almost 20% of that one with 10 g/l of NaCl. The decrease in methane produced was continue with the next two levels of NaCl until it reduced to 80% of that with 10 g/l of NaCl.the experiment was performed with period of 100 days, that may indicate if the adaptation period increased a better performane may be obtain as in case of Mende´z et al. (1995).

Sodium or salinity resulting from sodium, or other salt cations are not the only indication of anaerobic performance with saline wastewater. Electrical conductivity which an indicator of salinity can be used to evaluate the performance of anaerobic processes. Electrical conductivity gives a more general term of salinity.

Salinity inhibition in terms of electrical conductivity on anaerobic processes was investigated to indicate that an electrical conductivity of 35000 µS/cm could decrease methane production, while an electrical conductivity of 80000 µS/cm inhibits methane and CO_2 generation as well inhibiting the degradation of organic matter (Ogata et al., 2016).

3.2.7. Expended granular sludge bed reactor

Expended granular sludge bed reactor or as shortly known EGSB is a type of reactor classified as expended and fluidized bed anaerobic reactor, uses granular type of sludge. The EGSB uses the upflow regime with a circulation of the wastewater that will create an expansion in the granular sludge bed. The EGSB reactor is developed from a previous reactor version that uses the up flow regime, known as Upflow Anaerobic Sludge Blanket (UASB) reactor. The UASB reactor was first developed and introduced in 1970s by Lettinga and his team (Seghezzo et al., 1998). Since that time the UASB is used with wide range of wastewaters. The main concept of UASB is that all the biological treatment occurs in a dense bed of sludge that is formed and structured from the bacterial growth and the suspended solids introduced in the reactor influent. The upflow regime for feeding UASB helped to aggregate and form the anaerobic granules sludge (Hulshoff Pol, 1989). UASB reactor is described as a tank with a separation ability of three phases: wastewater, granular sludge and biogas at the top of the reactor. Influent enters the reactor from the bottom to pass through the biological reaction zone or granular anaerobic sludge bed. The granular sludge is made of anaerobic bacteria like, acidogens, acetogens and methanogens (Lettinga et al., 1980). Figure 3.8 illustrates the components of UASB reactor.

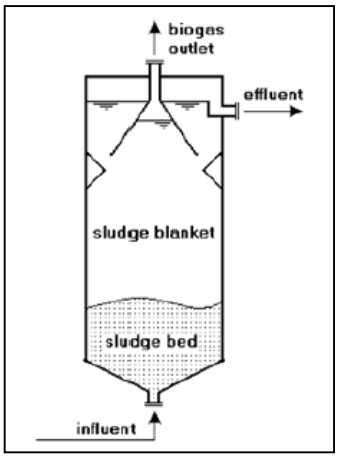

Figure 3.8 : UASB Reactor (adopted from De Lemos Chernicharo, 2007).

UASB reactor was designed to handle concentrated wastewater from agriculture and industrial wastewater, beside that it was used to treat municipal sewage. The UASB reactor uses a very low up flow velocity that usually ranges between 0.5 – 1.0 m/hr (van Lier et al., 2008). The minimum HRT required for the UASB reactor is reported to be 4 hr depending on the reactor volume, however it is not recommended to use the minimum HRT to avoid the sludge washout form the reactor which will lead to loss biological activity. The organic loading of UASB is usually in a wide range that starts from 1.5 kg COD/m^3.day and can reach to 32 kg COD/m^3.day (Van Haandel and Lettinga 1994; van Lier et al., 2008). In Van Haandel and Lettinga (1994), it was stated that it is hard to determine the most suitable HRT for UASB reactor by theoretical calculation and most of the HRT values depend on the field and experimental approaches. Thus it is suggested to have a minimum of 6 hr HRT for UASB reactors for regions that temperature exceeds 18°C, and for regions lower than 18°C it could be increased to 14hr (Van Haandel and Lettinga 1994). The height of the UASB reactor must be determined based on the economical and performance aspects, the most typical reactor height of UASB is 4 – 6 m for full scale application (Van Haandel and Lettinga 1994).

Studies indicated that using UASB reactors with low upflow velocity led to insufficient internal mixing, which end up with the formation of dead zones in the sludge bed leading to reduction in the removal efficiency (de Man et al., 1986; Seghezzo et al., 1998; van Lier et al., 2008).

In order to solve the problem observed with UASB reactor, it was suggested to make an improvement by using the entire available reaction volume. The suggestions included installing different inlets for the influent or introducing the feed into the reactor with a

higher up flow velocity. The second suggestion led to the invention of EGSB reactor, Figure 3.9 illustrates an EGSB component (van der Last & Lettinga, 1992; Kato, 1994; Kato et al., 1994; Seghezzo et al., 1998). EGSB reactor used a higher up flow velocity than 1 m/hr enhanced by the recirculation of the reactor effluent. The high up flow velocity caused an expansion in the granular sludge bed eliminating the dead zones and the earlier reports stated the use of 4 m/hr and higher velocities (van der Last & Lettinga, 1992; Lettinga et al; 1997). The new EGSB concept resulted in a taller reactor design than the previous UASB, with height to width ratio in range of 4 – 5 (Lim, S. J., 2009).

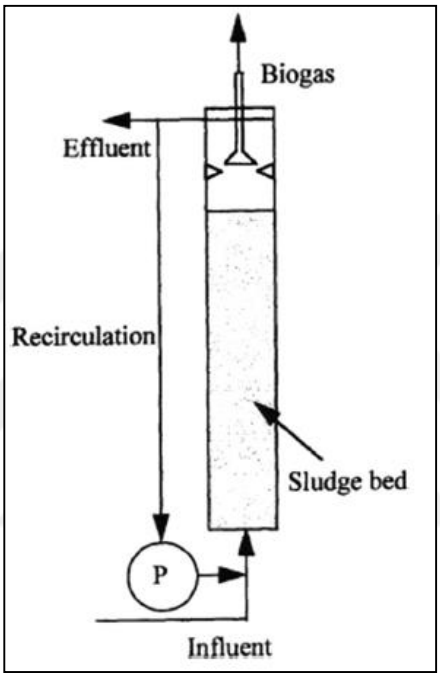

Figure 3.9 : EGSB reactor configuration (Seghezzo et al, 1998).

Seghezzo et al, (1998) gave the main characteristics of EGSB that is used generally in the literature. EGSB uses up flow velocities between 4 – 10 m/hr, with organic loading up to 40 kg COD/m^3.day. Expansion of the granular sludge bed must be observed with the up flow velocity. Granular sludge is the type of the anaerobic sludge used in this reactor with good stability, and the continues contact between wastewater and granular sludge keep the sludge active. Good internal mixing due to the circulation of the wastewater and the high upflow velocities is expected in EGSB. Poor quality in terms of suspended and colloidal solids removal can be observed together with possible escape of flocculent sludge from the reactor. Yet the up flow velocity is reported to be between 4-10 m/hr, (Saleh and Mahmood, 2004; Lim, S. J., 2009).

Table 3.6 shows the comparsion between UASB and EGSB. Both raectors depend on the anaerobic granular sludge for treating wastewater, the main differences is stated to be in the operation parameters, structure of the reactors and the applicabity (Lim, S. J., 2009).

As can be observed from the Table 3.6, the organic loading of EGSB is higher than that of UASB, as well the upflow velocity that ranged from 0.5 – 1.0 m/hr for UASB is tepically 6 m/hr for EGSB. It is to be kept in mind each case has it own operational conditions. High velocities must be avoided so that granular sludge does not escape from the reactor. The hydraulic retention time of UASB reactor was stated to be a minimum of 4 hr, while the range in EGSB was wide open from few hours to days, however the most important control parameter for hydraluic retention time selection is the washout of granular sludge. In terms of performance and applicability both UASB and EGSB showed a good results in terms of removal effciciency. According to (Kato et al., 1997), EGSB can endure low streangth wastewater in contrast to UASB. According to the same study, EGSB showed it could endure a very low COD concentrations even lower than 200 mg/l.

The results of EGSB treating organic matter in wastewater under different environmental and operational conditions was significantly reasonable in terms of efficiency. EGSB reactor was used to remove long chain fatty acids contained in wastewater. In one study (Hwu et al., 1998), the removal efficiency was up to 73% and 70% under thermophilic and mesophilic conditions respectively. This reveals the similar performance of EGSB under two different temperature conditions.

Table 3.6 : Comparison between UASB and EGSB.

Parameter	UASB	EGSB
Organic loading rate (kg COD/m^3.day)	1.5 – 32	Up to 45
Hydraulic retention time (hr)	4 (Minimum)	Not clearly stated but sludge washout should be taken in consideration
Up flow velocity (m/hr)	0.5 – 1.0	4 – 10, or over that one of UASB
Height (m)	5.5 – 6.5	12 - 18

EGSB was tested for removal of COD, fats and TSS from slaughterhouse wastewater by Nunez and Martinez, (1999). The results of this study showed no accumulation of fats in the reactor with removal efficiencies of 67% for COD, 85% for fats and 90% for TSS.

Another research focused on the performance of EGSB for the removal of short chain organic acids, and the removal efficiency was almost 100% under an organic loading of 10 kg COD/m^3.day when the feed was a mixture of maleic, furmaric, oxalic acid (Dinsdale et al. 2000). The performance in the same study was compared to the mixture of the feed containing butyric, benzoic, propionic, maleic and glyoxylic acid. The removal efficiency was reduced to 90% at the organic loading of 3 kg COD/m^3.day most probably due to the change in the feed components.

When an EGSB reactor was used in combination with the ANAMMOX process (anaerobic ammonium oxidation), the EGSB performance investigated showed a removal of total nitrogen over 50% combined with COD removal of 84% at 500 mg COD/l in the influent (Jianlong and Jing, 2005).

As mentioned before that Hwu et al, (1998) investigated the performance of EGSB reactor under mesophilic and thermophilic conditions. EGSB reactor performance was also investigated under psychrophilic conditions (Rebac et al., 1999; Enright et al., 2005; Connaughton et al., 2006). The studies showed that using EGSB under psychrophilic conditions is feasible in terms of avoiding energy savings to be provided at high temperature conditions for anaerobic processes. The EGSB performance under both psychrophilic and mesophilic conditions showed similar results when the organic loading of brewery wastewater was 4.5 kg COD/m^3.day. COD removal efficiency was reported to be the same in a range of 85 – 93% (Connaughton et al., 2006).

The EGSB reactor was studied for removal of phenol and production of biogas. The study conducted by Scully et al, (2006) tested the EGSB performance under 15°C, showed that 99% of phenol removal could be achieved at 2 kg COD/m^3.day loading and biogas production was up to 20 ml/g. day. Table 3.7 shows a summary of the EGSB performance found in the literature.

Table 3.7: Summary of literature survey about EGSB removal performance.

Treatment purpose	Wastewater	Performance	Reference
Removal of long chain fatty acids contained in wastewater	Synthetic wastewater	COD removal of 70 and 73% under mesophilic and thermophilic conditions respectively	Hwu et al., 1998
Removal of COD, fats and TSS	Slaughterhouse wastewater	removal efficiencies of 67% for COD, 85% for fats and 90% for TSS.	Nunez & Martinez, (1999)
Removal of short chain organic acids	Synthetic wastewater of short chain organic acids	90 – 100% removal efficiency with two different mixture of wastewater	Dinsdale et al. 2000
ANAMMOX process	Synthetic wastewater with granular sludge from brewery wastewater treatment plant	removal of total nitrogen over 50% with COD removal of 84%	Jianlong and Jing, 2005
EGSB performance under both psychrophilic and mesophilic	brewery wastewater	85 – 93% COD removal for psychrophilic and mesophilic respectively	Connaughton et al., 2006
Phenol removal	Synthetic industrial wastewater	99% of phenol removal	Scully et al, (2006)

4. MATERIALS AND METHODS

The aim of this work is to investigate the removal of organic matter from the residue of the ion exchange process with the suggestion of anaerobic processing for this goal. Different pieces in the literature investigated the removal and recovery of nutrients from source separated human urine using ion exchange method (Beler Baykal et al., 2004; Beler Baykal et al., 2009; Kocaturk, 2010; Kocaturk and Beler Baykal, 2012; Beler Baykal et al., 2011; Allar & Beler Baykal 2013; Allar 2015; Allar-Emek and Beler Baykal 2017). Those studies showed that the ion exchange/adsorption process was successful in terms of nutrient recovery of N, P with high efficiencies. The main motivation of this current work was received from a studies conducted on human urine using ion exchange/adsorption process with the aid of fixed bed clinoptilolite columns both in single stages and stage wise. A study was conducted by Allar, & Beler Baykal, (2015) on human urine to remove nutrients in a manner that will lead to higher amounts of nutrients to be removed, combined with improving the quality of the ion exchange liquid residue remaining after the ion exchange/adsorption processing. The results of stage wise operation successfully achieved a higher removal of nutrients leaving a liquid phase with no phosphorus and very small amounts of nitrogen. Yet the question is, what is the statues of the residue from this process in terms of organic matter. This work is motivated by the assumption that this remnant is still rich in organic matter and highly saline in addition to the residual nutrients remaining after the ion exchange/adsorption process. Anaerobic processing using EGSB reactor was suggested for removing organic matter from a human urine in which nutrients had been removed, yet the challenge in this case is the high salinity of this solution. In this work anaerobic granular sludge originally treating confectionary wastewater was adapted to this reside. The nature of human urine imposes a threat on the anaerobic microorganisms due to the high salinity, thus an adaptation is required. Fresh urine was used to adapt the anaerobic granular sludge to a high level of salinity. Then the adapted granular sludge was used to remove organic matter from the remnant of ion exchange process using EGSB reactor. To start with three configurations were suggested that will put together sorption processing and anaerobic process in a manner

that will lead to a concurrent recovery of nutrients and possibly energy from human urine.

4.1. Urine - The Liquid Phase

In this work mainly natural urine was used in to different modes: fresh and stored. The difference between the two being if it has gone under storage or not. Natural urine used in this research was collected from a separation system located in Istanbul Technical University at the Department of Environmental Engineering. The urine was collected from men's toilet by urinals that uses water flushes as shown in Figure 4.1. Then urine flows through a pipe line to be collected in two tanks placed at the end of the pipe line. One of the tanks was used to collect fresh urine and the other one was used to the as a storage tank for the urine to be hydrolyzed. Fresh urine was collected each two days in the fresh urine tank before using it as a feeding solution for the EGSB reactor during for the adaptation of anaerobic granular sludge received from the confectionery factory. The stored urine was collected in a separate tank as shown in Figure 4.1, and kept there long enough till the hydrolysis was completed, before it is used. Figure 4.2 shows the collection tanks used to collect fresh and stored urine.

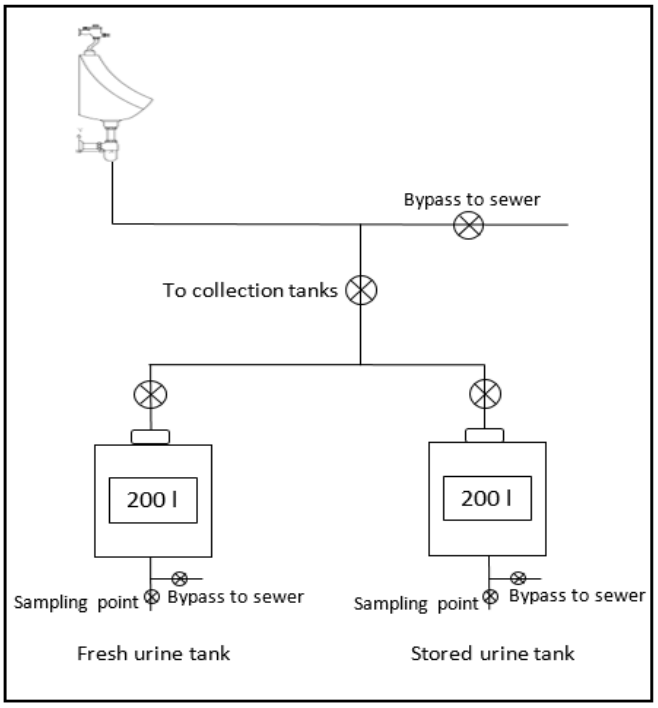

Figure 4.1: Urine collection system.

Figure 4.2: Urine collection tanks.

The characterization of fresh and stored natural human urine is shown in Table 4.1. Both types of natural urine were characterized for pH, electrical conductivity, total and soluble COD, ammonium, TKN, ortho-phospate, total phosphorus and potassium.

Table 4.1: Fresh and stored urine characterization.

Parameter	Unit	Fresh urine	Stored urine
pH	-	8.8 – 9.2	9.3 – 9.4
Electrical conductivity	µS/cm	25400 - 30300	32800 - 37000
Total COD	mg COD/l	4000 – 4520	4360 - 5300
Soluble COD	mg COD/l	3960 – 4500	4200 - 5250
Ammonium	mg NH_4^+-N/l	3000 – 4250	4100 - 4400
TKN	mg NH_3-N/l	7800 – 9250	4500 - 5250
Ortho-phosphate	mg PO_4^{3-}-P/l	275 – 295	165 - 210
Total phosphorus	mg PO_4^{3-}-P/l	290 – 320	175 - 230
Potassium	mg K/l	1100 – 1250	1200 - 1250

Synthetic urine was used in this work in the later stages to simulate natural stored urine from which nutrients had been removed from to provide control conditions for investigating the effect of salinity. The characteristics of synthetic urine were regulated to follow the characteristics of natural stored urine that was subjected to ion exchange/adsorption process run of 15 mg NH_4^+/g clinoptilolite initial loading. Synthetic urine was used as a feeding solution for the EGSB reactor to study the effect of salinity on organic matter removal. Table 4.2 shows the composition of the synthetic urine and the characteristics corresponding to the prescription used in this research. Sodium chloride (NaCl) was used a source of salinity measured by electrical conductivity. The synthetic urine components will be prepared using tap water and the pH will be adjusted using 1N NaOH solution.

Table 4.2: Chemical composition and corresponding concentrations.

Chemical composition	Amount (g/l)	Concentration
Citric acid ($C_6H_8O_7.H_2O$)	3.874	2700 mg COD/l
Potassium Chloride (KCl)	1.491	385 mg K^+/l
Ammonium Chloride (NH_4Cl)	3.0	985 mg NH_4^+/l
Sodium Dihydrogen Phosphate Monohydrate ($NaH_2PO_4.H_2O$)	0.15	33 mg PO_4-P/l
Magnesium Chloride, Hexahydrate ($MgCl_2.6H_2O$)	0.264	32 mg Mg^{2+}/l
Calcium Chloride, Dehydrate ($CaCl_2.2H_2O$)	1.103	300 mg Ca^{2+}/l
Sodium Chloride (NaCl)	150 - 45	-

4.2. Clinoptilolite - Solid Phase

The ion exchanger or adsorbent used in this research was clinoptilolite which is a natural zeolite. The used clinoptilolite originated from the mines of Gördes region in Manisa, Turkey, and was provided for scientific purposes by Rota Madencilik. As the clinoptilolite is known for being a cation exchanger, it was used in this research for the removal of ammonium and potassium cations through the ion exchange process beside the removal of phosphorus from the liquid phase the mechanism of which needs further research (Allar, 2015). The nutrient enriched clinoptilolite will be used as the input in the recovery stage. The chemical formula of the clinoptilolite is $(Ca,K_2,Na_2,Mg)_4Al_8Si_{40}O_{96}.24H_2O$ with the chemical composition shown in Table 4.3 (Rota Madencilik, 2018).

Table 4.3: Chemical composition of clinoptilolite (Rota Madencilik, 2018).

Chemical component	% weight
SiO_2	65 – 72
Al_2O_3	10 – 12
CaO	2.4 – 3.7
K_2O	2.5 – 3.8
Fe_2O_3	0.7 – 1.9
MgO	0.9 – 1.2
Na_2O	0.1 – 0.5
MnO	0 – 0.08
Cr_2O_3	0 – 0.01
P_2O_5	0.02 – 0.03

The form of the clinoptilolite used in this research was the sodium form as it is the most recommended form for ammonium removal from liquid phase (Cooney et al, 1999; Headstörm 2001; Yurtoglu, 2007) and in order to achieve this form, the clinoptilolite was conditioned with a NaCl solution following the procedure recommended by (Yurtoglu, 2007). Before conditioning, clinoptilolite was sieved to obtain the clinoptilolite size range of 1-2 mm, then washed with distilled water. During the conditioning process, a 9.0 cm diameter column was used and filled with clinoptilolite and a solution of 1M NaCl was passed through the clinoptilolite bed for 2 days using a peristaltic pump with a flow rate of 1 bed volume/h. After conditioning the clinoptilolite was dried at room temperature and then before using, it was dried at 103-105 °C to be brought to constant weight.

4.3. Anaerobic Granular Sludge

The anaerobic granular sludge to be used to treat the organic matter in human urine was originally provided from a real scale anaerobic processing unit. The granular sludge in the real anaerobic unit was operated at mesophilic temperature level and was used in confectionary plant to treat confectionary wastewater near Istanbul city. The granular size of the sludge is 1 – 4 mm. Figure 4.3 shows a sample of the anaerobic granular sludge of different sizes on a graph paper. The characteristics of anaerobic granular sludge are summarized in Table 4.4.

Figure 4.3 : Anaerobic granular sludge size distribuion.

Table 4.4 : Characterization of anaerobic granular sludge.

Parameter	Unit	Value
TSS	mg/l	39400
VSS	mg/l	34000
VSS/TSS	%	86
Granular Size	mm	1 – 4

4.4. Urine Collection and Storage

As mentioned in section 4.1, human urine was collected form a system collecting human urine from men's toilet at the Department of Environmental Engineering in Istanbul Technical University. Figure 4.1 illustrates the collection system used in this work. Source separated human urine was segregated using urinals that consume flush water The type of flushing in these urinals are the one that flushing water will flow as long as the person is pushing the flushing button, urine receives unknown amount water and thus diluted. Fresh urine was collected each two days to have enough to feed the EGSB reactor, and the excess fresh urine was discharged to the sewer through the bypass valve placed at the bottom of the tank. This work will investigate the use of source separated human urine in its stored or hydrolyzed form for the removal of organic matter and nutrients present as ammonium, phosphorus, and potassium. Storage of urine will be beneficial in terms of removing and recovering more nitrogen in the form of ammonium, due to the hydrolysis that takes place in the storage tank which converts urea to ammonium (Udert et al, 2003; Kocaturk and Beler Baykal 2012). Another reason which makes human urine storage beneficial is the pathogenic inactivation during storage period (WHO, 2006; Giresunlu and Beler Baykal, 2014). Inactivation of pathogens was not investigated in this work.

Source separated human urine must be stored for long enough time for the hydrolysis to be completed. Filling the storage tank with urine took about two weeks, and during this time no monitoring for the characteristics of urine was performed. On the first day of the storage characterization, pH, electrical conductivity, Ammonium, TKN, COD, Ortho-phosphate, total phosphorus, and potassium were monitored. Ammonium and TKN were the parameters that considered as the criteria for the hydrolysis to be completed. Two batches of stored urine were prepared and used in this research. The monitoring and characterization of stored urine extended beyond the completion of the hydrolysis for the parameters pH, electrical conductivity, ammonium, and COD to observe the changes the stored urine will be subjected to during longer storage periods.

It is to be mention that this work had put more effort on observations related to COD changes during storage than other references in the literature.

4.5. Processes

4.5.1. Ion exchange process

In this work ion exchange process was employed for nutrient removal and recovery. During the removal stage, ion exchange was performed using fixed bed clinoptilolite columns to concentrate nutrients on clinoptilolite surface by contacting human urine with clinoptilolite in 100% recycled feeding regime. The nutrient removal run was conducted for 4 days, as this time was enough to observe a stable concentration of all nutrients and a stable removal efficiency for nutrients in the liquid phase (Kocaturk, 2010; Beler Baykal et al, 2011; Kocaturk and Beler Baykal, 2012, Allar and Beler Baykal, 2013; Allar, 2015). Figure 4.4 shows a typical run for nutrient removal used in this work. Ion exchange was employed in this work for nutrient removal both in a single stage and in a stage wise operation. Single stage operation was used to remove the majority of the nutrients from the liquid phase, the quality liquid reside of this stage was monitored carefully for COD concentration because later on this will be the influent of anaerobic EGSB reactor. The stage wise operation of ion exchange with variable loadings was employed to improve the quality of the anaerobic effluent in which reside of single stage ion exchange was used as the influent.

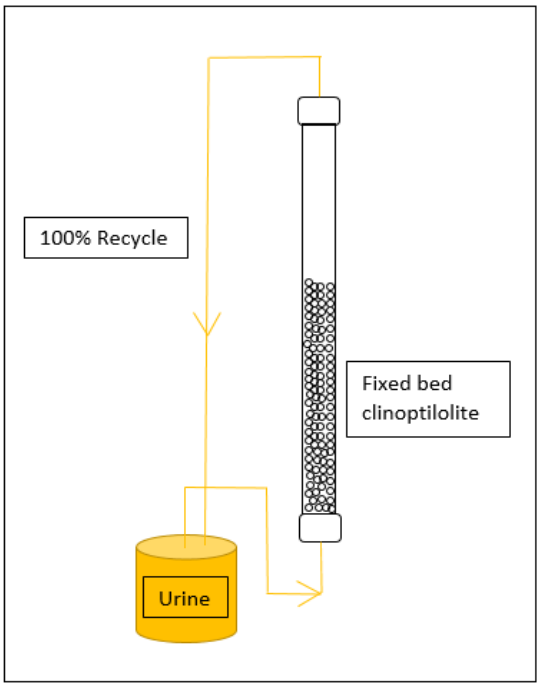

Figure 4.4 : Nutrient removal using fixed bed clinoptilolite column (adopted from Kocaturk and Beler Baykal, 2012).

Nutrient recovery was performed by employing desorption process on nutrient enriched clinoptilolite. The nutrients were recovered once the nutrient enriched clinoptilolite contacted with tap water, and then the nutrients were released from surface with tap water in a continuous feeding regime. Figure 4.5 shows a typical nutrient recovery run that was performed in this work.

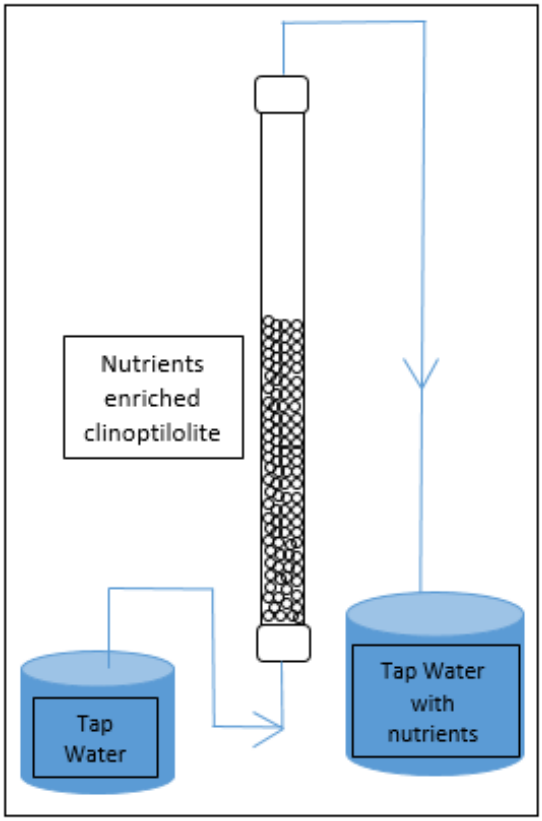

Figure 4.5 : Nutrient recovery by employing desorption on nutrients enriched clinoptilolite (adopted from Kocaturk and Beler Baykal, 2012).

4.5.2. Anaerobic process

The anaerobic process was employed to remove organic matter from source separated human urine. EGSB reactor was used with anaerobic granular sludge the characteristics of which are shown in Table 4.4. At the beginning, the anaerobic process was employed for the adaptation of anaerobic granular sludge from a low salinity confectionery wastewater to the highly saline stream i.e. human urine. The physical properties of the EGSB reactor will be discussed later in section 4.6 of this chapter. After the adaptation stage, anaerobic processes were applied with the adapted sludge to remove the organic matter from the residue of the single stage ion exchange process. Table 4.5 shows the operational conditions of the anaerobic process.

Table 4.5 : Operational conditions for anaerobic process.

Parameter	Value
HRT	40 hr
Up flow velocity	Near min limit (4 m/hr)
OLR	0.33 – 1.8 kg COD/m^3.day
Temperature	38°C

The hydraulic retention time (HRT) at all the times during the anaerobic process was set to be 40 hr. The organic loading (OLR) ranges from 0.33 – 1.8 kg COD/m^3.day, the change in OLR was due to the different urine concentrations at the influent that was used in this work. Regarding the circulation rate or up flow velocity of the EGSB reactor, the circulation pump was adjusted until suspension in the granular sludge was observed. The up flow velocity was close to the lower end of up flow velocity of EGSB reactor which is 4 m/hr. Higher up flow velocity was avoided in order to prevent the escape of sludge from the reactor. At all times the EGSB reactor was kept in a constant temperature room with a temperature of 38°C to maintain a mesophilic condition. The constant room temperature used for this purpose was located in Solid Waste Laboratory in the Department of Environmental Engineering of Istanbul Technical University. The pH of the feeding solution was always controlled before feeding it to the EGSB reactor. Hydrochloric acid was used to adjust the pH to a value around 7.5, as the suitable pH value for anaerobic process is 6.8 – 8.2 (Khanal, 2011).

4.6. Reactors

4.6.1. Fixed bed clinoptilolite columns

Fixed bed clinoptilolite columns were used for nutrient removal and recovery. The columns were all made from plexiglass. Two sizes of columns were used 9.0 cm and 3.6 cm with 100 cm height that fit the purpose of this research. Regarding single stage ion exchange for nutrients removal, 9.0 cm in diameter column was used. In multiple stages of ion exchange process for effluent quality control and in nutrient recovery experiment, columns with 3.6 cm in diameter and 100 cm column height were used. All columns were operated in upflow mode with 100% circulation for nutrient removal and continuous feeding mode for nutrient recovery.

4.6.2. Expended granular sludge bed (EGSB) reactor

Two lab scale EGSB reactors were used in this research, both of them are shown in Figure 4.6. The EGSB reactor No.1 was used for the treatment and adaptation of fresh urine. It has an effective working volume of 9.2 l, with a total height of 1.21 cm and 8.0 cm diameter of the lower column where the granular sludge is located, while the diameter of the upper part is 20 cm, which is designed for separation and collection of biogas. 30% of the lower column volume was filled with granular sludge from the confectionary wastewater treatment plant. Two pumps were connected to the column, one for feeding, the other one for circulation. The circulation pump was adjusted until the granular sludge was in suspension as it is one of the main characteristics of EGSB reactors.

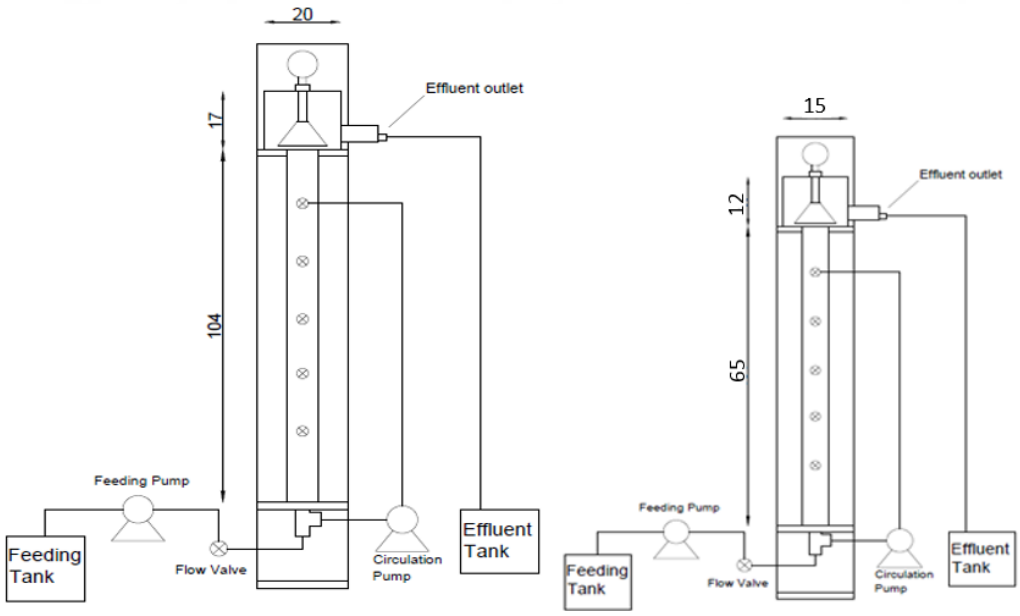

Figure 4.6 : Experimental setup of the EGSB reactors.

The EGSB reactor No.2 was used during the treatment of stored urine. Due to the limitation of getting enough stored urine, EGSB reactor No.2 was made smaller than EGSB No.1 but proportional in design. EGSB No.2 has an effective working volume of 2.7 l, with a total height of 77 cm, the diameter of the lower column part is 5 cm and the upper part is 15 cm for separation and collection of biogas. 30% of the lower column volume of the reactor was occupied by granular sludge and circulation arrangement in EGSB No.2 was similar to that one of EGSB No.1. Both of the reactors were located and operated in the same mesophilic temperature condition. Both reactors were connected to a gas meter to measure the amount of the biogas evolved.

The gas meter was of Milli Gascounter brand manufactured by Ritter with an electronic counter / LCD display. Table 4.6 describes the properties of the gas counter used in this research.

Table 4.6 : Properties of gas counter (Ritter, 2016).

Property	Value
Minimum flow rate Q min	1 ml/hr
Maximum flow rate Q max	1 l/hr
Measurement accuracy	± 3%
Min. measuring volume (resolution)	3 ml
Resolution of indication	0.01 ml
Gas temperature	10 – 60 °C
Maximum gas inlet pressure	100 mbar
Minimum gas inlet pressure	8 mbar
Display	6 digits [ml] + 2 decimals

4.7. Experimental Plan

4.7.1. Experiment configurations

The main aim of this work is to find a solution for a highly saline and organic rich residue of ion exchange process with clinoptilolite that is employed for nutrient removal from human urine. Adsorption/desorption by ion exchange process through fixed bed clinoptilolite columns was employed to remove and recover the nutrients embedded in this wastewater stream. Anaerobic processing is suggested to handle this residue of ion exchange process for removal of organic matter with possible biogas production. Different configurations were suggested to be tested during this research through the combination of ion exchange process and anaerobic process for both nutrients and organic matter removal. During the anaerobic process the ammonium release was monitored as it is a significant issue that will affect the recommendation of the best configuration to be followed that will lead to a concurrent nutrients recovery

and biogas production from source separated human urine. Figure 4.7 shows the suggested configurations that were tested.

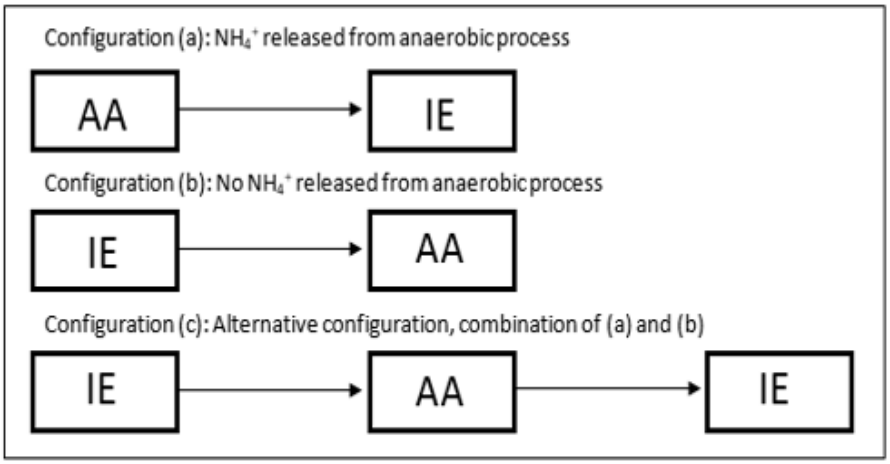

Figure 4.7 : Experiment configurations.

Configuration (a) was used for the adaptation of anaerobic granular sludge with fresh urine as feeding solution for the EGSB reactor. This configuration was intended to investigate the COD removal and to monitor any possible release of ammonium in the process. If a release of ammonium could be observed it would be logical to have nutrient removal through processing with clinoptilolite to come after the anaerobic process so that nutrient removal would be maximaized in a total of two stages.

In case of no ammonium release from the anaerobic process, configuration (b) would be recommended, in which urine will be subjected to one stage ion exchange for removal of nutrients, followed by anaerobic processing to remove organic matter in the liquid residue from processing with clinoptilolite.

The alternative configuration (c) is one in which stored human urine will be passing through a fixed bed clinoptilolite column to remove the majority of the nutrients from the liquid phase, followed by anaerobic process to remove the organic matter, followed by another stage of ion exchange. The second ion exchange process stage will be performed to enhance the quality of the anaerobic process effluent quality for environmental protection through the removal of the remaining nutrients if exists at an appreciable amount.

4.7.2. Adaptation of anaerobic granular sludge / configuration (a)

As human urine is a highly saline wastewater stream, an adaptation of the anaerobic granular sludge to high salinity level is a significant matter and it is a key factor for successful application of the anaerobic process. Fresh human urine was used at this stage as a feeding solution of the EGSB reactor No.1 shown in Figure 4.8. The adaptation included different stages based on different percentages of fresh urine in the feeding starting from 25% fresh urine and increasing this percentage in a stage wise manner until 100% fresh urine in feeding solution is achieved. The performance of the EGSB reactor No.1 for removal of organic matter would monitored. During this stage, the EGSB reactor was monitored for possible ammonium release. Shifting from one stage to another was based on the stabilization of the COD effluent concentration and removal efficiency. The bigger reactor was used at this stage to adapt more anaerobic granular sludge to be used later in this work. 30% of the reactor column's volume was filled with anaerobic granular sludge.

Figure 4.8 : EGSB reacotr No.1, actual set up used with fresh urine.

The hydraulic retention time (HRT) of the EGSB No.1 was set to be 40 hr, and the organic loading (OLR) changed in ascending manner from 0.72 to 1.80 kg COD/m^3.day according to the percent of fresh urine in the feeding solution. The EGSB reactor was fed with 5.5 l/day of feeding solution during this stage. Regarding the circulation rate or up flow velocity of the EGSB reactor, the circulation pump was adjusted until about 2 cm of suspension in the granular sludge was observed. At all times the EGSB reactor was kept in a constant temperature room with a temperature of 38°C to maintain a mesophilic condition.

The feeding solution during this stage was prepared every two days, by taking the required volume of fresh urine from the fresh urine tank. The dilution of the feeding solution was prepared by using tap water, starting with 25% of fresh urine in the feeding. The pH of the feeding solution was always controlled before feeding it to the EGSB reactor. Hydrochloric acid was used to adjust the pH to a value around 7.5. The pH adjustment of the feeding solution was adjusted for two reasons, to meet the suitable conditions for the anaerobic granular sludge and to keep the nitrogen in ammonium form as the ammonium changes to ammonia at pH levels higher than 8.5.

4.7.3. Urine storage and hydrolysis

This research mainly investigated the use of source separated human urine in its stored or hydrolyzed form for the removal of organic matter and nutrients present as ammonium, phosphorus, and potassium. The storage of urine would be beneficial in terms of removing and recovering more nitrogen in the form of ammonium, due to hydrolysis that take place in the storage tank that coverts the urea to ammonium (Udert et al, 2003; Kocaturk and Beler Baykal 2012; Allar, 2015). In order to do so, source separated human urine must be stored for long enough a time for the hydrolysis to be completed. Filling the storage tank took about two weeks, and during the filling time no monitoring for the characteristics of urine was performed. Characterization started on the first day of storage by monitoring pH, electrical conductivity, Ammonium, TKN, COD, Ortho-phosphate, total phosphorus, and potassium. Ammonium and TKN were the parameters that considered as the criteria for the hydrolysis to be completed. Two batches of stored urine were prepared and used in this research. The monitoring of the characterization of the stored urine extended beyond the completion of the hydrolysis for the parameters pH, electrical conductivity, ammonium, and COD to observe the changes the stored urine will be undergoing during longer storage periods.

4.7.4.Ion exchange – anaerobic process / configuration (b)

Following the urine storage and completion of hydrolysis, nutrient removal through single stage ion exchange using fixed bed clinoptilolite colomns was initiated. The previouse experince of the Segregated Streams/ECOSAN group of Istanbul Technical University was used to perform this experiment regarding the operational conditions that should be used (Beler-Baykal et al, 2004; Beler Baykal et al, 2009; Beler Baykal et al, 2011; Kocaturk, 2010; Kocaturk and Beler Baykal 2012; Allar 2015; Allar et al, 2015; Allar-Emek and Beler-Baykal 2017). Fixed bed clinoptilolite columns were used

to accomplish this task and nitrogen as ammonium was taken as the basis for initial loading. 15 mg NH_4^+/g clinoptilolite was used as the initial loading during the nutrient removal process (Allar, 2015; Allar and Beler Baykal, 2015). This stage for nutrient removal was performed at 100% recycle until no appreciable removal in the liquid phase was observed. Each ion exchange run at this stage was performed in a period of 4 days. Figure 4.9 shows the experimental set up of the ion exchange for nutrient removal.

Figure 4.9 : Experimental set up of ion exchange for nutrient removal.

Table 4.7 shows the operational conditions of the single stage ion exchange process for nutrient removal. The pH of the stored urine was adjusted at this stage to a pH value around 7.5 to keep the nitrogen in the ammonium form and prevent its conversion to ammonia. The pH adjustment will help to concentrate more ammonium ions on the clinoptilolite surface and eventually will lead to recover more nitrogen as ammonium to be used as a fertilizer. At the end of each ion exchange run the stored urine without nutrients was stored separately and kept in cold room of 4°C to be used later as a feeding solution of the EGSB reactor No.2.

The anaerobic processing stage with stored urine in which nutrients had been removed as feeding solution was performed under the same operational conditions of HRT, circulation condition, mesophilic temperature of EGSB No.1 mentioned previously. OLR ranged from 0.33 – 1.60 kg COD/m^3.day, the change in OLR values depends on the percentage of the stored urine without nutrients in feeding solution.

Table 4.7 : Operational condition of single stage ion exchange for nutrient removal.

Initial loading	
Ammonium (mg NH_4^+/g clinoptilolite)	15.0
Ortho-Phosphate (mg PO_4^{3-}/g clinoptilolite)	0.59
Potassium ((mg K^+/g clinoptilolite)	3.39
Chemical Oxygen Demand (mg COD/g clinoptilolite)	15.07 – 9.04
Experimental set up	
Column diameter (cm)	9.0
Column height (cm)	100
$m_{clinoptilolite}$ (g)	4600
Flow rate (ml/min)	10
$Vol._{urine}$ (l)	13000

The anaerobic process was performed first using the same sludge that was adapted with fresh urine, the feed solution was prepared as 50% stored urine, then increased to 75% and the performance of this sludge was monitored. The old adapted sludge was replaced with a sludge from the same source of confectionary wastewater treatment plant and the adaptation was started over again with stored urine. In the main runs, the sludge from confectionery wastewater treatment plant was adapted with stored urine starting from 25%, and increased stage wise to 35%, 50%, 75%, until 100% stored urine as feeding for the EGSB reactor No.2 was achieved. The OLR was changed according to the COD concentrations with each stage corresponding to the percentages in each stage. The EGSB No.2 at this stage was fed with 1.6 l/day of stored urine to maintain the same HRT of 40 hr that was used.

Figure 4.10 : EGSB reactor No.2, actual set up used with stored urine.

4.7.5.Ion exchange – anaerobic process – ion exchange / configuration (c)

This configuration can be considered as a continuation of configuration (b) with ion exchange following anaerobic process. The aim of this configuration was to enhance the effluent quality of the anaerobic process before disposal for environmental protection. Multiple runs of ion exchange process with different initial loadings were performed after of anaerobic process with different concentrations of stored urine. The effluent of the EGSB reactor was used as the feeding solution for the fixed bed clinoptilolite columns in the final stage. Effluent of the EGSB of each of different stored urine concentration stage were collected separately and stored in a cold room of 4°C before using them for the final ion exchange runs. To improve the effluent quality, multiple stages of ion exchange were used under many cases. Variable initial loadings were used during the stage wise operation due to the significant removal that can be observed in a stage wise manner compared to that of constant loading (Allar & Beler Baykal, 2015). Three different loadings were used, 15, 10 and 5 mg NH_4^+/g clinoptilolite. The operation mode was batch mode 100% recycle similar to that one of the initial ion exchange stage prior to anaerobic process. The pH was not adjusted after the anaerobic process but kept as it was coming out of the EGSB. Table 4.8 describes the operational conditions of each ion exchange run that was carried out after the anaerobic process in configuration (c).

Table 4.8 : Operational condition of multiple stages ion exchange process of stored urine after anaerobic process.

AA process stage	Int. loading	Number of IE stage	Column dia.(cm)	Bed height (cm)	Clinoptilolite mass (g)	Urine vol. (l)	Flow rate (ml/min)
25% Stored urine	15	1	3.6	12	95.3	5	10
35% Stored urine	15	1	3.6	27	220	10	10
50% Stored urine – 1st trial	15	1	3.6	47	383	10	10
	5	2	3.6	52	420	10	10
50% Stored urine – 2nd trial	15	1	3.6	29	240	5	10
	5	2	3.6	36	290	5	10
75% Stored urine	15	1	3.6	32	263	5	10
	5	2	3.6	37	300	5	10
100 % Stored urine	15	1	3.6	45	370	5	10
	5	2	3.6	58	445	5	10
	10	1	3.6	68	555	5	10
	5	2	3.6	44	330	5	10

4.7.6.Nutrient recovery

Regarding nutrient recovery from the surface of nutrient enriched clinoptilolite was due to desorption process. In the recovery experiment, stored urine from batch 2 was used. The clinoptilolite that was used for recovery experiment was used to process stored urine from Batch 2 in the first stage of ion exchange. Table 4.9 shows the characteristics of the nutrients enriched clinoptilolite that was used for the nutrient recovery experiments. The nutrient recovery experiments were performed in continues feeding mode. Figure 4.11 shows the setup of continues mode nutrient recovery experiments. Ammonium, ortho-phosphate, potassium, COD, pH and electrical conductivity were the parameters that were monitored during the recovery experiments. Recovery efficiencies were determined based on the amount of ammonium, ortho-phosphate and potassium released from the clinoptilolite surface. Two parallel columns were used in this stage as duplicates, both of 3.6 cm in diameter, both operated under the same operational conditions. Two different contact times used in the continues mode 5 min and 300 min. The two contact time was intended to simulate two different infiltration rates based on dripping irrigation (Allar, 2015).

Table 4.9 : Characteristics of nutrient enriched clinoptilolite used in nutrient recovery experiment.

Parameter	Initial loading mg / g clinoptilolite	Actual loading mg / g clinoptilolite
Ammonium	15.0	12.0
Ortho-Phosphate	0.59	0.58
Potassium	3.39	2.27
Chemical Oxygen Demand	12.7	4.19

Figure 4.11 : Experimental set up of the nutrient recovery experiment.

For the continues modes nutrient recovery experiment, an auto sampler device was always used that enabled more frequent samples to be collected at the beginning of the recovery period. Figure 4.12 shows the auto sampler device used the during experiments. The auto sampler was set to collect a sample each 30 min then the settings were changed to take a sample each hour. After the release was stable, two samples were collected per day till the end of the recovery experiment.

Figure 4.12 : Auto sampler device used in nutrient recovery experiment.

For testing potassium recovery, batch reactors of 250 ml volume were used for monitoring the release of potassium from the clinoptilolite surface. 8 batch reactors with tap, rain, drinking and deionized water were employed for this purpose with 15 g of nutrient enriched clinoptilolite in each. Of the total of the 8 samples of clinoptilolite 4 came from the removal column without any further treatment to represent nutrient enriched clinoptilolite over soil to receive either irrigational water or rain water. The other 4 came from nutrient removal followed by recovery for about three weeks, to mimic the case for rain water desorption after being distributed on the soil. Figure 4.13 shows the 8 batches on a shaker with 50 rpm and 25.0°C and samples were taken every day to measure potassium concentration.

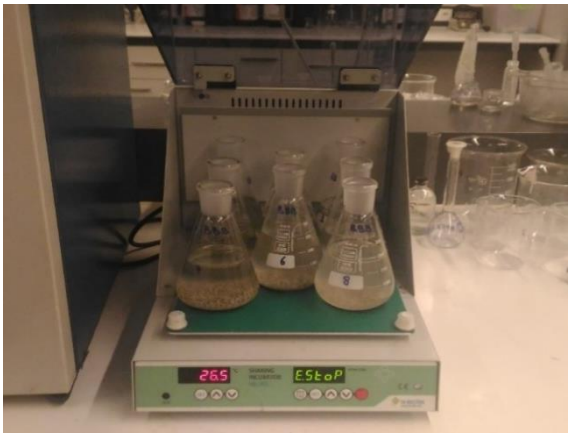

Figure 4.13 : Batch mode of nutrient recovery experimnet.

The characteristics of the four types of liquid phase i.e. tab, rain, drinking and deionized water are shown in Table 4.10. All the water types have no phosphorus and almost no ammonium. Tap water has the highest potassium concentration and electrical conductivity among the other types of water, while deionized water has no potassium at all and ignorable electrical conductivity level.

Table 4.10 : Characteristics of tap and rain water used in nutrient recovery experiment.

Parameter	Tap water	Rain water	Deionized water	Drinking water
pH	7.0 – 7.8	6.0 – 6.5	6.0	7.6
Electrical conductivity	420 – 575	24 – 30	0.33	144
Ammonium	0.2 – 0.35	0.1 – 0.2	0	0
Ortho-Phosphate	0	0	0	0
Potassium	2.4 – 3.0	0.5 – 0.9	0	2.0

4.7.7.Salinity effect – anaerobic process

The effect of salinity on the removal of organic matter through anaerobic processing is investigated in this part of this work using synthetic solution simulating natural stored urine that was subjected to single stage ion exchange with an initial loading of 15 mg NH_4^+/g clinoptilolite. The composition of the synthetic urine was mentioned in section 4.1, electrical conductivity used as a measure of salinity. In order to determine the effect of salinity measured as electrical conductivity on organic matter removal using anaerobic processing, different salinity levels were introduced with a constant COD concentration. To begin with the level of electrical conductivity was similar to 100% stored urine, eventually it was decreased to match the electrical conductivity 75%, 50% and 25% stored urine, respectively. The anaerobic granular sludge that was used in the EGSB was used in this stage which is already adapted to 100% natural stored urine from which nutrients had been removed. The parameters that were monitored closely in this stage are COD and electrical conductivity. At all times during this stage COD concentration will be 2700 mg/l. Figure 4.14 shows the expected operation plan of the anaerobic process with synthetic urine.

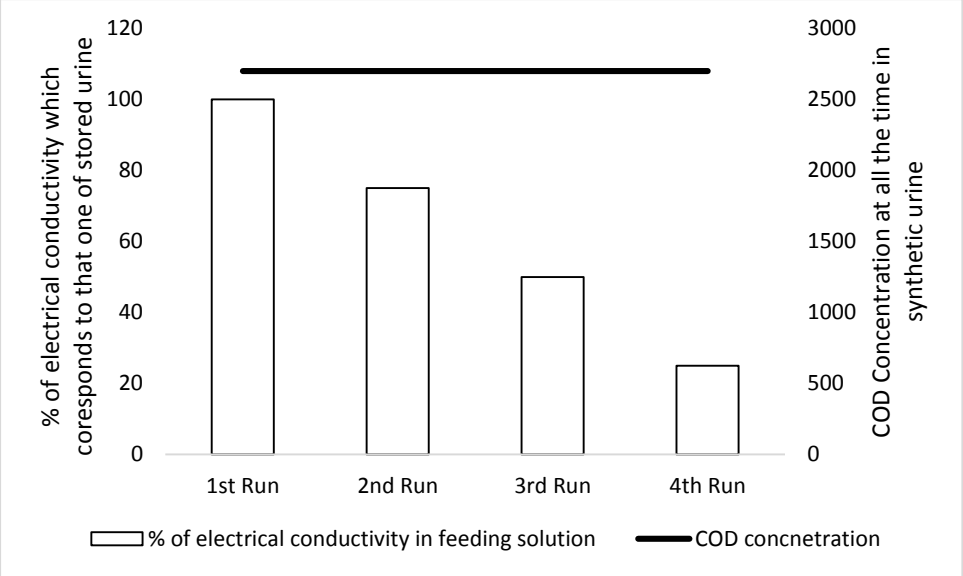

Figure 4.14 : Operation plan of anaerobic process with synthetic urine under controlled conditions.

4.8. Plant Experiments

Plant tests were performed using nutrient enriched clinoptilolite to be used as fertilizer, produced during this thesis in the initial stage of ion exchange. Pepper and tomato were used for this purpose, which are flowering plants that are easy to grow.

Pepper and tomato seedlings were purchased from Emirgan nursery. First, 800 grams of soil was placed in each pot during planting. Then a small pit was opened in the middle of the soil and the seedling was placed properly and 200 g more of soil was added in order to hold the seedlings in the soil firmly. The experiment was carried out using a total of 12 pots, each set of pepper and tomato contained 2 pots as duplicates for control without any fertilizer, 2 pots of clinoptilolite fertilizer and 2 pots of synthetic fertilizer (20:20 Composite).

Nitrogen, phosphorus and potassium content of the fertilizers used are 12 mg NH_4/g clinoptilolite, 0.58 mg PO_4/g clinoptilolite and 2.27 mg K/g clinoptilolite. 86 g of clinoptilolite was used for each pot in which clinoptilolite to be used as a fertilizer, while 250 mg of synthetic fertilizer was used for each pot of pepper and tomato in which synthetic fertilizer is used (Dogan, 2015).

4.9. Analytical Methods

The parameters measured in this research were, pH, electrical conductivity (as an indicator of salinity), COD, ammonium, TKN, ortho-phosphate, total phosphorus, and potassium. pH was measured using a pH probe of Hanna instruments brand with a product No. HI 1332. Electrical conductivity was measured using HACH CDC 401 probe. Ammonium concentration was measured using Orion 720 ion meter and ammonia electrode, product code Thermo Orion 9512. TKN was measured using Macro Total Kjeldahl Nitrogen method. Phosphorus analysis measured using tin chloride method. Potassium measured by using flame photometry device. Total and soluble COD measurements were performed by using open reflux method. Solid analysis was performed for anaerobic granular sludge and samples of influent and effluent of the EGSB reactors (Standard Methods, 2005). Samples for soluble COD, othro-phosphate, potassium and ammonium were filtered by using 0.45 µm plastic filters with syringe. Table 4.11 shows a summary of the analytical methods used in this research.

Table 4.11 : Analytical methods of the parameters measured in the research.

Parameter	Analysis method	Standard
pH	pH probe method	
Electrical conductivity	Conductivity probe method	
Ammonium	Ammonia probe method	
TKN	Macro Total Kjeldhal Nitrogen method	Standard
Ortho-phosphate	Tin chloride method	Methods, 2005
Total phosphorus	Tin chloride method	
Potassium	Flame photometry method	
COD	Open reflux method	
TSS	Gravimetric method	

5. RESULTS AND DISCUSSION

5.1. Characterization of Urine

Human urine as fresh and stored were characterized for pH, electrical conductivity, COD, ammonium, TKN, ortho-p, total phosphorus and potassium. Table 5.1 shows the characterestics of fresh and stored natural human urine.

Table 5.1: Characterization of fresh, stored and synthetic urine (averages).

Parameter	Unit	Fresh urine	Stored urine
pH	-	9.0	9.35
E. conductivity	µS/cm	28000	34500
Total COD	mg/l	4260	4830
Soluble COD	mg/l	4230	4725
Ammonium	mg NH_4^+-N/l	3625	4250
TKN	mg NH_3-N/l	8525	4875
Ortho-p	mg PO_4^{3-}-P/l	285	190
TP	mg PO_4^{3-}-P /l	300	205
Potassium	mg K^+/l	1225	1225

The COD of both fresh and stored urine used in this study was almost similar and almost all COD in the human urine was in the soluble form with 98% of soluble COD. The average of total COD concentration in fresh and stored human urine was 4260 and 4830 mg/l respectively, and these values fall within a wide range of COD in human urine that starts from around 1500 mg/l up to 12000 mg/l (Larsen and Gujer, 1996; Beler Baykal et al, 2011; Allar and Beler Baykal, 2015).

Ammonium concentration in fresh human urine was higher than the concentrations reported in the literature which was at the most 1160 mg/l (Kabdaslı et al, 2006) and the majority of the nitrogen in form of urea (Beler Baykal et al, 2011; Kocaturk and Beler Baykal, 2012). In this work, ammonium concentration of fresh urine is 3625 mg/l, comparing this value to the TKN concentration of fresh urine it can be concluded that around 40% of the nitrogen in the fresh urine was in the form of ammonium. This reveals that the fresh urine has under gone a partial hydrolysis through the collection pipe line, which confirms the results that was found by Udert et al. (2003), in which it was indicated that through the pipe lines of a collection system hydrolysis of urea is expected due to the presence of urease enzyme. The partial hydrolysis that occurred in

the pipelines explains the high pH and electrical conductivity of fresh urine in this work compared to what was reported in the literature.

Regarding phosphorus, the majority of the phosphorus in natural human urine is in the ortho phosphate from with about 95%. Ortho-p in fresh urine was higher than that of stored urine due to the precipitation of calcium phosphate and spontaneous struvite formation in the pipe lines and collection system. The amount of reduction in ortho-p between fresh and store urine is around 30% that matches the percentages mentioned in previous studies (Udert et al, 2003; Kucaturk, 2010). Potassium is the parameter that shows no change at all between fresh and stored urine with an average concentration of 1225 mg/l and this concentration is consistent with the previous studies in the literature (Kocaturk and Beler Baykal, 2012; Allar, 2015).

It can be observed form Table 5.1, that both fresh and stored urine have the same pH value, and this observation is in contrast to many of studies that were conducted on fresh urine in which the pH value of fresh urine falls in a range of 6.0 – 7.3 (Larsen and Gujer 1996; Kabdaslı et al, 2006; Beler Baykal et al, 2011; Kocaturk and Beler Baykal, 2012). The electrical conductivity on another hand was not similar the stored urine which has a higher electrical conductivity, that more or less matches with what was reported previously by other studies (Allar and Beler Baykal, 2013; Allar, 2015; Allar & Beler Baykal 2015). Electrical conductivity of fresh urine was higher than the value reported in another study in which the electrical conductivity was 22500 µS/cm while in this work it is 27850 µS/cm (Beler Baykal et al, 2011).

5.2. Adaptation of Anaerobic Granular Sludge / Configuration (a)

In this work anaerobic granular sludge was used in an EGSB reactor to treat the residue of stored human urine after ion exchange process were nutrients had been removed. Anaerobic granular sludge was brought from a confectionery wastewater treatment plant treating a wastewater of characteristics shown in Table 5.2. Source separated human urine has totally different characteristics than the confectionery wastewater that anaerobic granular sludge originated from. Fresh and stored human urine is considered as a highly saline solution with an electrical conductivity range from 13000 to over 55000 µS/cm (Beler Baykal et al, 2009; Beler Baykal et al, 2011), while the confectionary wastewater has much lower a value which does not exceed 8% the electrical conductivity of human urine at the lower end. Comparing other parameters

of urine to confectionary wastewater, it can be found that COD more or less falls in the range of confectionary wastewater. However, NH_4^+ in human urine is much higher and makes up about hundred times of that one of confectionary wastewater.

Table 5.2 : Characteristics of confectionery wastewater compared to urine (Larsen and Gujer, 1996; Kocaturk and Beler Baykal, 2012; Ozgun et al, 2012; Allar and Beler Baykal, 2013; Allar and Beler Baykal 2015).

Parameter	Unit	100% Fresh urine	100% Stored urine	Confectionery WW
pH	pH unit	6.0 – 7.3	8.9 – 9.8	3.83 - 6.48
EC	µS/cm	13000 – 22500	36700 – 57000	252 - 689
COD	mg COD/l	1534 – 12000	4300 – 7275	6540 - 37180
Ammonium	mg NH4+-N/l	160 – 1160	3660 – 8570	0.22 – 15.4
TKN	mg N/l	5700 - 9760	5666 - 8600	16 - 95

The anaerobic sludge and bacteria are very sensitive for the changes in the environmental conditions. As the two liquid phases have different natures, adaptation is required. In the case of this work, salinity imposes a threat and challenge for the success of anaerobic granular sludge to handle such high salinity level compared to that one of confectionery wastewater.

In order to adapt the granular sludge to high level of salinity, fresh urine was used as a feeding solution of the EGSB reactor at first. The adaptation was performed stage wise starting from 25% fresh urine in the feeding solution and then increased to the next level. For adaptation stage with fresh urine configuration (a) in Figure 4.7 was used. This configuration was also intended to check the ammonium release from the anaerobic process as well.

At all the times during this work, the pH of the influent of EGSB reactor was adjusted to a pH of around 7.5, to maintain a suitable pH condition for the anaerobic microorganisms (Speece 1983; Speece 1996; Khanal, 2011) and to prevent the loss of ammonium in form of ammonia further more as ion exchnage is the mechanism of nitrogen removal total ammonia nitrogen should be in the form of ammonium to enable ion exchnage. Figure 5.1 illustrates the pH changes in the EGSB reactor at 25% fresh urine adaptation stage.

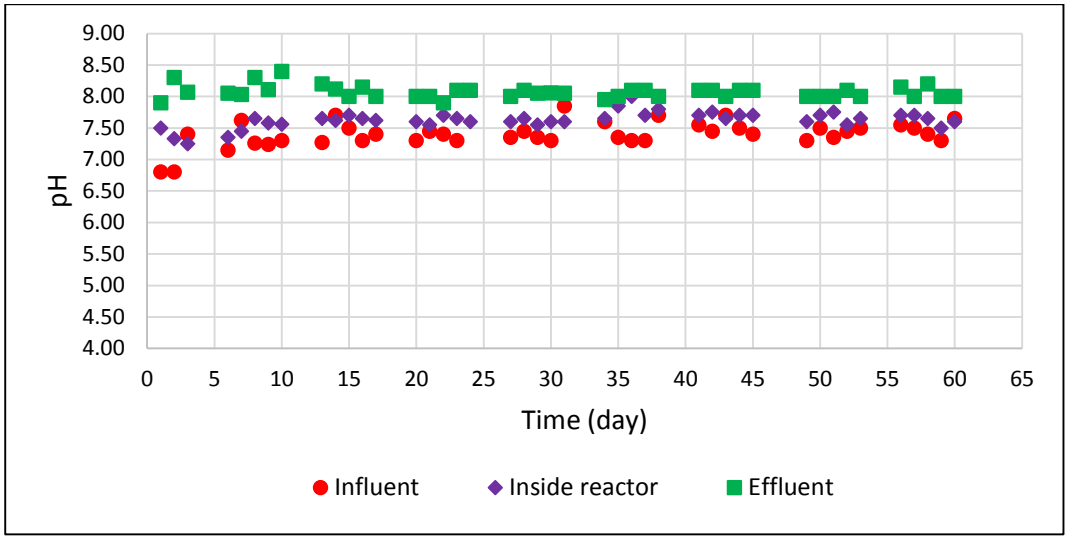

Figure 5.1 : pH of EGSB reator at 25% fresh urine adaptation stage.

The pH inside the reactor showed a small increase compared to pH value in the influent as it can be expected that alkalinity was produced in the reactor. The effluent pH value was always around 8.0, which is an acceptable value for the prevention of losing the ammoium form. No drop in pH was observed inside the reactor to show there was no accumulation of volatile fatty acids inside the reactor. The electrical conductivity was measured at the influent and effluent to observe any changes; the electrical conductivity of the influent was close to 9000 µS/cm and effluent showed a slight change of about 7% as shown in Figure 5.2.

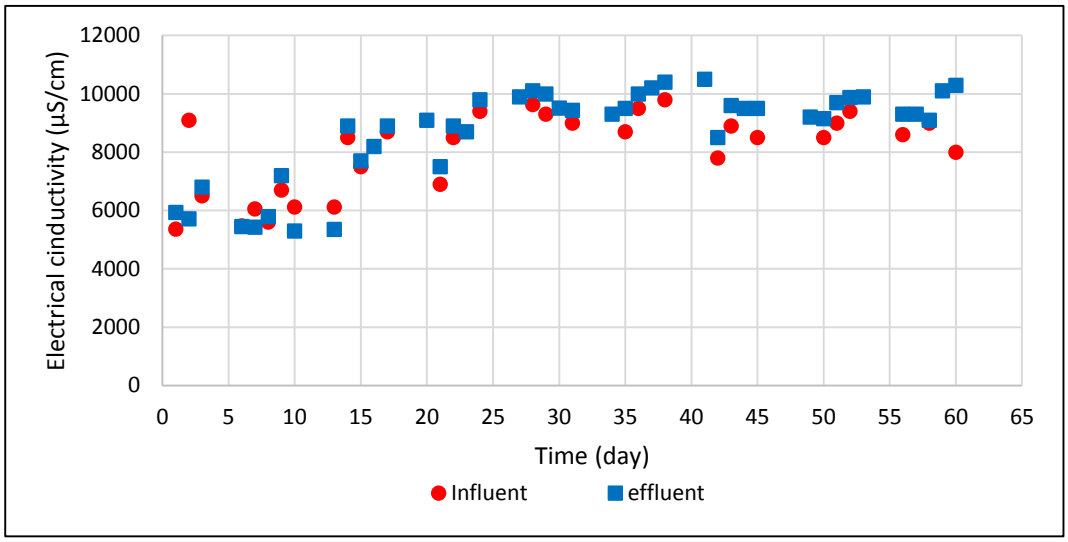

Figure 5.2 : Electrical conductivity of 25% fresh urine adaptation stage.

Under the experimental conditions employed in this study, the results revealed that with 25% fresh urine, COD removal efficiency fluctuated in the first month of the adaptation period, but stabilized thereafter as shown in Figure 5.3. Tiny particles were

observed in the effluent that was most probably particles from the sludge escaping from the reactor. Upon this observation, both total and soluble COD concentrations were analyzed at the effluent. The COD of the influent was 1200 mg/l COD an averages. In the effluent, the total COD was around 550 mg COD/l at the end of the first month of adaptation, which after one month started to stabilize at a concentration of 440 mg COD/l and a soluble COD of 300 mg COD/l. The results have revealed that EGSB reactor was reasonably successful in terms of reducing COD concentrations with a reduction of 60% for total COD, and 75% for soluble COD, as shown in Figure 5.4.

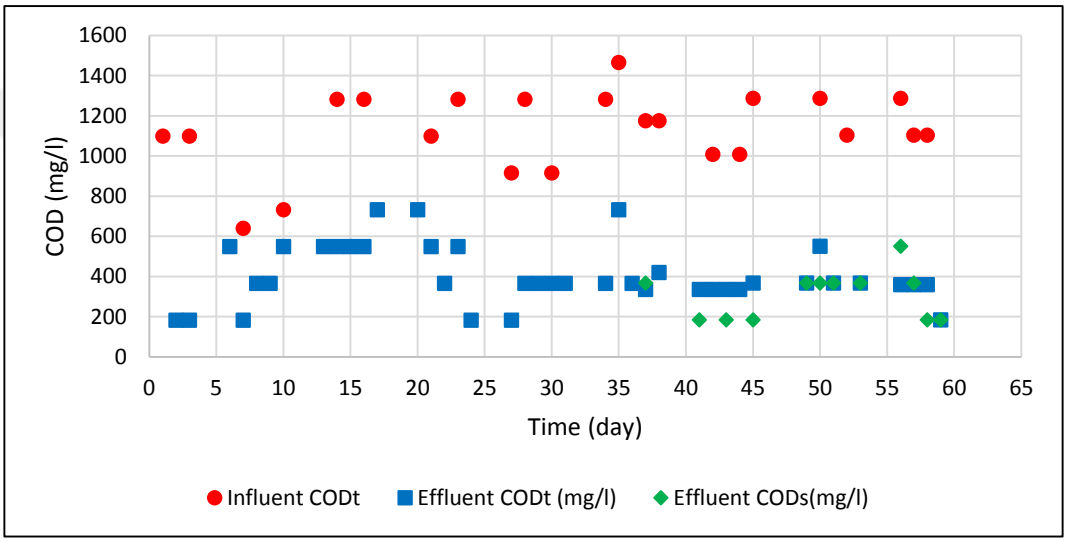

Figure 5.3 : COD Concentrations at 25% fresh urine adaptation stage.

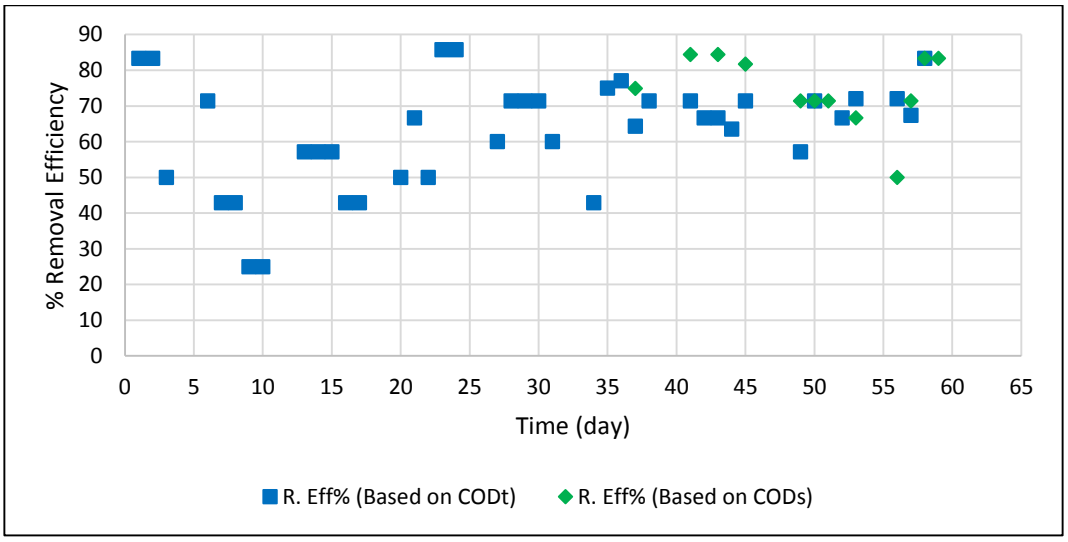

Figure 5.4 : COD removal efficiency of 25% fresh urine adaptation.

The results obtained at this stage was compared to other studies performed using EGSB with similar COD concentrations. The results were in line with Yang et al, (2018) in which EGSB reactor was used to treat low strength synthetic municipal wastewater. The OLR of this stage of adaptation was 0.72 kg COD/m^3 and it was lower than that of Yang et al, (2018) which was up to 2.7 kg COD/m^3, but the removal efficiencies were similar. Another study used EGSB reactor with a synthetic wastewater simulating low strength wastewater of a 600-800 mg/l of COD showed removal efficiencies around 80% and 66% could be achieved with an OLR of 6.5 and 12 kg COD/m^3 day respectively (Yoochatchaval et al, 2008). It is important to note that, in both of these studies salinity is supposed to be much lower than the salinity of urine employed at this stage as the liquid phase involved simulated domestic wastewater. Based upon COD conversions, theoritecal methane production for this system was calculated that about 1.7 l/day of methane can be produced as an average when a stable COD removal efficiency was observed The 1.7 l of CH_4/day is corresponding to 0.3 l CH_4/l urine, as shown in Figure 5.5.

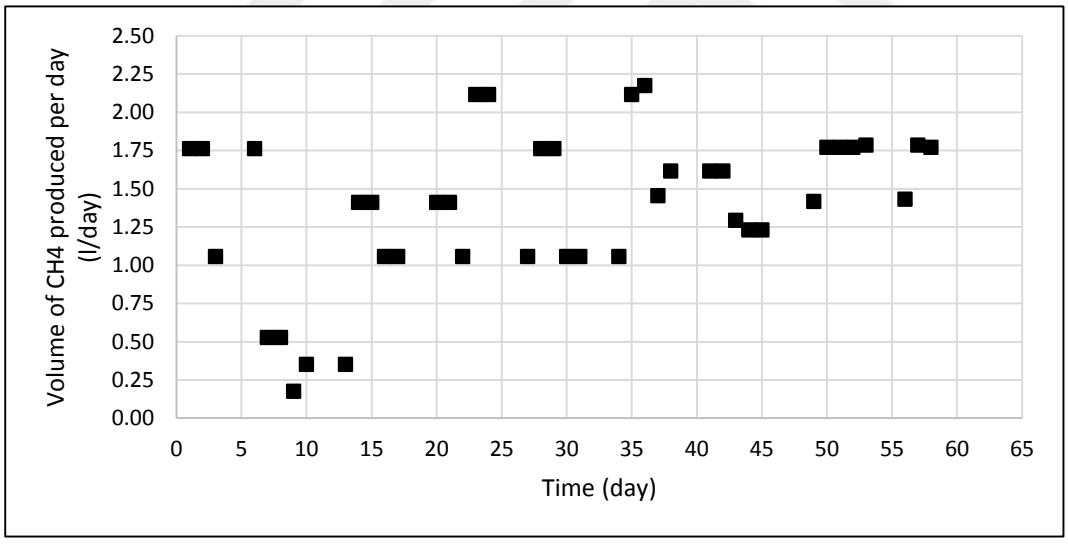

Figure 5.5 : Calculated amount of methane based on COD removed from 25% fresh urine adaptation stage.

Ammonium was monitored to check for release from the anaerobic process at the effluent of the EGSB reactor. The results of this adaptation stage revealed that 6% of release could be expected revealing that the ammonium increase at the effluent was relatively low as shown in Figure 5.6. Ammonium results were comparable to TKN results that showed low increase of 3% at the effluent. The ammonium concentration at this adaptation stage did not reach the inhibition concentration in terms of

ammonium and TAN which is reported to be 3000 mg/l for ammonium (McCarty, 1964; De Lemos Chernicharo, 2007; Khanal, 2011) and 1500 – 7000 mg/l for TAN (McCarty and McKinney, 1961; Lettinga, 1988; Bujoczek et al, 2000; Hejnfelt and Angelidaki, 2009).

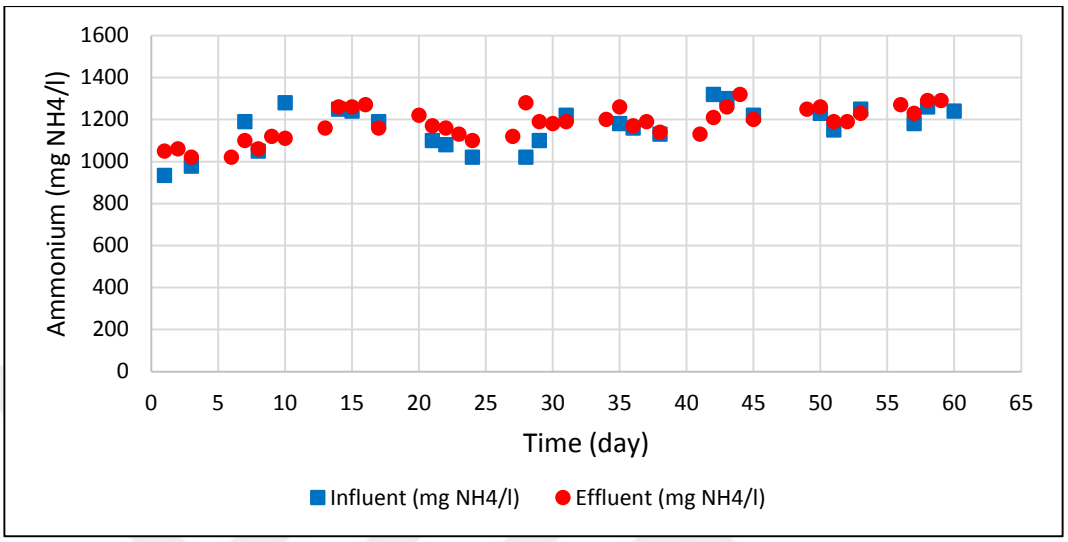

Figure 5.6 : Ammonium concetration at 25% fresh urine adaptation stage.

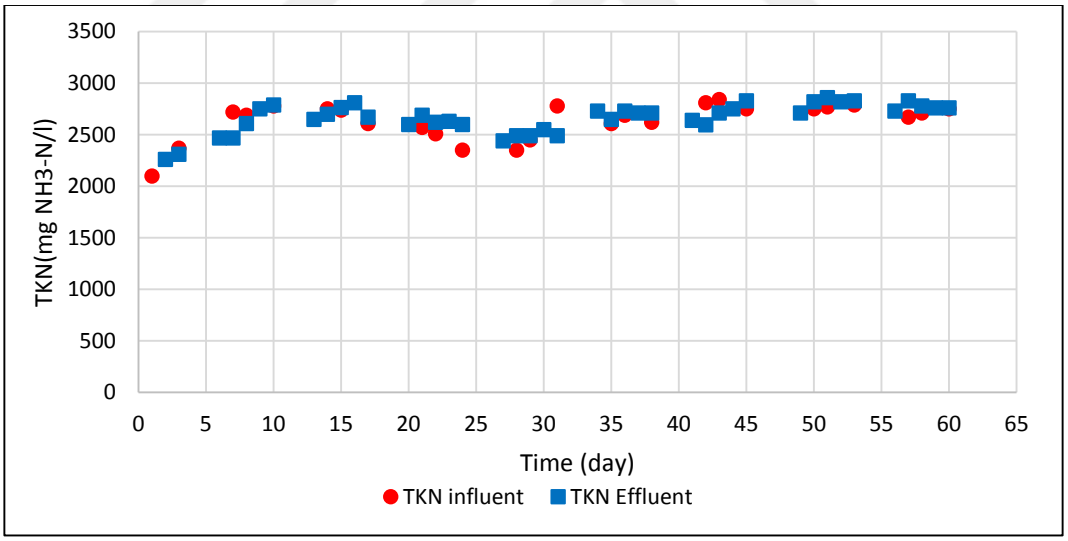

Figure 5.7 : TKN concentrations at 25% fresh urine adaptation stage.

The granular sludge showed a considerable performance at this stage of adaptation with a salinity around 9000 µS/cm which is at least 13 fold over that one of confectionery wastewater, however, the inhibition limits of electrical conductivity were not reached which is 35000 µS/cm (Ogata et al., 2016).

After two months of adaptation with 25% fresh urine in the influent, and after the stabilization of COD removal efficiency, the fresh urine concentration in the influent

was increased to 50%. The concentrations at this stage were doubled of that one of 25%. The performance of the EGSB reactor was monitored for the same parameters of pH, electrical conductivity, COD, ammonium and TKN. Regrding the pH of 50% fresh urine adaptation stage, it was similar to the previous stage with controlled pH at the influent to be around 7.5, slight increase inside the reactor and pH of around 8.0 at the effluent, as show in Figure 5.8.

The salinity at this stage increased to about 20000 µS/cm, the threshold for the electrical conductivity inhibition which is 35000 µS/cm (Ogata et al., 2016) was not reached at this stage but the electrical conductivity was doubled compared to the previous one. Figure 5.9 presents the electrical conductivity of 50% fresh urine the adaptation stage.

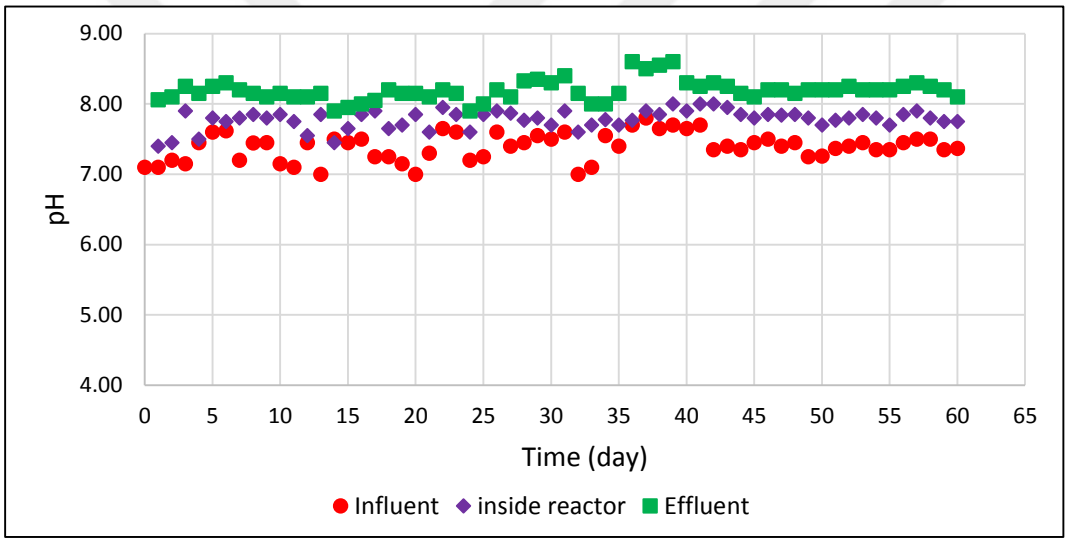

Figure 5.8 : pH of 50% fresh urine adaptation stage.

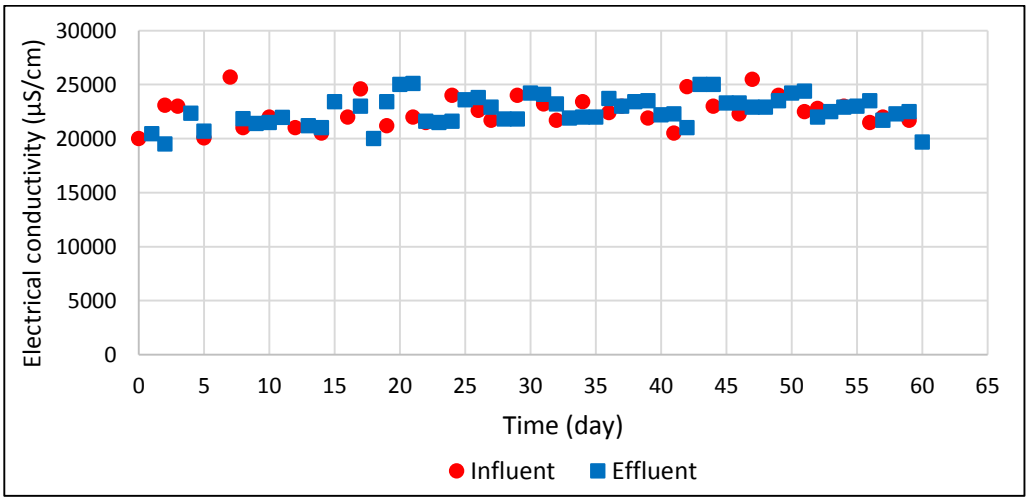

Figure 5.9 : Electrical conductivity of 50% fresh urine adaptation stage.

The performance of the EGSB reactor under 50% fresh urine adaptation stage was monitored and the results revealed that the first week of this stage witnessed a drop in the removal efficiency to reach values of less than 20%, but the week to follow the removal efficiency started to increase. This can be attributed to the sudden increase of electrical conductivity from 9000 to 20000 µS/cm. It took about a month for the granular sludge to stabilize and show a stable COD removal at the effluent. The COD at the effluent which was 1250 mg/l for total COD and around 750 mg/l for soluble COD as an average, reduced from a COD concentration at influent around 2110 mg/l, as shown in Figure 5.10. The COD removal efficiency at this stage was at an average based on total COD was around 45% and based on soluble COD was around 60% as illustrated in Figure 5.11 which was lower than that of 25% . The difference between total and soluble COD was attributed to the tiny particles of sludge that escaped from the reactor, and the analysis of total suspended solids showed an increase at the effluent compared to influent as shown in Figure 5.12 supporting the assumption of escaping sludge.

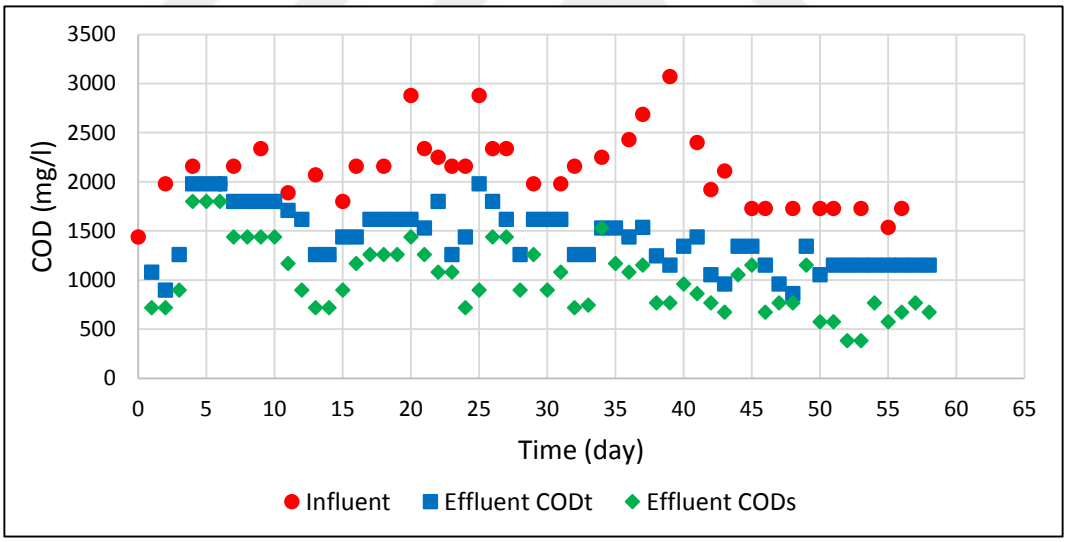

Figure 5.10 : COD Concentrations at 50% fresh urine adaptation stage.

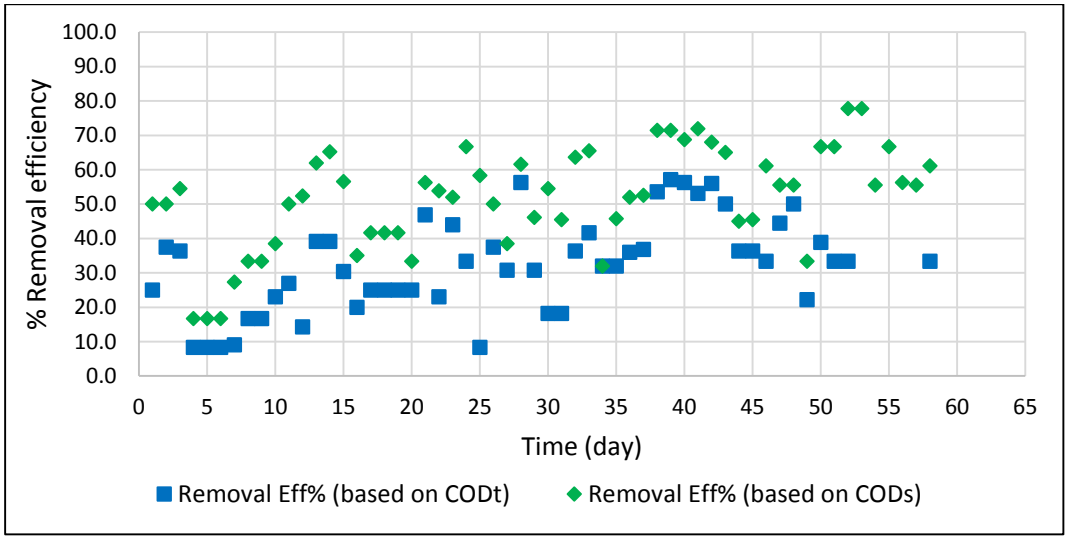

Figure 5.11 : COD removal efficiency of 50% fresh urien adaptation.

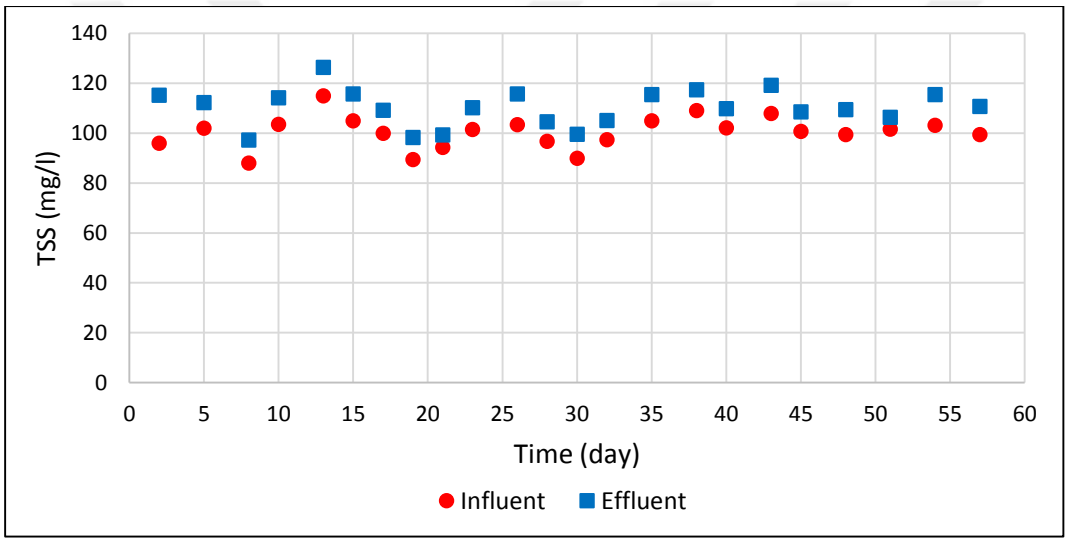

Figure 5.12 : Total suspended solids analyis of 50% fresh urine adaptation stage.

The calculated volume of the methane produced based on the amount of COD removed showed that 2.0 l CH_4/day can be produced from the reactor at this stage as shown in Figure 5.13. Based on another interpretation 0.36 l CH_4/l urine can be produced from the EGSB reactor with 50% fresh urine in the influent.

Ammonium concentration of this stage in the effluent was around 2300 mg/l. The release of ammonium at this stage was not appreciable with only 1% of increase as an average through the adaptation period of this stage. As it is shown in Figure 5.14 the influent and effluent concentration almost overlap with each other.

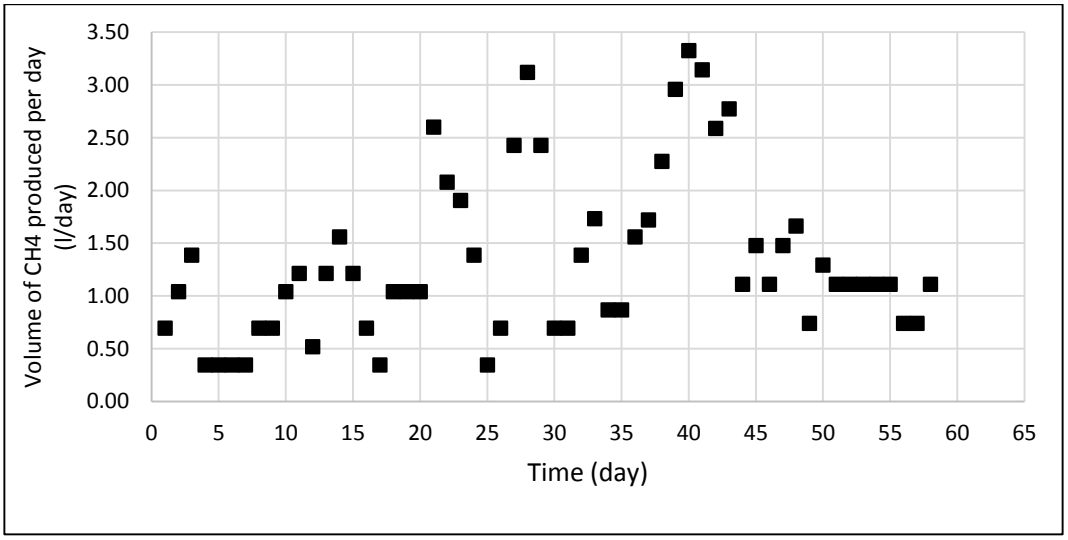

Figure 5.13 : Calculated amount of methane based on COD removed from 50% fresh urine adaptation stage.

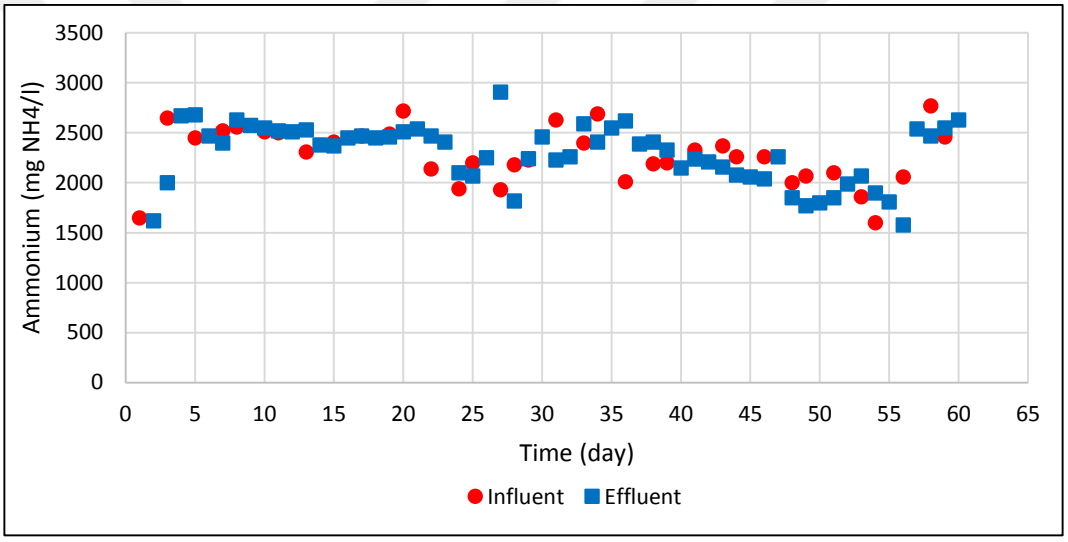

Figure 5.14 : Ammonium concetration at 50% fresh urine adaptation stage.

Noting that the pH of the influent was around 7.5 that means all the nitrogen in ammonium form. The ammonium concentration at this adaptation stage was over the inhibition limit in terms of TAN which is 1500 mg/l however it was below the inhibition level in terms of ammonium only of 3000 mg/l (McCarty and McKinney, 1961; Lettinga, 1988; Bujoczek et al, 2000; Hejnfelt and Angelidaki, 2009). TKN results at this stage did not give any indication upon ammonium release as the TKN concentration between influent and effluent was more or less the same and the increase at the TKN value was not observed. Figure 5.15 illustrates the TKN concentrations in 50% fresh urine stage.

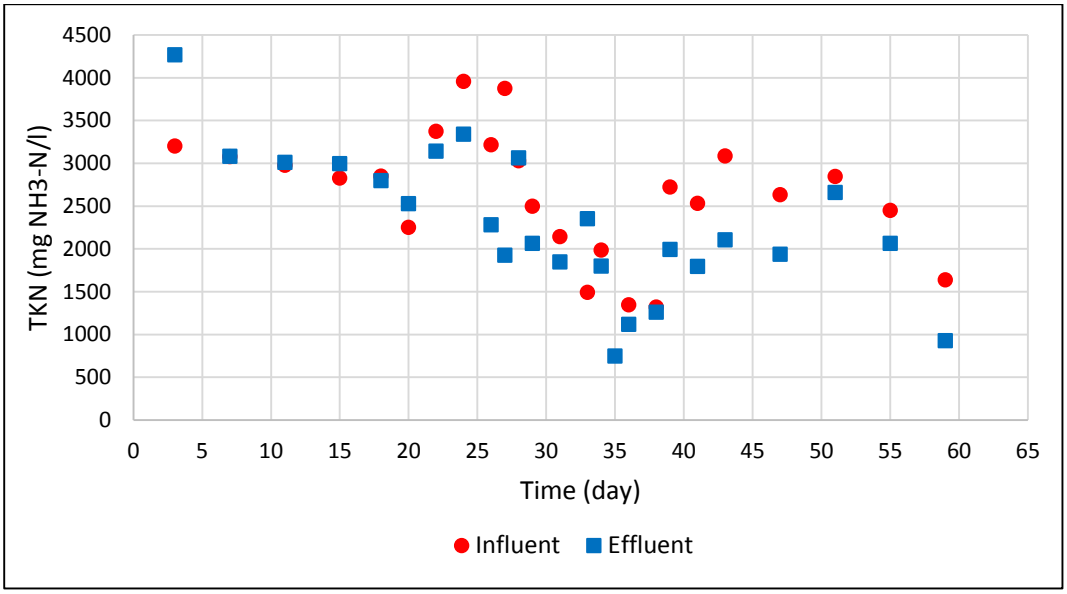

Figure 5.15 : TKN concentrations at 50% fresh urine adaptation stage.

After two months of adaptation with 50% fresh urine, it was observed that increasing the fresh urine concentration by doubling it did not give good result as the salinity in terms of electrical conductivity was increased which possibly imposed more stress on the anaerobic granular sludge. Not only salinity but also ammonium was increased. Even though that the ammonium inhibition in terms of TAN was almost at the lower end and far from inhibition related to ammonium only.

Upon the obtained results from 50% fresh urine adaptation stage, the fresh urine concentration was increased at this stage to 65% in order to introduce the anaerobic granular sludge to a small increase in terms of salinity and ammonium. The pH of this stage was unchanged similar to the previous two stages as shown in Figure 5.16.

The electrical conductivity of this stage was increased to an average of 25500 µS/cm. The electrical conductivity was still on the safe side for inhibition which is 35000 µS/cm (Ogata et al., 2016). A slight increase in the electrical conductivity value at the effluent occurred as it can be observed from Figure 5.17.

Regarding the performance of EGSB reactor and the granular sludge for the removal of COD, the removal efficiency was decreased more at this stage to be around 40% based on total COD and 50% based on soluble COD. The influent COD concentration was almost 2900 as an average, while the COD at the effluent was 1720 mg/l and 1430 mg/l based on total and soluble COD respectively.

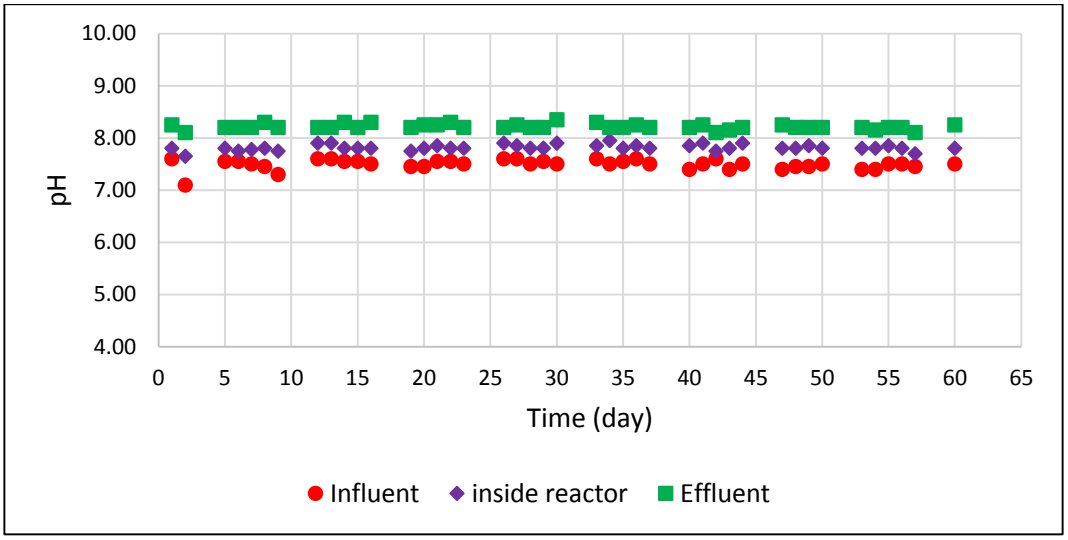

Figure 5.16 : pH values of 65% fresh urine adaptation stage.

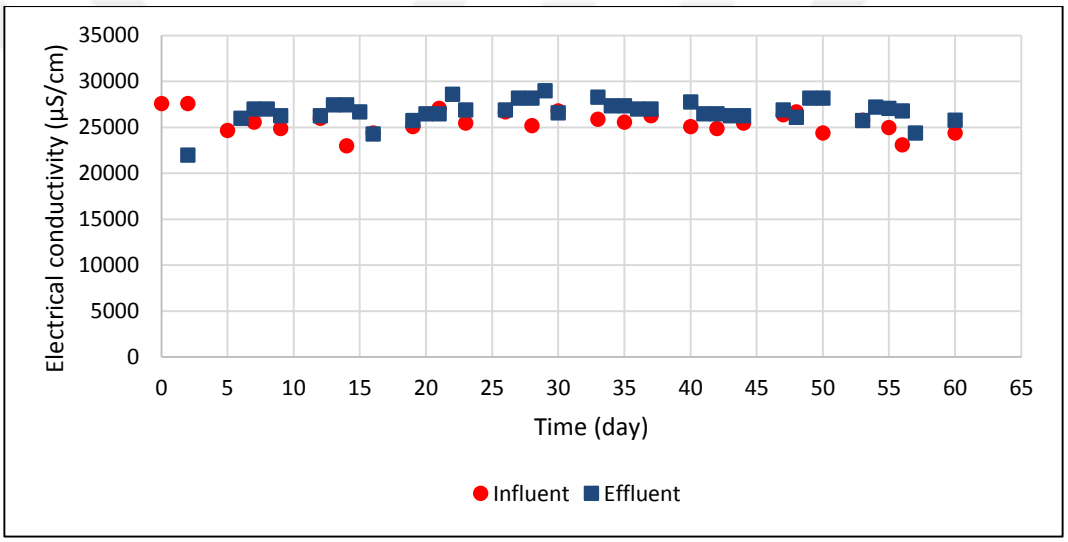

Figure 5.17 : Electrcial conductivity of 65% fesh urine adaptation stage.

Figure 5.18 and 5.19 show the concentrations and removal efficiencies of 65% fresh urine adaptation stage. The decrease of the COD removal efficiency can be attributed to the increased level of salinity and ammonium concentration and by checking the ammonium concentration at this stage, it could be noticed that the ammonium concentration was almost 4000 mg/l as shown in Figure 5.22, that means the suggested level of ammonium inhibition which is 3000 mg/l was exceeded (McCarty, 1964; De Lemos Chernicharo, 2007; Khanal, 2011). Regarding salinity, a level of 25500 µS/cm may impose a stress on the granular sludge but the value indicated in the literature for electrical conductivity inhibition threshold was not approached yet which is 35000 µS/cm (Ogata et al., 2016). The total suspended solids analysis for this stage showed an increase in the TSS value at the effluent, justifaying the difference between total

and soluble COD. Figure 5.20 shows the TSS analysis for 65% fresh urine adaptation stage.

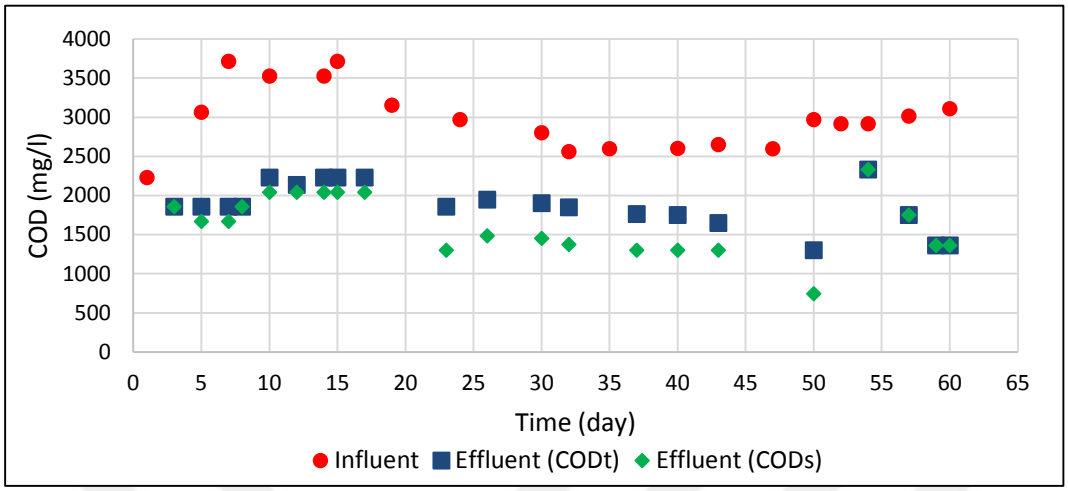

Figure 5.18 : COD Concentrations at 65% fresh urine adaptation stage.

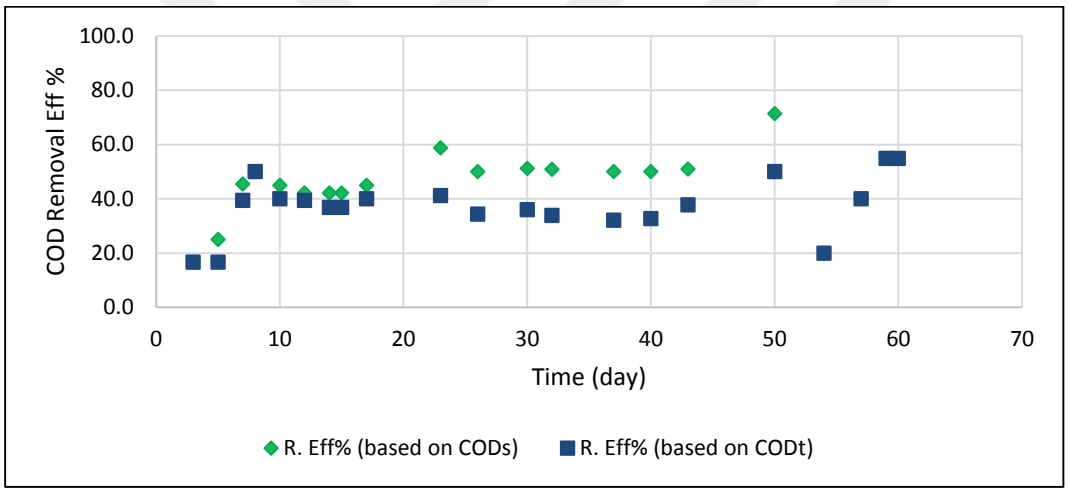

Figure 5.19 : COD removal efficiency of 65% fresh urien adaptation.

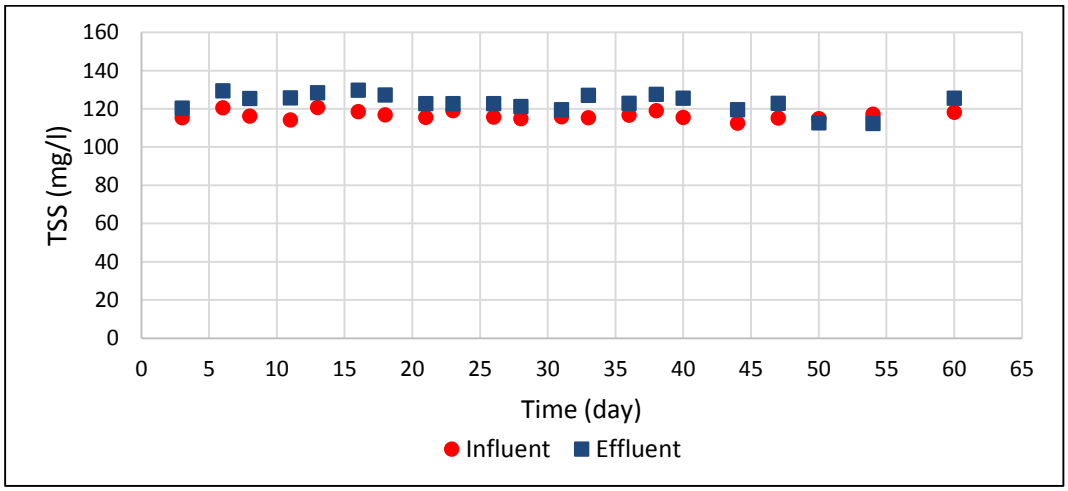

Figure 5.20 : Total suspended solids analyis of 65% fresh urine adaptation stage.

The gas counter at this stage was connected to the reactor and set to measure the amount of biogas produced from the reactor. The measurements revealed that biogas was observable but the measured quantity was not comparable with the amount of methane calculated theoretically. Figure 5.21 shows the amount of methane calculated theoretically with a start to show those days that biogas was observed by the gas counter on a qualitative bases. Theoretical calculation of methane production from the EGSB reactor with 65% fresh urine revealed that 2.2 l CH_4/day can be produced at stable COD removal efficiency, which corresponds to 0.4 l CH_4/l urine can be produced.

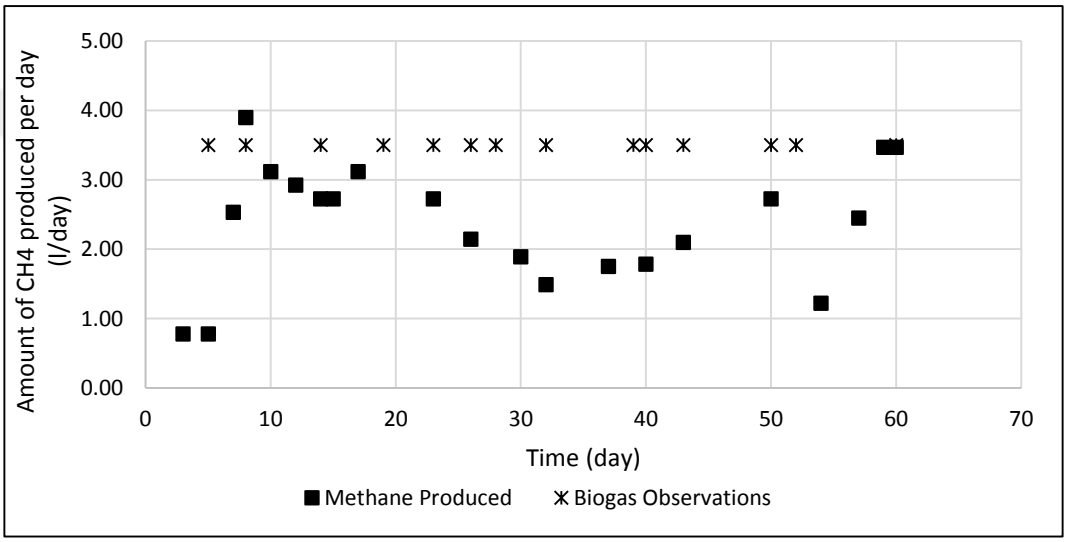

Figure 5.21 : Calculated amount of methane based on COD removed from 65% fresh urine adaptation stage.

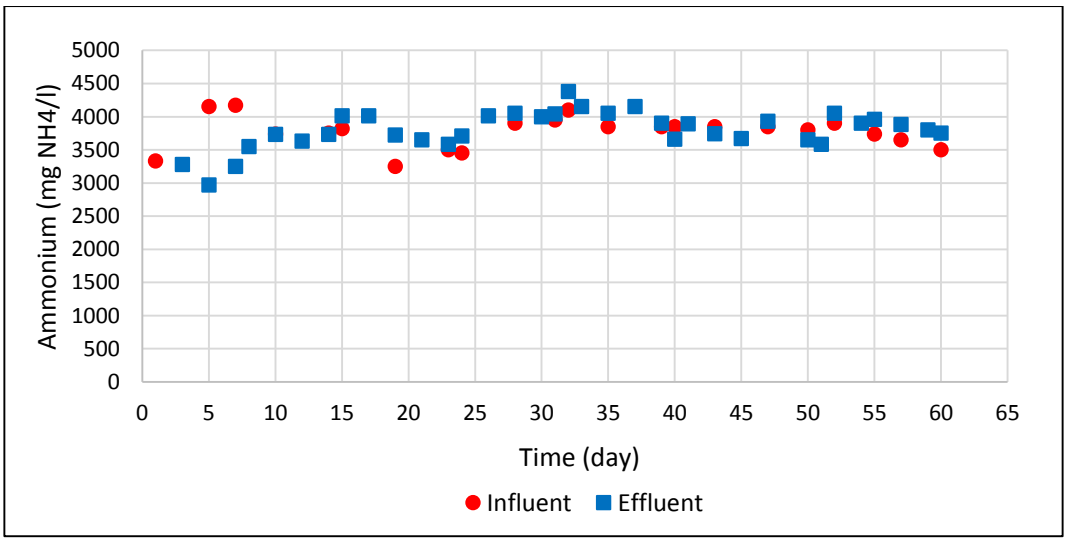

Figure 5.22 : Ammonium concetration at 65% fresh urine adaptation stage.

The release of ammonium in this stage from the anaerobic process was not appreciable, the analysis of ammonium indicated an increase of 1% only at the effluent, the same thing was observed by TKN analysis. Figure 5.22 and 5.23 shows the ammonium and TKN analysis for 65% fresh urine adaptation stage.

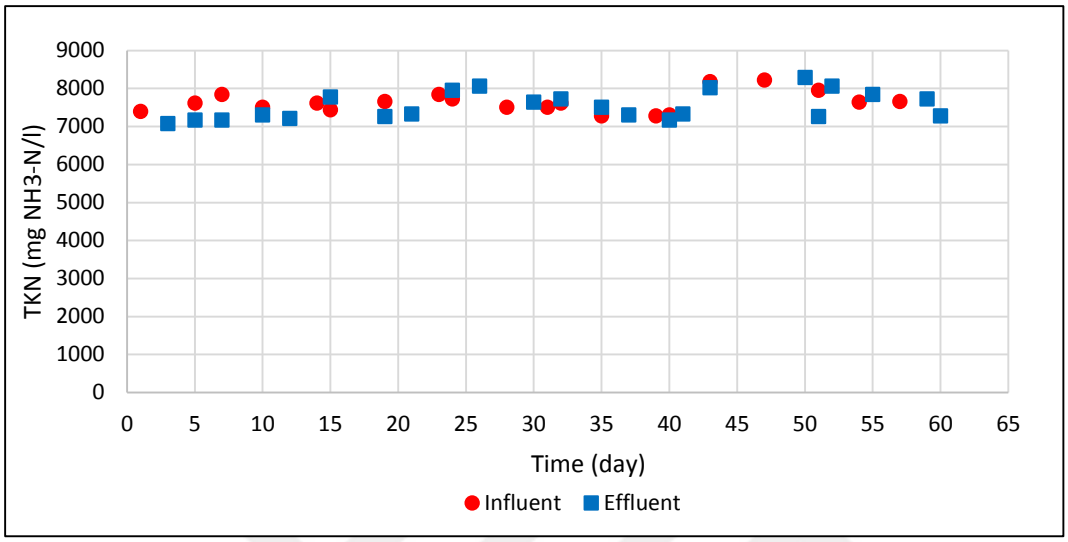

Figure 5.23 : TKN concentrations at 65% fresh urine adaptation stage.

The adaptation of anaerobic sludge using fresh urine revealed that at a low concentration of 25% fresh urine the anaerobic process performed better than the other two adaptation stages. The COD removal efficiency was 75% with 25% fresh urine, while with 50% and 65% fresh urine stages the removal efficiencies were 60% and 40% respectively. The reduction in the COD removal efficiency could be attributed to the increased concentration ammonium and salinity. During the adaptation period, it was observed that a sudden increase in salinity by increasing urine concentration in the feeding solution does not seem to be beneficial as in the case of increasing the fresh urine concentration from 25 to 50% fresh urine. The low removal efficiency of COD with higher fresh urine percentages in the influent can be attributed to the effect of increasing ammonium concentration that can cause an inhibition at 3000 mg/l (McCarty, 1964; De Lemos Chernicharo, 2007; Khanal, 2011). However, salinity measured as electrical conductivity imposes a stress on the anaerobic granular sludge but the maximum electrical conductivity used in adaptation was 25500 µS/cm that still below 35000 µS/cm which is indicated as the threshold of salinity inhibition of anaerobic process in terms of electrical conductivity (Ogata et al., 2016).

The release of ammonium was rather low, 6 % at the most indicating that the configuration (a) in Figure 4.7 will not generate benefits for the application

comboining anaerobic and sorption processes. The possible ammonium inhibition as well provides another reason that configuration (a) will not be recommended as the ammonium needs to be eliminated or reduced to a level that will not inhibit the anaerobic granular sludge for a better COD removal.

5.3. Urine Storage and Hydrolysis

The main aim of this work is to investigate the removal of organic matter from the liquid residue of ion exchange/adsorption process of stored urine employed for nutrient removal/recovery. In order to achieve that, first of all human urine must be stored for the hydrolysis of urea to be completed. Although storgae is recommended to aid the pathogens inactivation with a recommendation of 6 months' period (WHO, 2006), the urine must be stored for increasing the ammonium concentrations through the hydrolysis in which conversion of urea to ammonium takes place (Kocaturk and Beler Baykal, 2012; Allar, 2015), so that ion exchange will occur. Two batches of 200 l of human urine was prepared. The urine was collected at Department of Environmental Engineering in Istanbul Technical University from men's toilet. The urine collected received dilution as it was collected from urinals that uses flush water, the amount of dilution was undetermined due to the fact that the urinals uses the type of flush that continues as long as the flush button is pressed. Each batch took about two weeks to be filled.

During storage, urine was monitored for ammonium, TKN, ortho - p, total phosphorus, pH, electrical conductivity and COD. Ammonium and TKN were the main criteria for completion of hydrolysis. Figure 5.24 and 5.25 shows the ammonium and TKN concentrations during the storage period. The hydrolysis of urine was completed in about a month from the first day of storage which confirms the recommended storage period for hydrolysis to be completed in the literature (Kocaturk and Beler Baykal, 2012; Allar, 2015). At the beginning of the storage period NH_4^+/TKN was around 70% in batch 1 and 80% in the second batch. After one month of storage, hydrolysis was completed and the ammonium concentration was stabilized at 4350 mg NH_4^+-N/l in batch 1 and 4300 NH_4^+-N/l in batch 2. Ammonium was constituted 82% and 92% in batch 1 and batch 2 respectively at the end of one-month storage.

Udert et al. (2006) stated that 90% of the nitrogen in stored urine is in the form of ammonia, as urea in urine is converted to ammonia during storage and, similar results were obtained in this study especially in batch 2. Since the conversion of urea in urine to ammonia begins in the pipeline, the conversion is completed in a shorter time during storage as indicated by Udert et al. (2006).

The observation of ammonium and TKN concentration was carried longer to obtain if any further changes occur. Batch 1 was monitored for a period of 50 days and batch 2 was monitored for 100 days. In both batches, ammonium and TKN concentrations were stable at the end without a large fluctuation from the initial value. This indicates that there is no loss of ammonium during the observation period of storage after hydrolysis was completed.

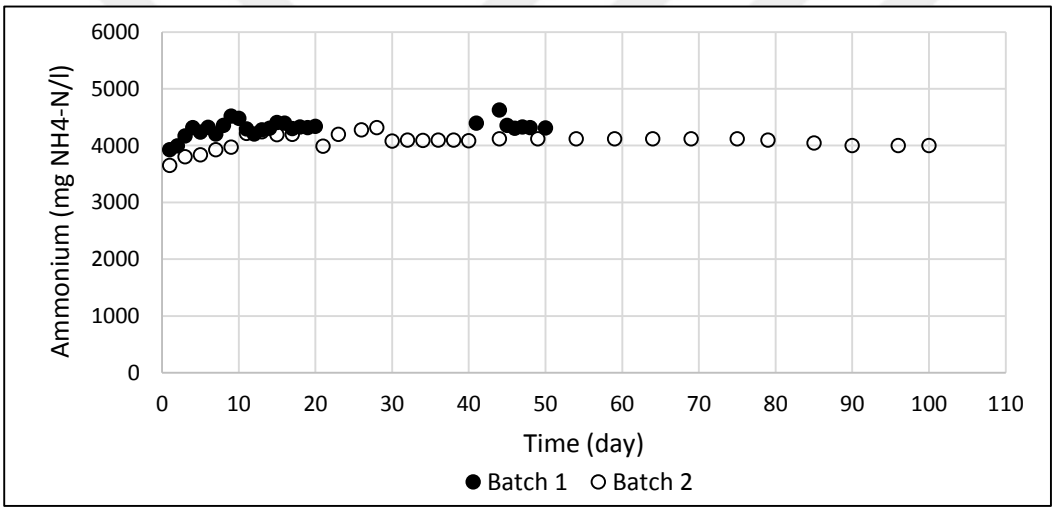

Figure 5.24 : Ammonim concentration during storage of human urine.

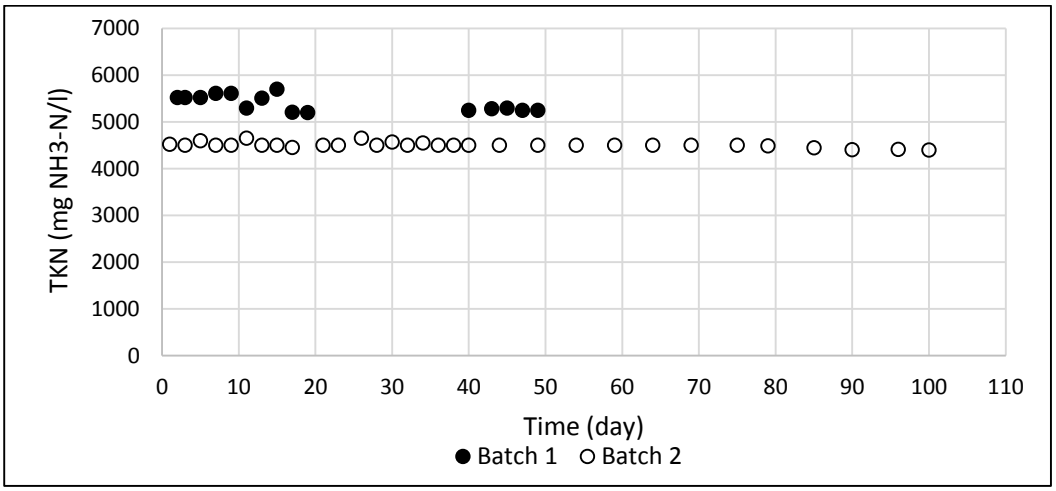

Figure 5.25 : TKN concentration during storage of human urine.

Phosphorus analysis of ortho-p and total phosphorus revealed that during storage a very small change was obtained especially in batch 2, where the ortho-p was started with a concentration of 225 mg/l and ended at a concentration of 210 mg/l. The decrease of phosphorus is attributed to the calcium phosphate precipitation and spontaneous struvite formation (Udert et al, 2003; Kocaturk, 2010; Allar 2015). The loss of ortho-p due to the precipitation in collection system is estimated to be 35 – 40% (Udert et al, 2003; Kocaturk, 2010), while the loss of ortho-p in this work is 6% which is lower than the reported percentages, leaving the assumption that more ortho-p precipitated in the pipes during collection. The percentage of ortho-p to total phosphorus in human urine was observed to be 93 % and 91% in batch 1 and 2 respectively, confirming the previous results obtained by other studies (Udert et al, 2006; Kocaturk 2010; Kocaturk and Beler Baykal 2012; Allar 2015). Based on this observation ortho-p was used through out this work to characterize the phosphorus content. Figure 5.26 illustrates the concentration of ortho-p and total phosphorus during storage.

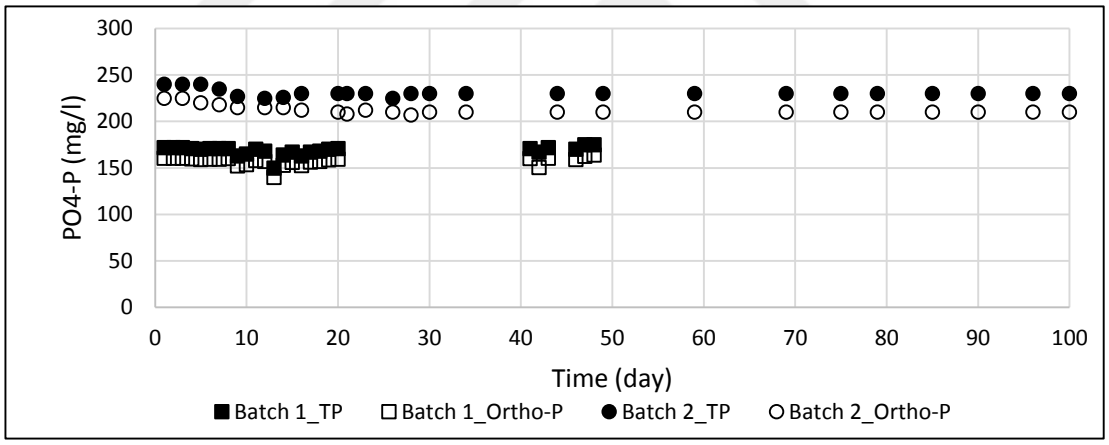

Figure 5.26 : Ortho-p and total phosphorus concentrations during storage.

Figure 5.27 shows the results of potassium analysis of both batch 1 and batch 2 during storage. Potassium seems to be unchanged during the storage both batches are almost similar with a concentration around 1200 mg/l.

pH of human urine in storage changes due to the hydrolysis of urine and conversion of urea to ammonium, that will be accompanied by the release of bicarbonate ions (Udert et al, 2003). Different pieces in the literature reported that the pH will start to raise from a value of near 7.0 and end with pH values of over 9.0 (Kocaturk, 2010; Kocaturk and Beler Baykal 2012; Allar 2015). The results from this work showed that at the beginning of storage the pH was around 8.5 then increased and stabilized around

9.3 due to the use of urine collected from a pipeline. Figure 5.28 shows the changes in pH during the storage period of both batches.

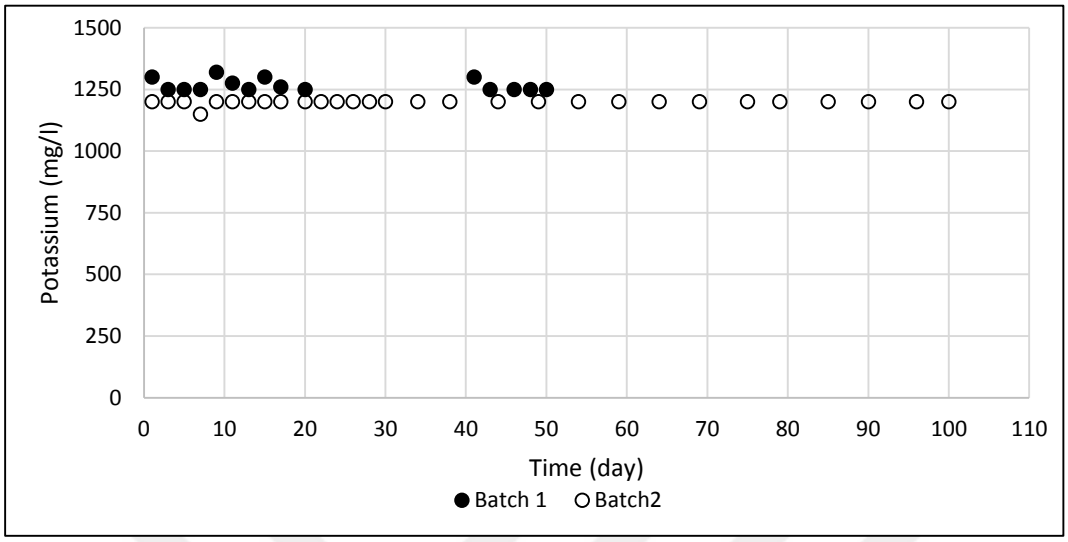

Figure 5.27 : Potassium concentation during storage period.

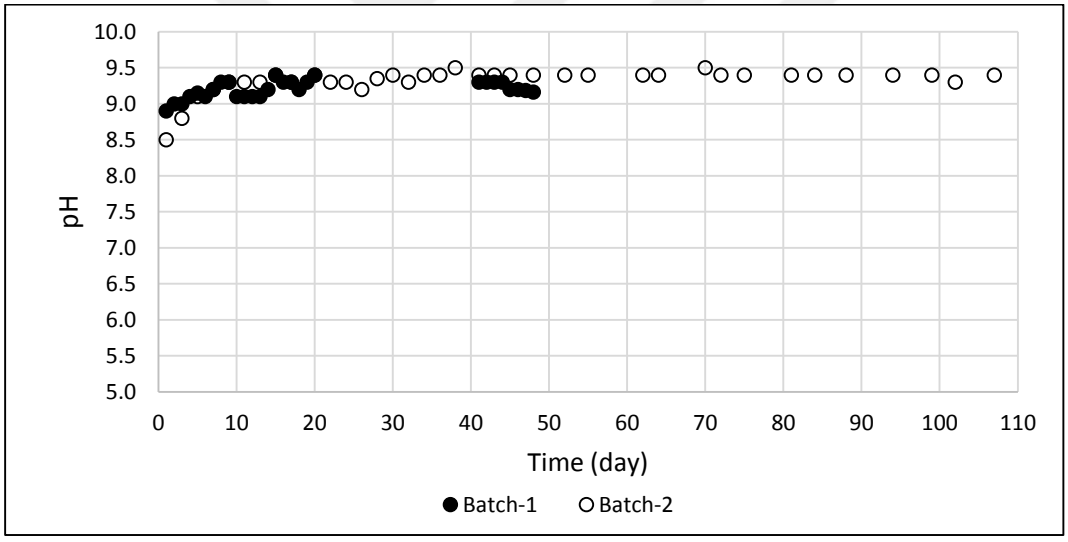

Figure 5.28 : pH changes during storage period.

A change was observed as well in the electrical conductivity as shown in Figure 5.29, in which it increased from around 30000 µS/cm to around 37000 µS/cm for batch 1. In batch 2, electrical conductivity stared from 25000 µS/cm and stabilized around 32000 µS/cm. Due to the high salinity of stored urine, a direct application of urine as a fertilizer must be accompanied by dilution before application in order to protect the plants from the high salinity that might be lethal at such high levels especially for those that are sensitive to salinity. More about the salinity of stored human urine related to the subject of this work, is that the salinity in terms of electrical conductivity of stored urine was observed to be around the inhibition threshold of anaerobic process which

is 35000 µS/cm (Ogata et al., 2016), thus this matter requires a careful attention as salinity seems to be a challenge for anaerobic processes.

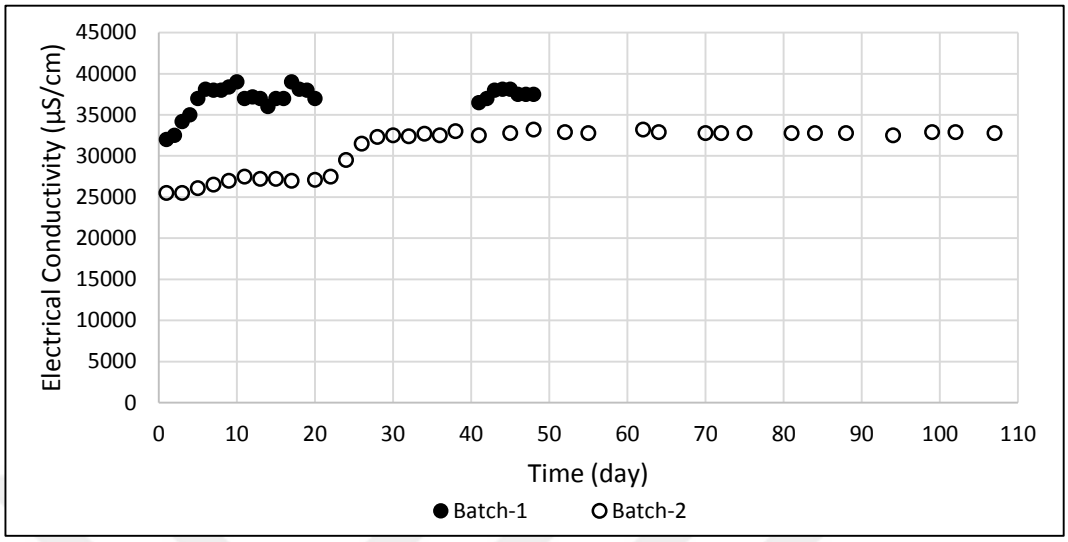

Figure 5.29 : Electrical conductivity of human urine during storage period.

COD was monitored during the storage period to understand the changes occurring in the storage period for this important parameter for anaerobic processing. The COD during the hydrolysis period showed almost no change with a stable concentration of about 4200 mg/l and 5300 mg/l for batch 1 and batch 2 respectively. After 2 months of storage COD started to decrease a concentration around 4500 mg/l. This change was observed clearly in batch 2. The reduction in COD then continued and in a period of almost 4 months the COD concentration of stored human urine was reduced to about 60% in batch 1 and 65% in batch 2 of its initial concertation. The COD reduction in urine was not reported by other studies that investigated the storage of human urine as a part of their research (Beler Baykal et al, 2009, Kocaturk, 2010; Kocaturk and Beler Baykal, 2012, Allar & Beler Baykal 2013; Allar, 2015). The COD reduction during long storage time is a critical observation as it affects the choice of treatment method to eliminate organic matter after being stored or processed further for nutrient removal. Figure 5.30 shows the changes of COD in stored urine during 170 days of storage. Both total and soluble COD were analyzed, and the analysis revealed that the majority of the COD in stored human urine was in soluble form with a 98% of soluble COD. Table 5.3 summaries the characteristics of stored urine after the completion of hydrolysis in a storage period of one month.

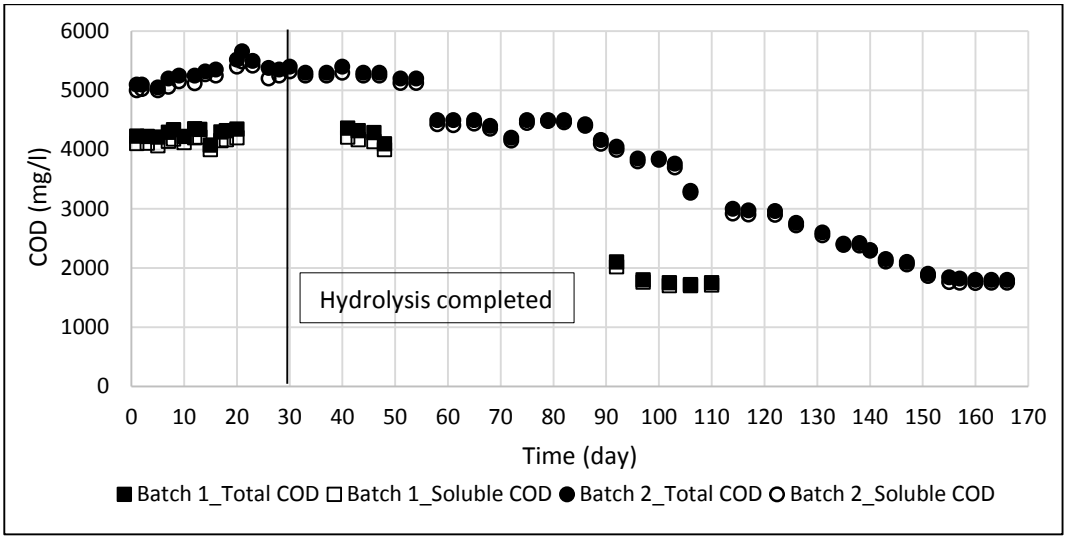

Figure 5.30 : COD chnages of stored human urine during 170 days storage period.

The observation about reduced COD concentration is important in case anaerobic process was intended to be use to handle organic matter in human urine. a lower concentration in the storage tank means a lower concentration will be introduced to the anaerobic bacteria hence a lower potential of biogas production. On the other hand, the reduction in COD in the storage tank may be beneficial in terms of environment pollution control in which much lesser concentrations will be expected as compared to its initial status.

Table 5.3 : Summary of the characteristics of stored urine after hydrolysis.

Parameter	Unit	Batch 1	Batch2
pH	-	9.4	9.4
E. Conductivity	µS/cm	37000	32000
Total COD	mg/l	4345	5320
Soluble COD	mg/l	4200	5250
Ammonium	mg NH_4^+-N/l	4300	4100
TKN	mg NH_3^+-N/l	5200	4500
Orth-p	mg PO_4^{3-}-P/l	162	210
TP	mg PO_4^{3-}-P /l	172	230
Potassium	mg/l	1250	1200

5.4. Ion Exchange – Anaerobic Process / Configuration (b)

Configuration (b) that was shown in Figure 4.7 was tested for removal of nutrients and organic matter using a single stage of ion exchange followed by anaerobic processing. This configuration is based on using ion exchange process via fixed bed clinoptilolite columns to remove nutrients from stored human urine, then the residue of the nutrient removal stage will be subjected to anaerobic processing for removal of organic matter. After hydrolysis of urea was completed, the stored urine was ready for ion exchange with fixed bed clinoptilolite columns.

Stored urine from batch 1 was used for nutrient removal after two months while stored urine from batch 2 was used directly after one month of storage when hydrolysis was completed. The pH of stored urine required an adjustment to a level that will not allow for a loss of ammonium in form of ammonia and thus the chances will be higher to concentrate more ammonium on the clinoptilolite surface. The pH was always adjusted to around 7.5 before stored urine was used with fixed bed clinoptilolite columns.

The aim of this stage was to remove the nutrients from liquid phase and concentrate them on the clinoptilolite surface in order to produce nutrients enriched clinoptilolite that can be used later as an alternative fertilizer. It was given in the literature review that ion exchange with clinoptilolite in removal and recovery of nutrients from human urine was a successful practice and that in some studies almost all the nitrogen, phosphorus and potassium was removed from the liquid phase (Beler Baykal et al, 2004; Beler Baykal et al, 2009, Kocaturk, 2010; Kocaturk and Beler Baykal, 2012, Allar & Beler Baykal 2013; Allar, 2015).

The parameters monitored in this part were ammonium, phosphorus, potassium and COD. It is to be mentioned that previous research using human urine for, but ignored organic matter. As organic matter was one of the main parameters of this work due to its effect on the efficiency of anaerobic processing, special attention was devoted to COD. The investigation upon organic matter is a sensitive issue due to the threat that this pollutant imposes on the environment if it is disposed without treatment. This work investgates concurren organic matter removal upon processing with clinoptilolite for nutrient removal and recovery.

Ion exchange with fixed bed clinoptilolite was performed in a single stage in this configuration and with initial loading of 15 mg NH_4^+/g clinoptilolite based on (Allar and Beler Baykal, 2015). The nutrient removal stage was performed with 100% recycle and each nutrient removal run lasted for 4 days as no more appreciable removal was observed after this period. Removal efficiency results revealed that 80% of ammonium, almost 100% of phosphorus and 70% of potassium was removed from the liquid phase at the end of the 4^{th} day. Figures 5.31 – 5.47 illustrate the nutrient removal results of both batch 1 and 2.

The majority of the removal had occurred in the first day of operation. The removal percentages at the first day of each run performed was about 75% for ammonium, 95% for phosphorus and 60% for potassium. The final removal efficiencies for ammonium, phosphorus and potassium were in line with previous studies that were performed under the similar operational conditions (Beler Baykal et al, 2009, Kocaturk, 2010; Kocaturk and Beler Baykal, 2012, Allar & Beler Baykal 2013; Allar, 2015).

The removal of COD was also monitored during the ion exchange process and the results revealed that there was a considerable amount of COD removed during this stage. The removal efficiency ranged between 45 – 50 % in batch 1, while results obtained from batch 2 was between 25 – 35%. Figure 6.43 – 6.46 shows the concentrations and the removal efficiencies of COD from batch 1 and batch 2.

This observation is important for anaerobic processes as the amount of organic matter expected to be treated was reduced, thus may affect the EGSB reactor performance. However, this observation may contribute more to environmental protection as the organic matter laod and consequently pollution is reduced upon processing with clinoptilolite which is mainly used to removal and recovery of nutrients. More effort should be concentrating on the possibilities of organic matter removal during ion exchange process using fixed bed clinoptilolite columns.

The mechanism of removal of organic matter in fixed bed clinoptilolite columns was not studied in this work. However, it is possible that during processing with clinoptilolite, physical adsorption on the clinoptilolite surface could had occurred that caused an accumulation of organic matter on the surface of clinoptilolite which resulting in COD reduction.

The nutrient removal stage produced a clinoptilolite loaded with nutrients, each gram of nutrient enriched clinoptilolite contained a 12 mg NH_4^+, 0.58 mg PO_4^{3-}, and 2.27 mg K^+ and 4.19 mg COD corresponding to the removal efficiencies from batch 1 and batch 2. Table 5.4 shows the initial loading and final surface concentration after single stage ion exchange for nutrient removal.

Table 5.4 : Initial and final surface concentraton after single stage ion exchnage.

Parameter	Initial loading mg / g clinoptilolite	Surface concentration mg / g clinoptilolite
Ammonium	15.0	12.0
Ortho-Phosphate	0.59	0.58
Potassium	3.39	2.27
Chemical Oxygen Demand	12.7	4.19

All in all, the liquid phase residue of single stage ion exchange process is a liquid phase in which nutrients had been removed with partial removal of organic matter as well. In terms of nutrients remaining in the liquid phase, ammonium was 1000 mg/l, phosphorus about 5 mg/l and 400 mg/l for potassium. The COD concentration in the liquid residue was at a considerable level with about 1000 mg/l for liquid residue in batch 1 and ranged between 2200 - 3800 mg/l in batch 2. It can be observed that the liquid residue has a considerable concentration of ammonium but very low concentration of phosphorus, this indicates that an addition of phosphorus is required to sustain the microbial growth of the anaerobic granular sludge. Table 5.5 shows the summary of the characteristics of the ion exchange liquid residue which is stored urine without nutrients.

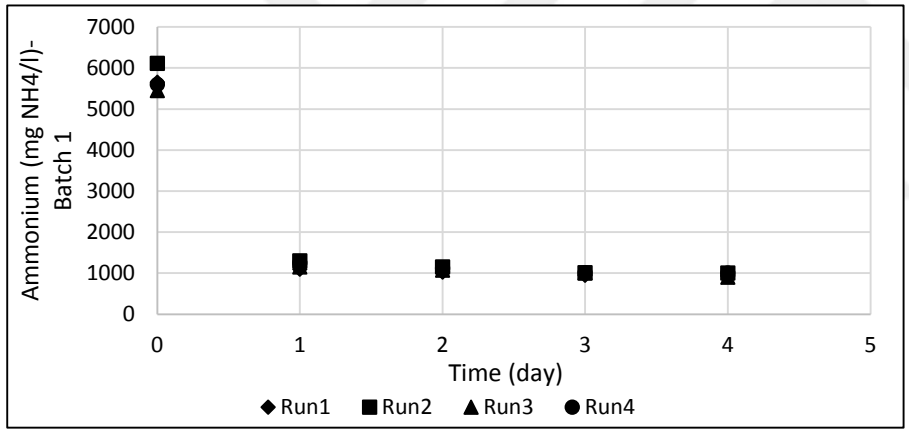

Figure 5.31: Ammonium concentration during ion exchange process of batch1.

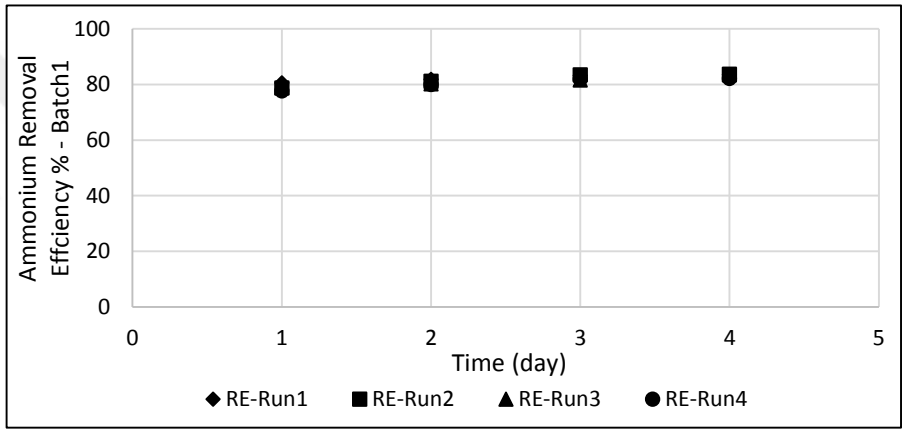

Figure 5.32: Removal efficiency of ammonium during ion exchnage process of batch1.

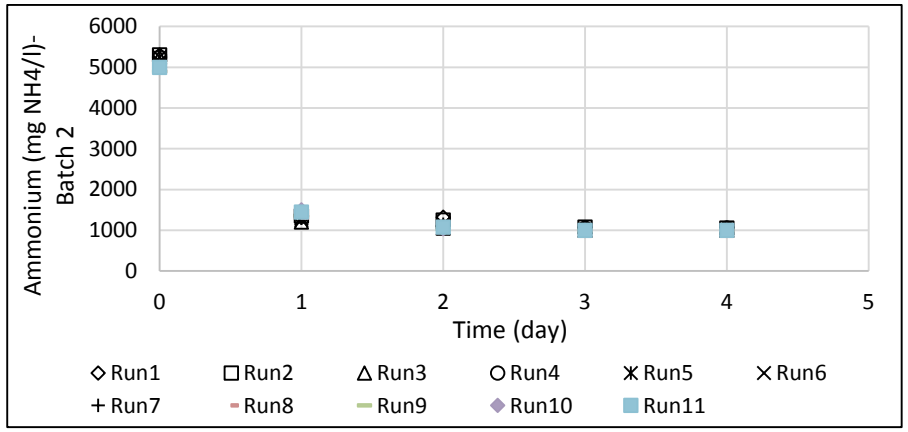

Figure 5.33: Ammonium concentration during ion exchange process of batch2.

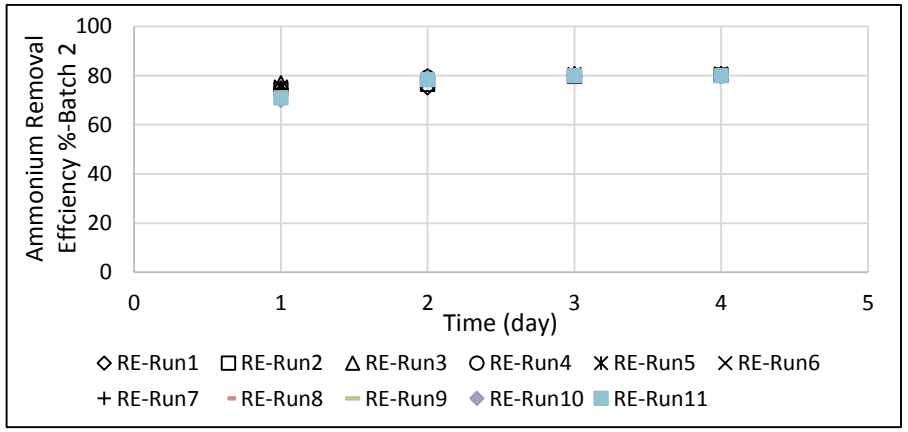

Figure 5.34: Removal efficiency of ammonium during ion exchnage process of batch2.

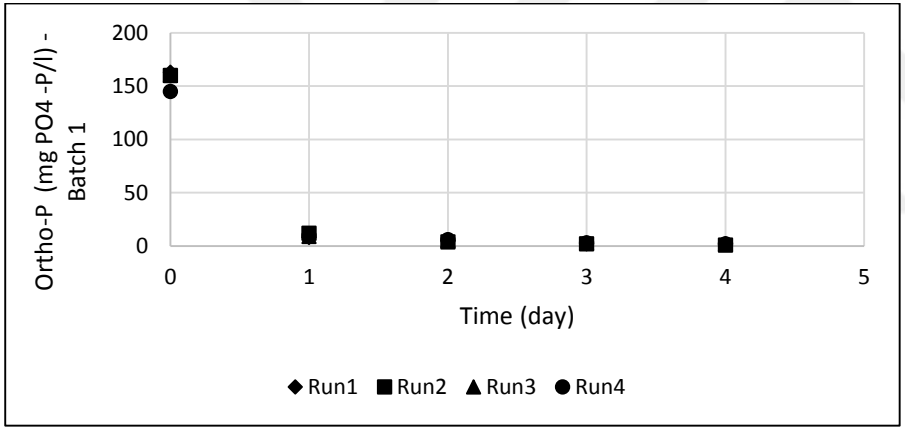

Figure 5.35: Phosphorus concentration during ion exchange process of batch1.

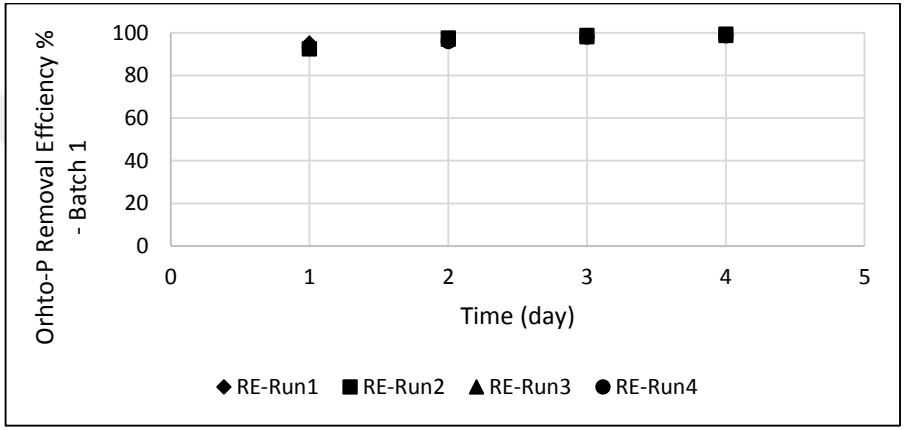

Figure 5.36: Removal efficiency of phosphorus during ion exchnage process of batch1.

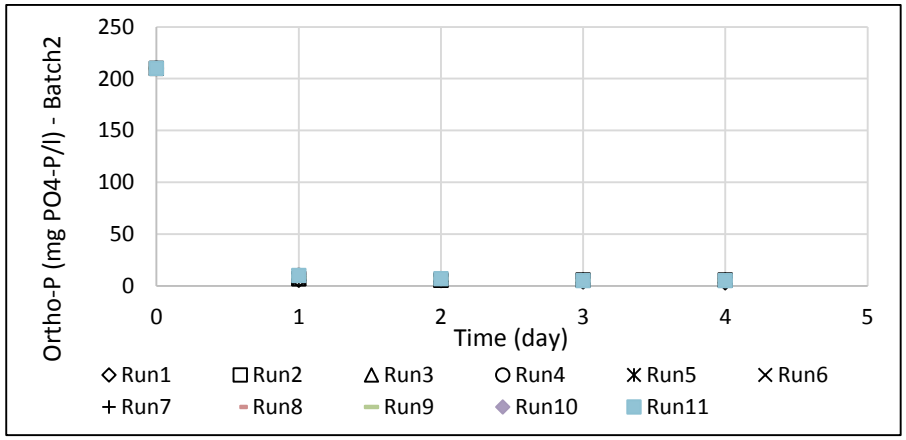

Figure 5.37: Phosphorus concentration during ion exchange process of batch2.

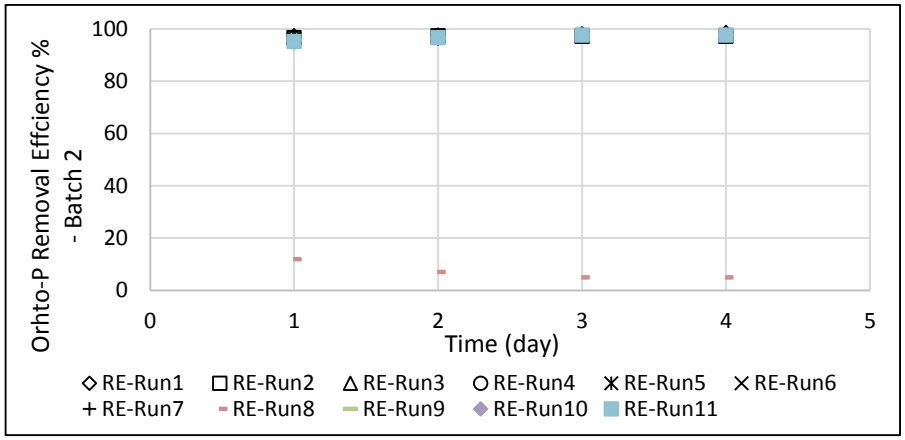

Figure 5.38: Removal efficiency of phosphorus during ion exchnage process of batch2.

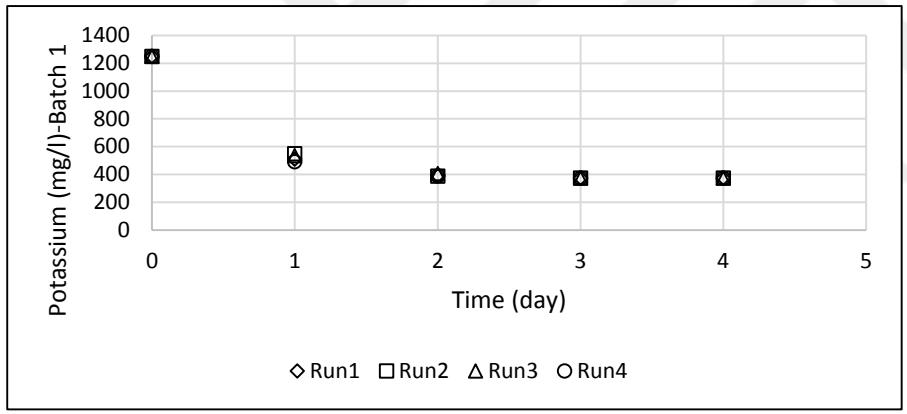

Figure 5.39: Potassium concentration during ion exchange process of batch1.

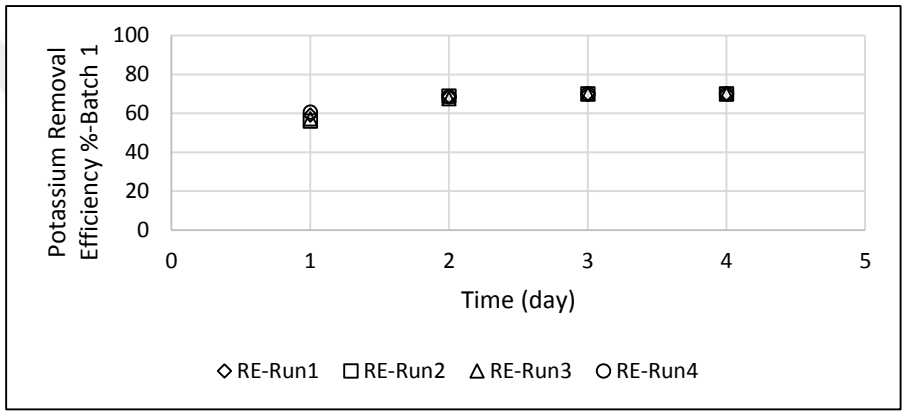

Figure 5.40: Removal efficiency of potassium during ion exchnage process of batch1.

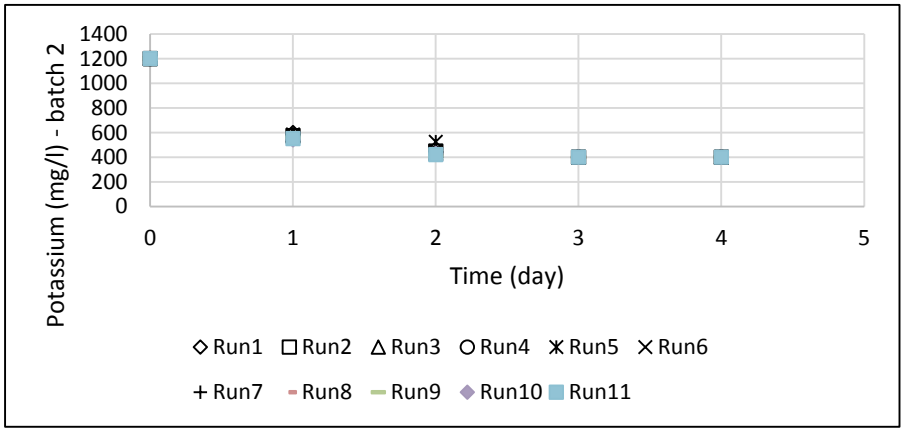

Figure 5.41: Potassium concentration during ion exchange process of batch2.

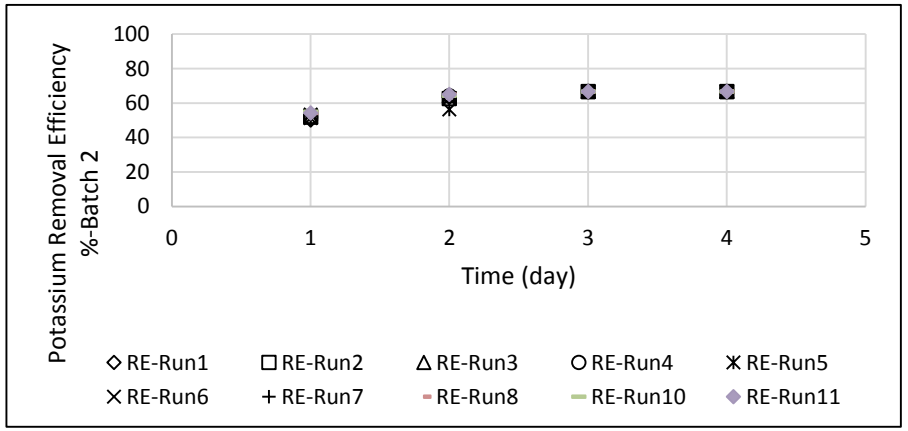

Figure 5.42: Removal efficiency of potassium during ion exchnage process of batch2.

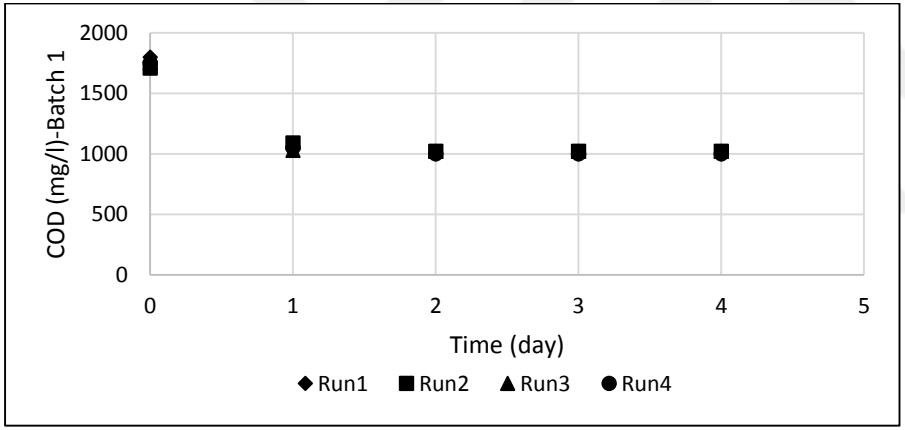

Figure 5.43: COD concentration during ion exchange process of batch1.

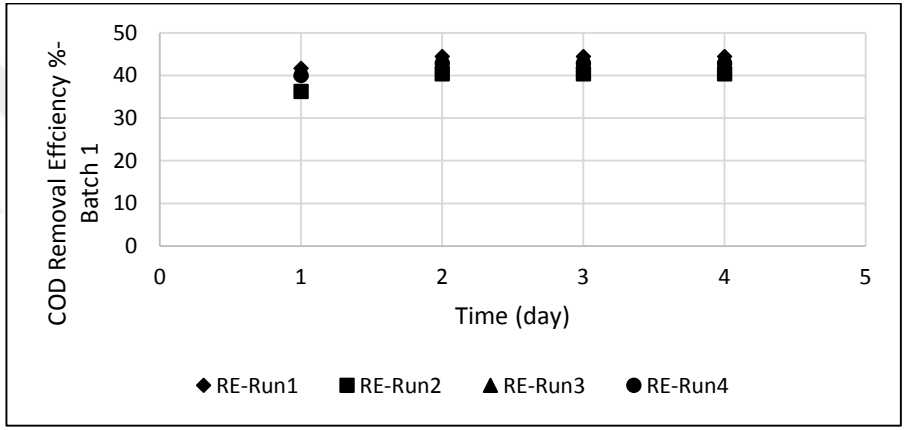

Figure 5.44: Removal efficiency of COD during ion exchnage process of batch1.

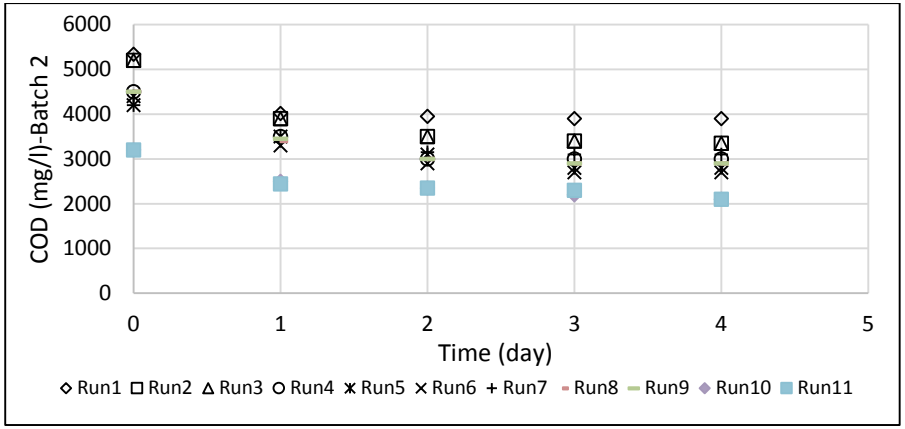

Figure 5.45: COD concentration during ion exchange process of batch2.

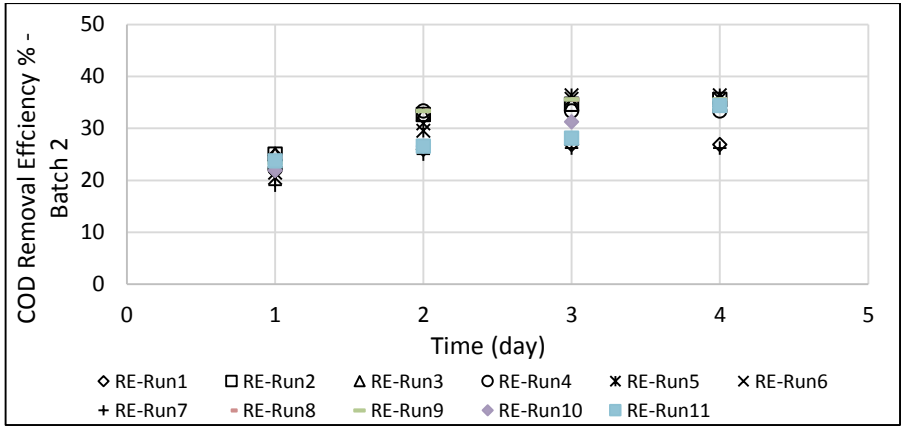

Figure 5.46: Removal efficiency of COD during ion exchnage process of batch2.

Table 5.5 : Characteristics of single stage ion exchange remnant of batch 1 and 2.

Parameter	Unit	Batch 1		Batch2	
		Initial	Remnant	Initial	Remnant
pH	-	7.5	7.5	7.5	7.5
E. Conductivity	µS/cm	37000	37000	32000	32000
COD	mg/l	1800	1000	5300-3200	3900-2200
Ammonium	mg/l	5500	1000	5300	1000
Orth-p	mg/l	162	5	210	5
Potassium	mg/l	1250	400	1200	400

The next stage of configuration (b) is to treat the liquid residue of ion exchange process with EGSB reactor to remove the organic matter. After each run of ion exchange, the residue was stored separately in a cold room of 4°C temperature to be used later as the feeding solution of EGSB. The EGSB reactor with 2.7 l effective volume was used at this stage. pH adjustment was not required as the pH remaind unchanged after ion exchange process with 7.5. A few milliliters of phosphoric acid was added to increase the amount of phosphorus in the influent to maintain a sufficient amount of phosphorus for the anaerobic microbial culture which did not change the pH of the feeding solution.

Anaerobic processing of the feed solution was started by feeding the EGSB reactor with 50% stored urine of batch 1. The anaerobic granular sludge used in this stage was previously adapted with fresh urine to a level of 65% fresh urine in the feeding. The pH results revealed that the pH inside the reactor was more or less similar to the pH of the influent and the pH of the effluent increased to a maximum level 8.2 as shown in Figure 5.47. The electrical conductivity of the influent was around 18000 µS/cm which still below the inhibitory limits of electrical conductivity at 35000 µS/cm as shown in Figure 5.48.

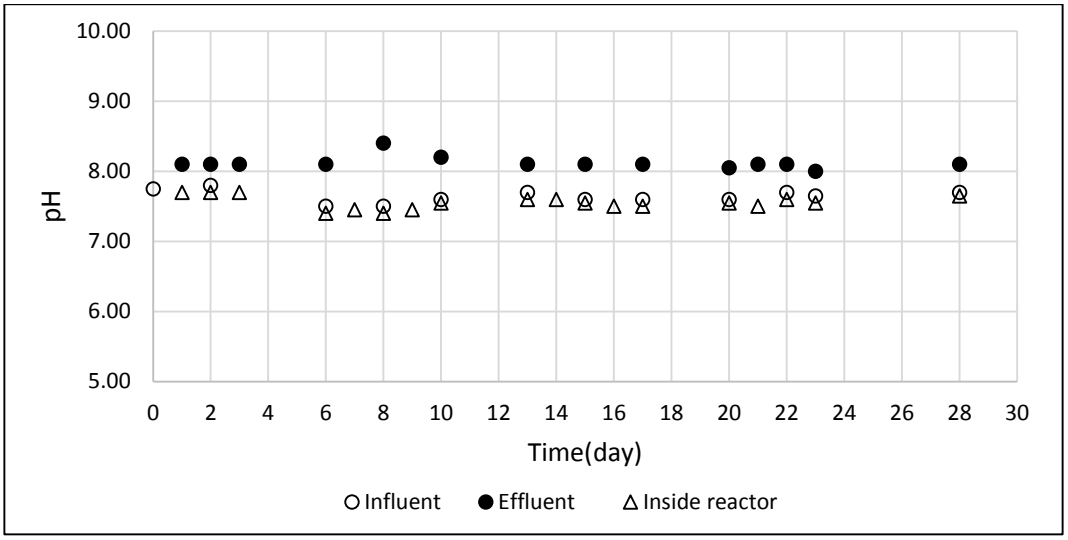

Figure 5.47 : pH of 50% stored urine w/o nutrients stage from batch1.

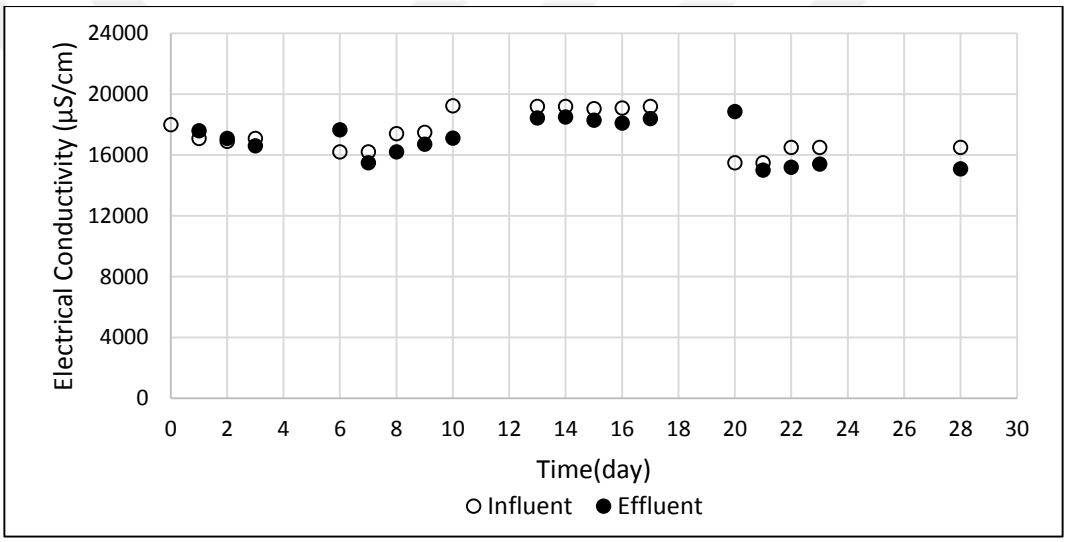

Figure 5.48 : Electrical conductivity of 50% stored urine w/o nutrients from batch1.

The COD concentration of the influent was about 600 mg/l with an average COD at the effluent of 300 and 360 mg/l of soluble and total COD, respectively. The COD removal efficiency was around 50% for soluble COD and around 30% for total COD. When the removal efficiency was compared to the 50% fresh urine adaptation stage it was observed to be less under the same conductivity level with lower ammonium concentration. However, the difference in COD concentration in the influent is considerably lower at this stage of 50% stored urine, pointing the impact of COD concentrations. Figure 5.49 and 5.50 illustrate the COD concentration and removal efficiency of 50% stored urine w/o nutrients from batch 1. Regarding ammonium concertation at this stage, the influent concentration was 500 mg/l as shown in Figure 5.52, and according to the literature this level of ammonium does not impose any

inhibition threat for the anaerobic sludge. After one month of operation with 50% of stored urine and stable performance in terms of COD removal. The concentration in the feeding was increased to 75%.

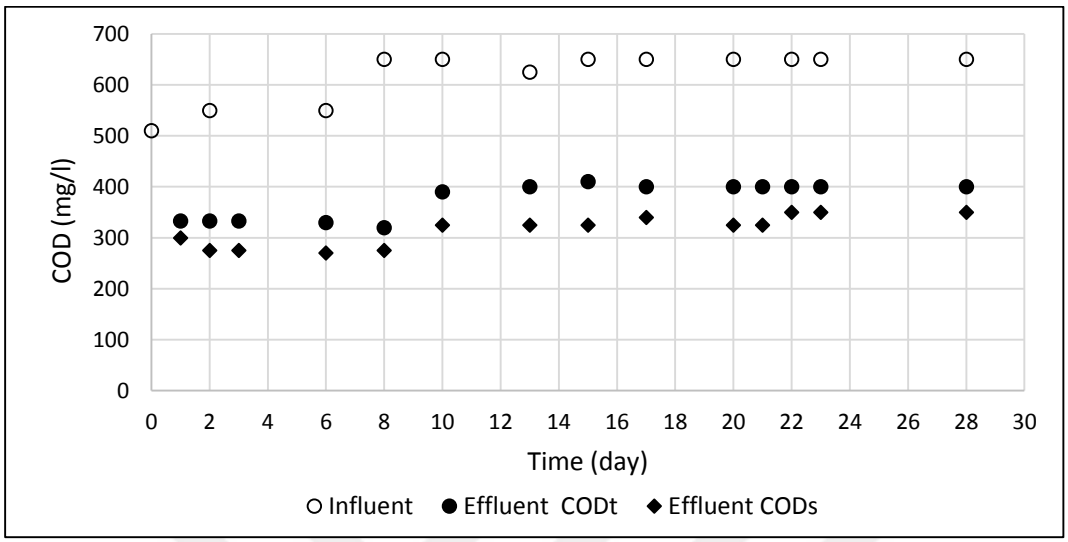

Figure 5.49 : COD concentration of 50% stored urine w/o nutrients.

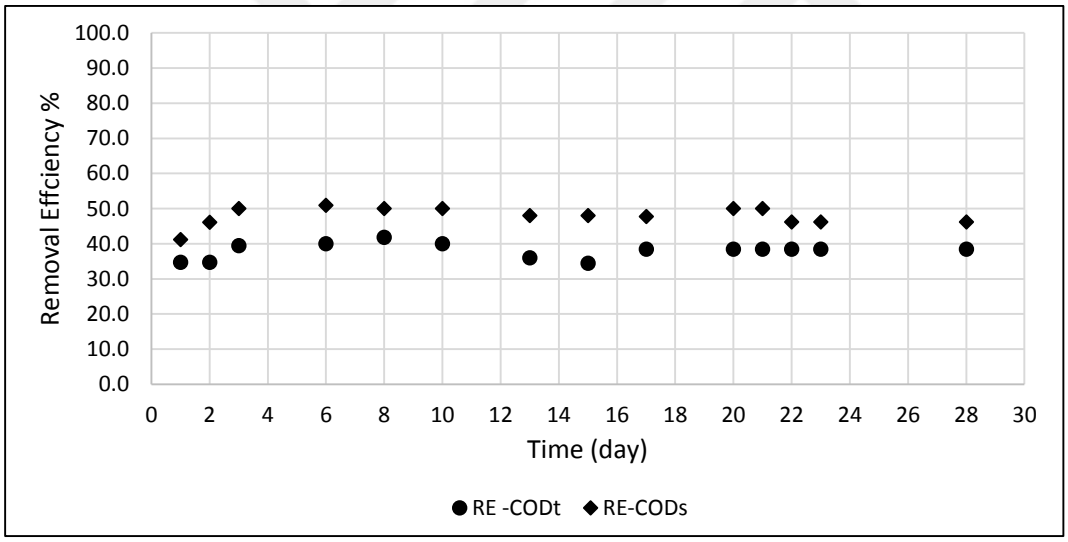

Figure 5.50 : COD removal efficeincy of 50% stored urine w/o nutrients.

The influent COD of 75% feed was 700 mg/l as shown in Figure 5.52. This stage showed no improvement of the COD removal efficiency, in fact the COD removal efficiency was decreased to be around 25% as shown in Figure 5.53. Electrical conductivity of the influent was about 25000 µS/cm, and ammonium was around 700 mg/l, both of these inhibition factors are still below the limits to impose a threat to anaerobic processing.

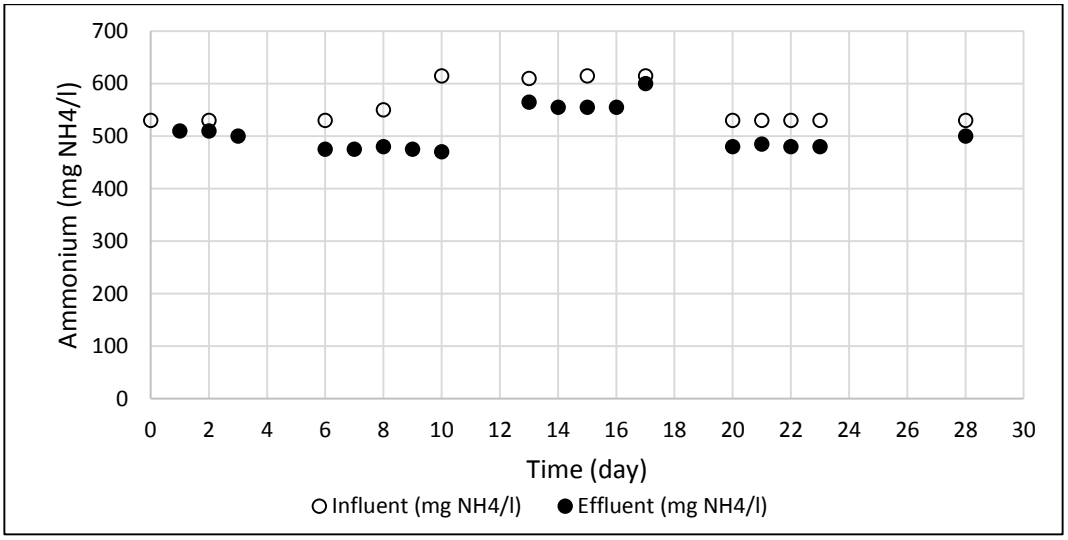

Figure 5.51 : Ammonium concentration of 50% stored urine w/o nutrients satge.

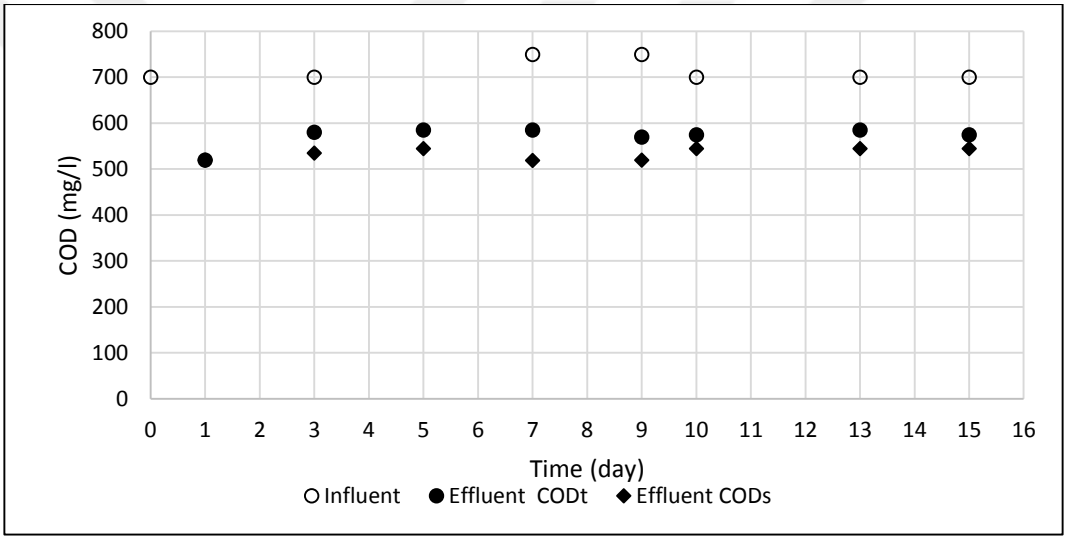

Figure 5.52 : COD concentrations of 75% stored urine w/o nutrients.

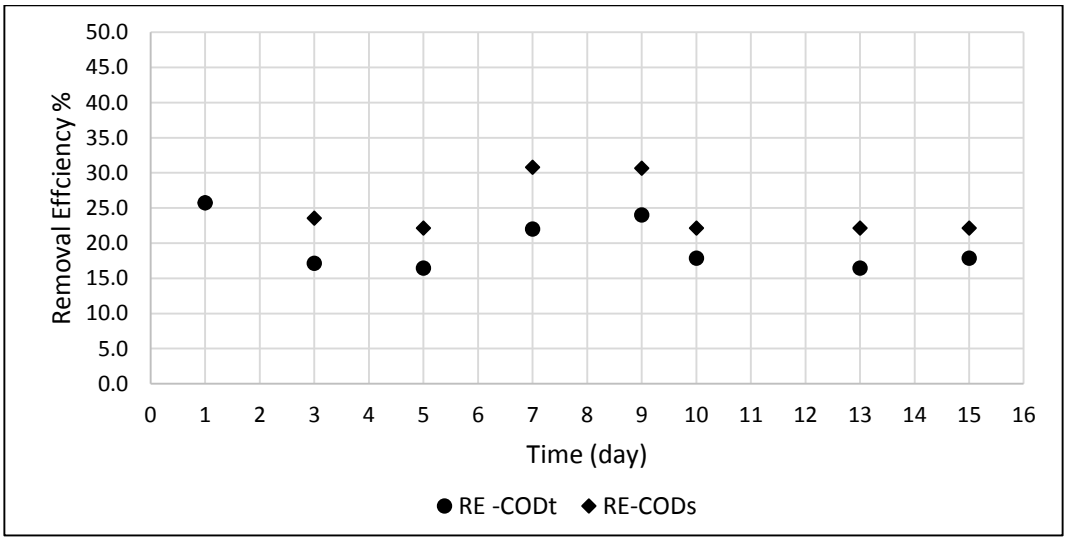

Figure 5.53 : COD removal efficeincy of 75% stored urine w/o nutrients.

The poor performance of the EGSB reactor at these two stages i.e. 50 and 75% of stored urine from batch 1, with operational conditions similar to that one of the adaptation stages with fresh urine may be attributed to the low COD concentration in the feed at these two stages. However, 50 and 75% stored urine did not reach the threshold inhibition for electrical conductivity and ammonium recommended by the literature. In a study focusing on domestic wastewater by Yoochatchaval et al. (2008), anaerobic EGSB reactor was fed with a low COD concentration of 600 – 800 mg/l and COD removal efficiency was up to 80%. However, In this study, the salinity level is supposed to be similar to that one of domestic wastewater which is far lesser than the salinity of human urine. This indicates the negative impact of higher salinity.

Due to the deteriorated performance of EGSB reactor in terms of COD removal, a feeding solution from batch 2 was prepared with 25% stored urine in an attempt to introduce a lower salinity which more over had a higher COD concentration than that one of batch 1. The COD concentration in the influent with 25% feed from batch 2 had a concentration of 900 mg/l which is higher than those of 50 and 75% feed prepared from batch 1 as shown in Figure 5.54. Electrical conductivity of this new influent was 8800 µS/cm, which is similar to that one of 25% fresh urine of adaptation stage. The ammonium concentration was 250 mg/l, which is far below any inhibition that can be caused by ammonium. The COD removal efficiency at this stage showed a little improvement in which the removal efficiency increased to 50% for soluble COD and 35% for total COD using the same sludge as shown in Figure 5.55.

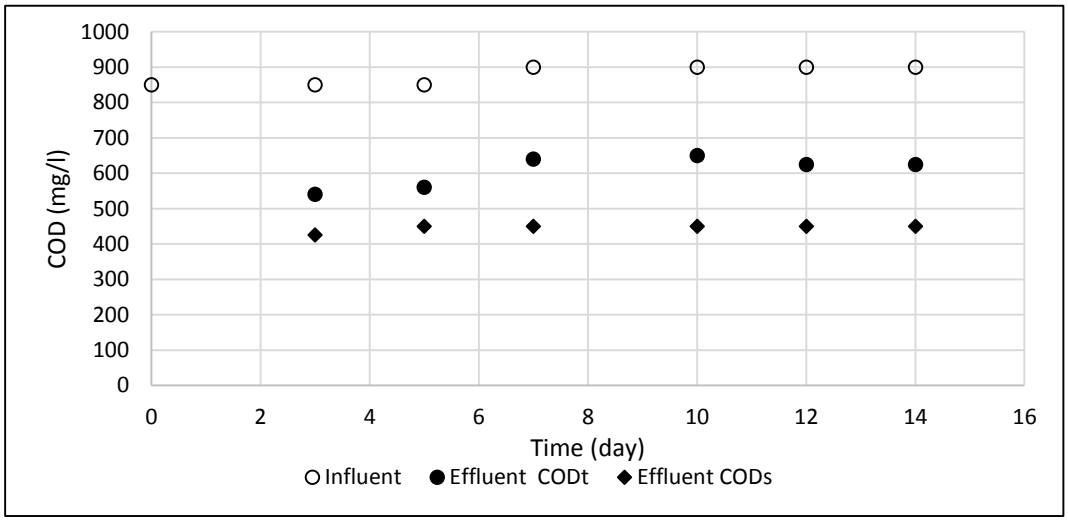

Figure 5.54 : COD concentrations of 25% stored urine w/o nutrients from batch 2.

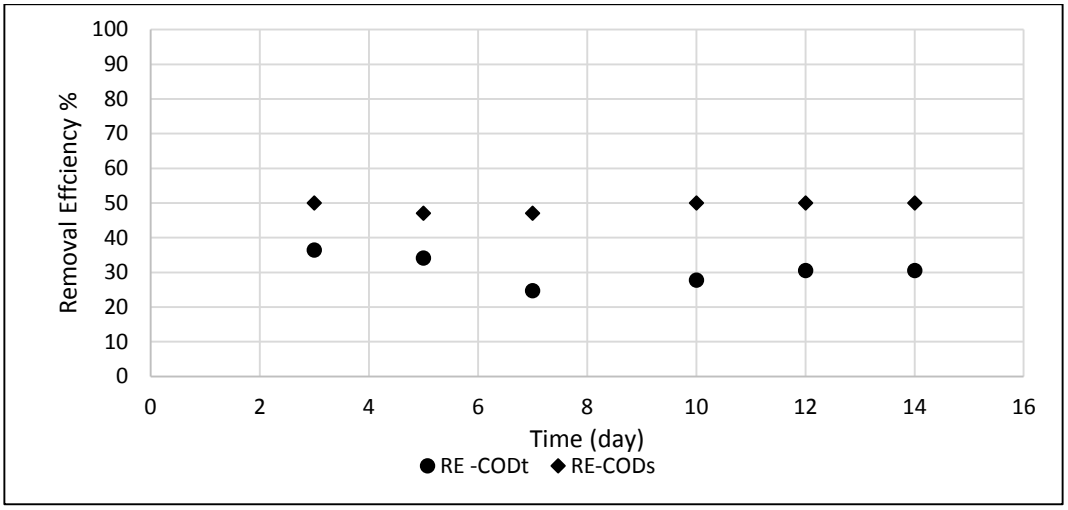

Figure 5.55: COD removal efficeincy of 25% stored urine w/o nutrients from batch2.

After two weeks of operation under 25% feed from batch 2, the removal efficiency was stable with 50% and no increase was observed. The performance of EGSB treating liquid residue of ion exchange process with adapted anaerobic granular sludge was not satisfactory possibly due to the harsh condition of high salinity introduced with very low COD. For this reason, the adapted sludge with fresh urine was replaced by a new sludge from the same source of confectionery wastewater treatment plant and a new adaptation stage was started with stored urine w/o nutrients from batch 2.

According to Lefebvre et al. (2007), who studied the effect of salinity on anaerobic bacteria, the adaptation with salinity should be carried in a stage wise manner as was done in this work with small changes between stages. This recommendation was the basis that the adaptation of the new sludge was established on. 30% of the EGSB reactor column volume was filled with new anaerobic granular sludge and the adaptation was started with 25% of stored urine w/o nutrients from batch 2.

Figure 5.56 illustrates the salinity level measured as electrical conductivity in each stage starting with 9000 µS/cm for 25% concentration of stored urine w/o nutrients and ending with 32000 µS/cm for 100% concentraton. The ammonium concertations in these new stages were always below the inhibition threshold as the maximum concentration obtained at 100% concentration was 1000 mg/l as shown in Figure 5.57. The pH of the influent was maintained at all the stages around 7.5, and inside the EGSB reactor no drop was observed to show no accumolation of volatial fatty acids but a slight increase as was in the previous stages. At effluent the pH was around 8.0 during all the stages. COD was monitored in the experiments, and the results revealed that

with 25% stored urine the average removal efficiency was 80% for soluble COD and 66% for total COD. COD concentration at the influent was 800 mg/l, while at the effluent the COD concertation was reduced to an average 150 mg/l for soluble COD and 220 mg/l for total COD as shown in Figure 5.58. This stage lasted for 17 days. After a stable performance was observed in terms of COD removal, urine concertation in feed was increased to 35%. COD concentration in the influent was 1100 mg/l. The COD removal efficiency and COD concentration at the effluent were similar to that one of the previous stage of 25% stored urine w/o nutrient. COD removal efficiency was around 80% for soluble COD and 78% for total COD. COD concentrations at the effluent were 200 mg/l for soluble COD and 250 mg/l for total COD, as shown in Figure 5.58. The electrical conductivity was increased to 11000 µS/cm at this stage so the introduced change in salinity was about half of that one from the previous stage. There was no difference could be detected in COD removal efficiency between 25% and 35% urine solutions under conditions employed. Upon the stable performance of the EGSB reactor the percentage of urine in the feed was increased to 50%. The electrical conductivity was increased to 18000 µS/cm as shown in Figure 5.56. The performance of the EGSB reactor was remarkable at this stage, with a removal efficiency reached to an average of 85% for soluble COD and 80% for total COD. The COD concentration at the influent was 1500 mg/l and reduced to 235 and 300 mg/l for soluble and total COD, respectively, as shown in Figure 5.58.

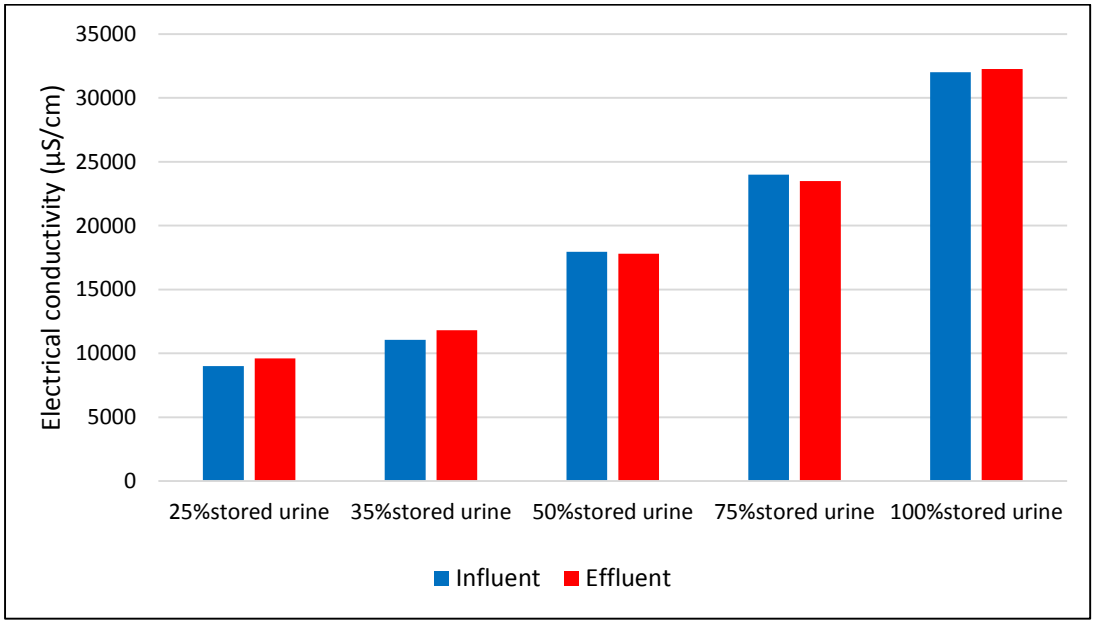

Figure 5.56 : Electrical conductivity corresponding to stage of stored urine w/o nutirents from batch 2.

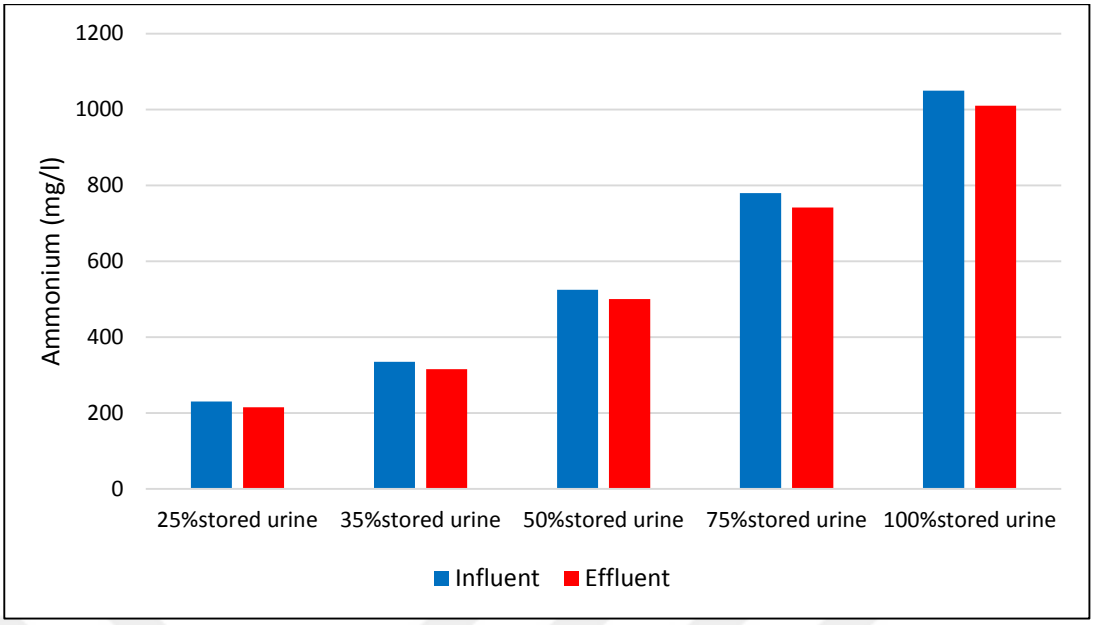

Figure 5.57 : Ammonium concentration corresponding to stage of stored urine w/o nutirents from batch 2.

After stabilization of the COD removal efficiency, the urine percentage in the feeding solution was increased to 75%, the electrical conductivity was 24000 µS/cm as shown in Figure 5.56. A reduction in the removal efficiency was observed at this stage which dropped to stabilize around 70% for both soluble and total COD, which is still a resonable level. The COD in the influent was 2000 mg/l and reduced to 600 for soluble COD and 625 mg/l for total COD as shown in Figure 5.58 and 5.59. As the ammonium concentration at this level is almost 750 mg/l which is below the threshold of inhibition, salinity of 24000 µS/cm was attributed to be the reason of COD removal reduction. A stable performance at this stage was obtained within three weeks and then 100% of urine in the feeding solution was introduced.

The last stage with 100% urine in the feeding was critical as the salinity level was approaching the threshold of salinity inhibition indicated by electrical conductivity which is 35000 µS/cm (Ogata et al, 2016). The electrical conductivity was measured as 32000 µS/cm. The COD removal efficiency was 60% for both soluble and total COD. COD in the influent ranged between 2700 – 2200 mg/l as which is due different storage times of the feed solutions which were used in the single stage ion exchange runs. This change in COD concentration at the influent was related to the change of COD concentration in the storage tank.

It was discussed in section 5.3, that long storage times will lead to a reduction in COD concentration which was refleted in this outcome. The salinity effect is observed to be more appearent at this stage.

Ammonium concentration was around 1000 mg/l so no inhibition was expected at this concentration. It seems that the lower the urine concentration in the feeding the better the results. However that means more dilution required to eliminate the salinity effect, but at the same time COD concentration in the influent will be reduced as well which generally had a negative effect on organic matter removal in anaerobic procesing.

All in all, 50 % feed gave a better result compared to other dilutions. Even though the 100% store urine stage had the highest COD concentration, it showed a lower COD removal efficiency most probably due to the high salinity level that approaches the threshold inhibition level.

Configuration (b), that employs ion exchange followed by anaerobic processing revealed that such a combination of sorption and anaerobic processes is possible and can provide a good suggestion for removal of nutrients and organic matter from stored human urine. During the use of configuration (b), production of biogas was expected in the experiments however it was hardly observed.

The gas counter recorded few milliliters of biogas, while according to the amount of COD removed and through theoretical calculations, the biogas produced should be between 0.3 – 0.8 l CH_4/day as shown in Figure 5.60, which corresponds to 0.19 – 0.5 l CH_4/l urine.

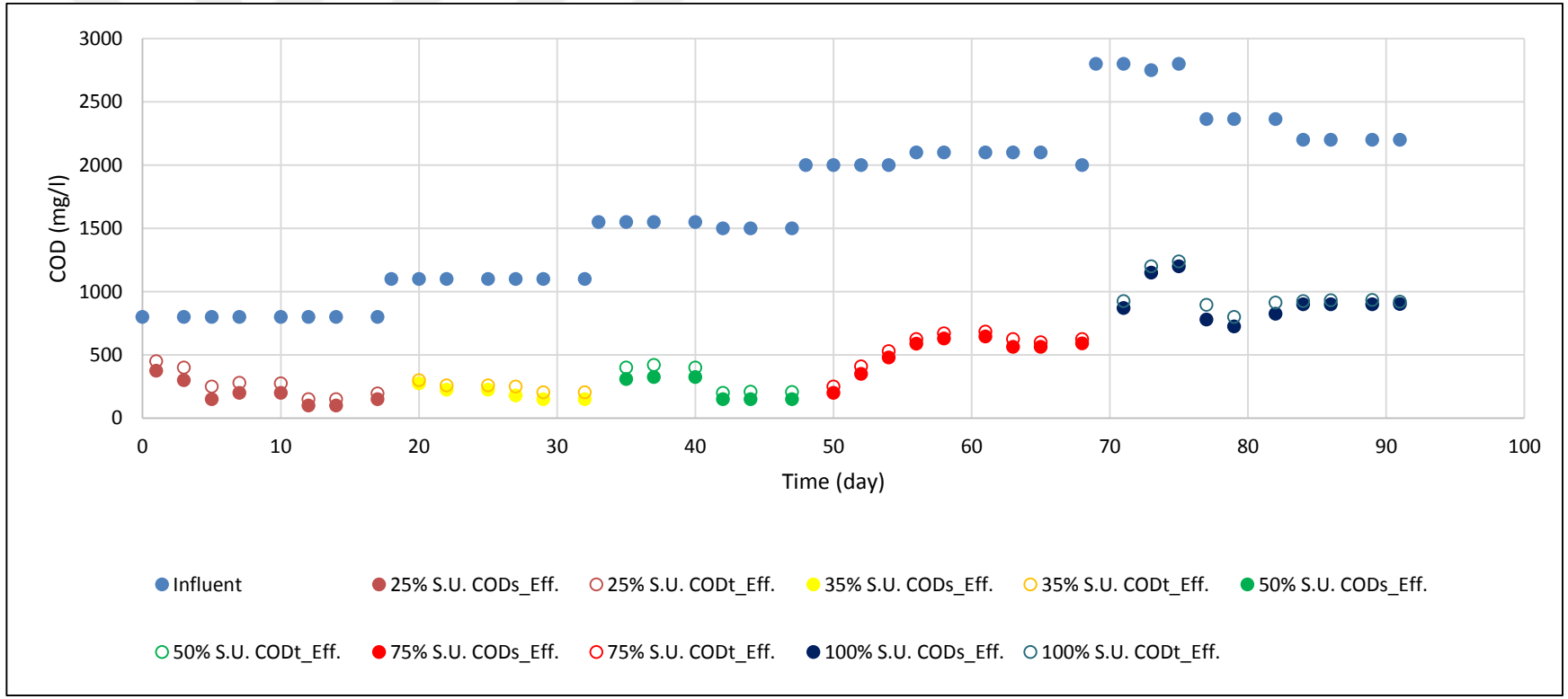

Figure 5.58 : Cummulative COD concnetraion of 25, 35, 50, 75 and 100% stored urine w/o nutrients from batch 2 performed with unadapted sludge.

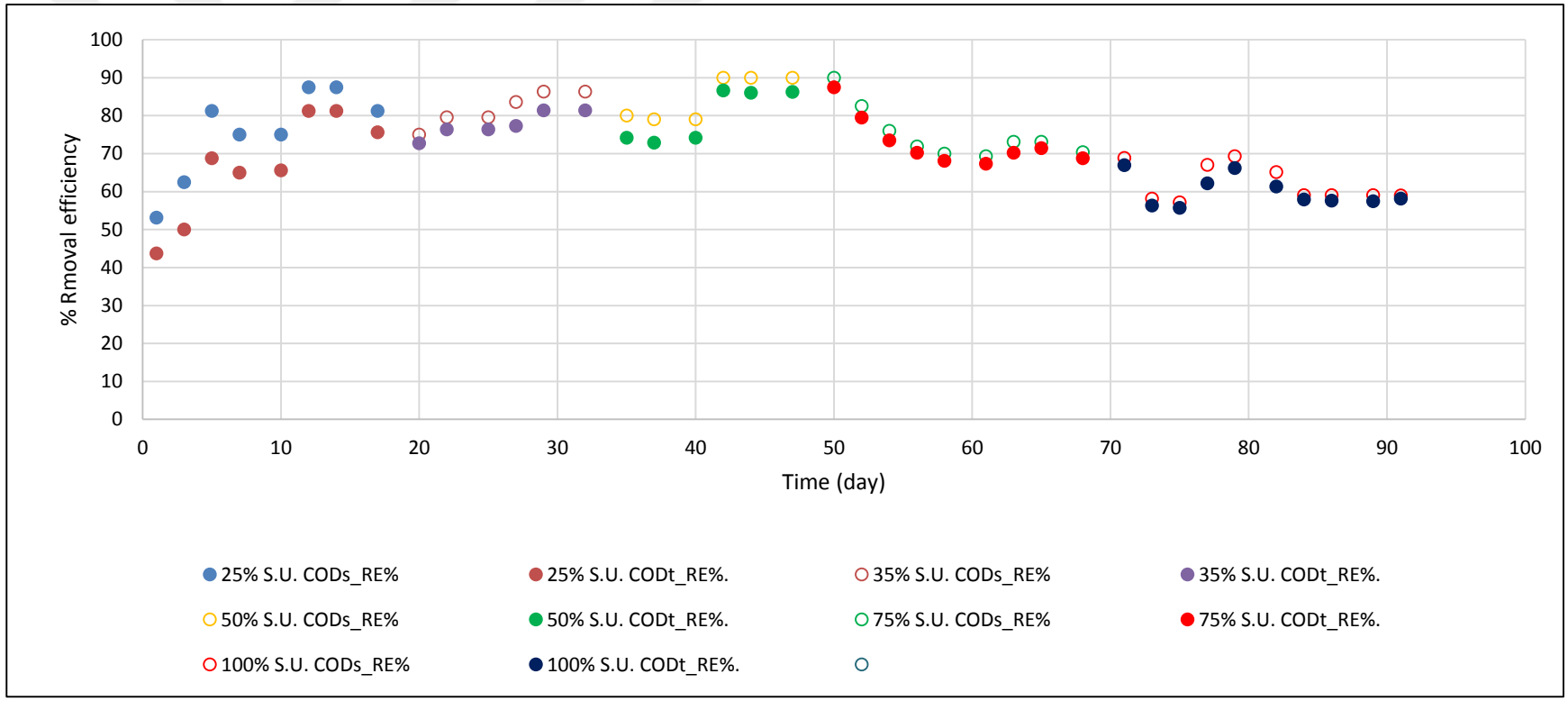

Figure 5.59: Cummulative COD removal efficiency of 25, 35, 50, 75 and 100% stored urine w/o nutrients from batch 2 performed with unadapted sludge.

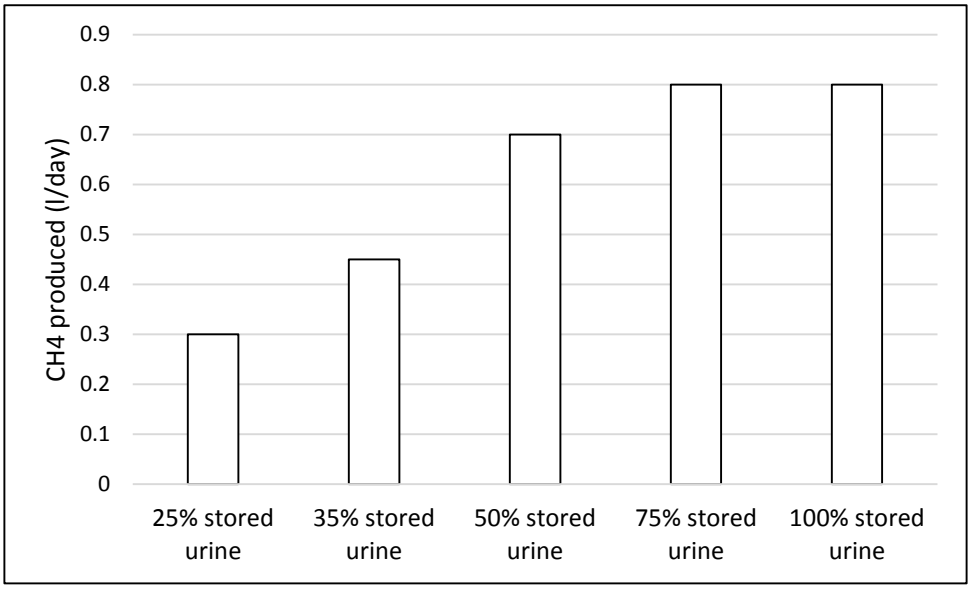

Figure 5.60 : Methane produced theoritically during the use of configoration (b).

As phosphorus was almost totally removed from the stored urine with single stage ion exchange. External source of phosphorus was added to the feeding solution to sustain the growth of anaerobic microorganisms. During the stages in which stored urine w/o nutrient from batch 2 was used as a feed for the EGSB reactor, the phosphorus showed a small decrease as shown in Figure 5.61.

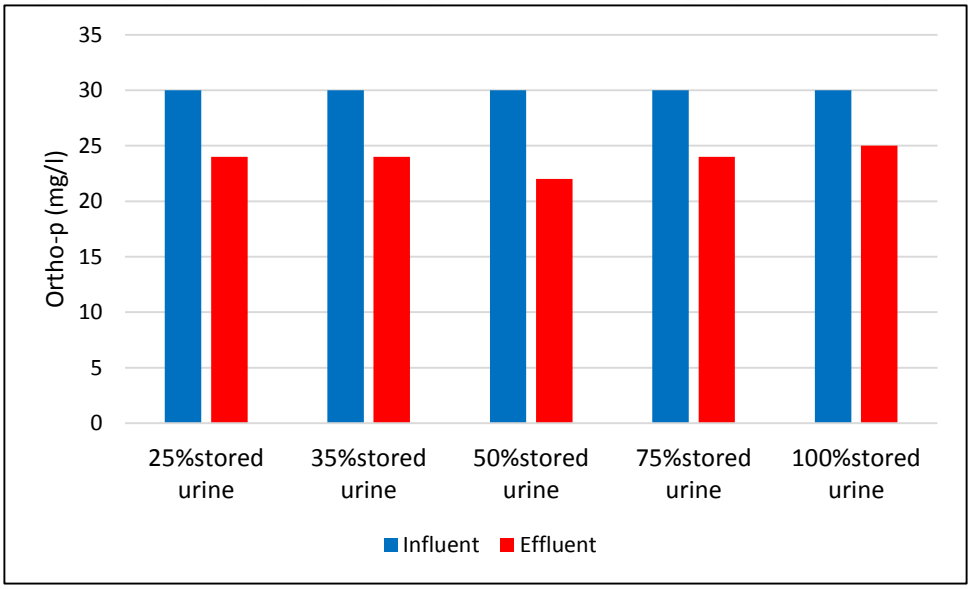

Figure 5.61 : Phosphorus concentration corresponding to stage of stored urine w/o nutirents from batch 2.

Another run was performed to confirm the performance of the 50% stored urine w/o nutrient stage that showed a 85% COD removal efficiency. Due to the changes in COD concertation in the storage and the removal of COD in the single stage ion exchange process, stored urine w/o nutrients used at this stage had a lower COD concertation. In order to maintain the same COD concentration of the previous 50% feed that was used in the first trial, the dilution in the second trial was made to fit the COD concentration in the 50% of the previous trial. Figure 5.62 and 5.63 shows the COD analysis and removal efficiency of both trials. The results from the second trial revealed that 75% removal efficiency could be achieved while in the first trial it was 85%.

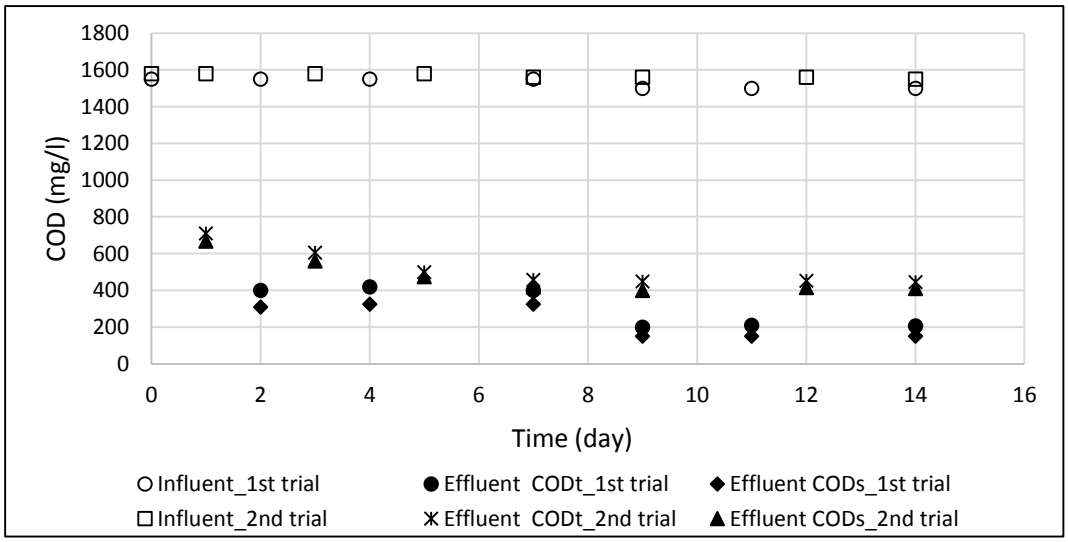

Figure 5.62 : COD analysis of first and second trial of 50% stored urine w/o nutrient stage.

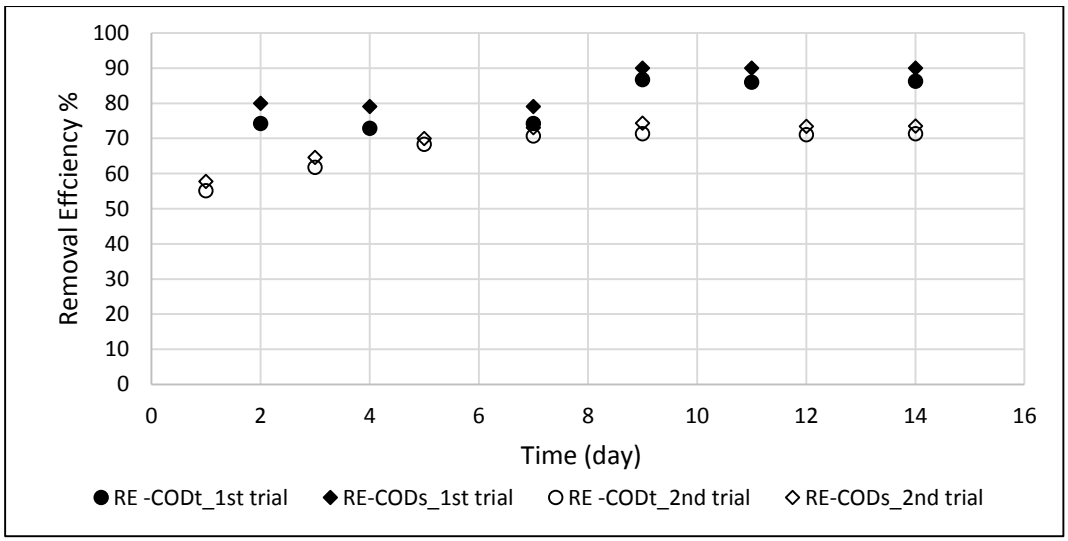

Figure 5.63 : COD removal efficiency of first and second trial of 50% stored urine w/o nutrient stage.

The difference in removal efficiency is attributed to the change in dilution, as the second trial has higher salinity and ammonium concentration which looks similar to the one of previous 75% trial. The effect of salinity on COD removal efficiency is observed at the second trial in which a 25% increase in the salinity lead to a reduction in COD removal efficiency from 85% to 75% with the same COD concentration in the influent. The salinity in the first and second trials were 18000 and 24000 µS/cm, respectively.

5.5. Ion Exchange – Anaerobic Process – Ion Exchange / Configuration (c)

The evaluation of the effluent obtained at the end of each stage through configuration (b), is indicating that a further treatment is required to remove the remaining ammonium, COD and phosphorus for environmental protection. Table 5.6 shows the summary of the effluent concentration of each stage in configuration (b).

Table 5.6 : Summary of effleunts quality of configuration (b) stages.

Parameters	Units	25% S.Urine	35% S.Urine	50% S.Urine	75% S.Urine	100% S.Urine
Ammonium	mg/l	218	320	495	740	1000
COD	mg/l	200	200	235	510	915
Phosphorus	mg/l	24	24	22	24	25
EC	µS/cm	9500	11000	18000	24000	32000

Configuration (c), seems to be a continuity of configuration (b) in which another ion exchange stage will be added after the anaerobic process stage for treating the remnant of the first ion exchange process stage. The ion exchange process could be performed in a stage wise manner to remove the reaming ammonium as recommended by Allar and Beler Baykal, (2015). COD removal may be possible at this configuration as it was shown previously in this work that ion exchange can remove about 25 – 35 % of the COD in the liquid phase. Configuration (c) is applied more to improve the quality of the effluent of anaerobic process and to protect the environment by discharging a liquid phase which is less in terms of ammonium, COD and phosphorus. Figure 5.63 shows the ammonium removal efficiencies obtained by applying different stages with variable loading ion exchange process.

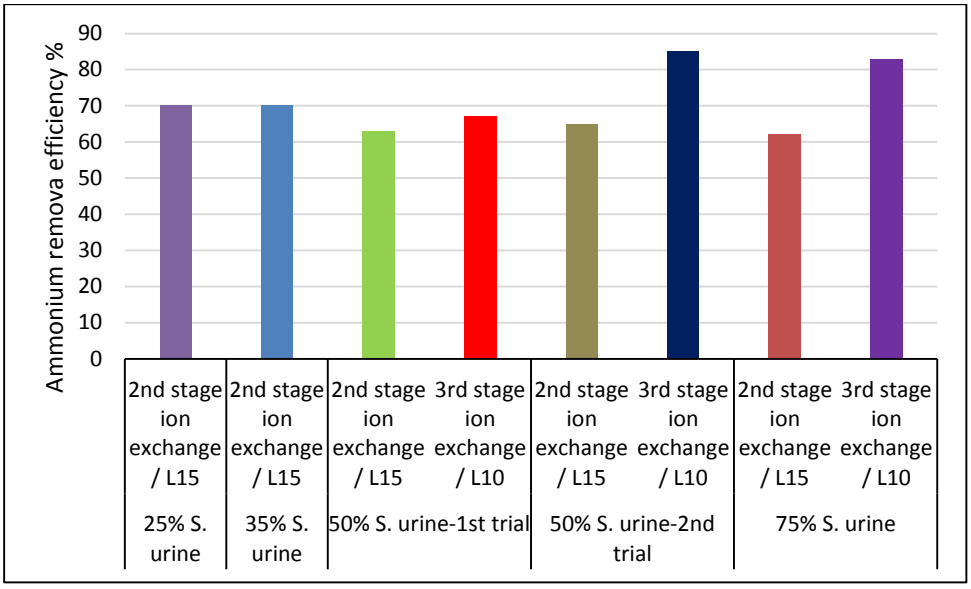

Figure 5.64 : Stage wise ammonium removal for EGSB effleunt from configuaration (b).

Applying ion exchange after anaerobic process successfully reduced the ammonium concertation and improved the quality of the effluent that may be discharged to sewer systems. Ammonium concentrations for 25 and 35% stages were reduced from 286 mg/l to 85 mg/l for 25% stage and 330 mg/l to 100 mg/l in 35% stage. 50 and 75% stages were treated with 2nd and 3rd stage and the ammonium concertation was reduced from 557 to 70 mg/l at the end of the 3rd stage for 50% stored urine stage and from 790 to 50 mg/l at the end of 3rd stage for 75% stored urine stage.

Regarding COD for 25, 35, 50 and 75% stages of stored urine, the COD removal efficiencies were as shown in Figure 5.64. For 25 and 35 % stages of stored urine COD removal efficiencies were 25 and 29%, respectively. The COD concentrations were reduced from 220 to 165 mg/l for 25% stage and from 280 to 165 mg/l for 35% stage of stored urine. The COD removal in 50 and 75% stages of stored urine were obtained at the end of the 3rd stage as 43% and 58%, respectively. The COD concentrations remained at the end of the 3rd stage were 112 mg/l for 50% stage of stored urine and 130 mg/l for 75% stage of stored urine which is similar to low streangth domestic wastewater.

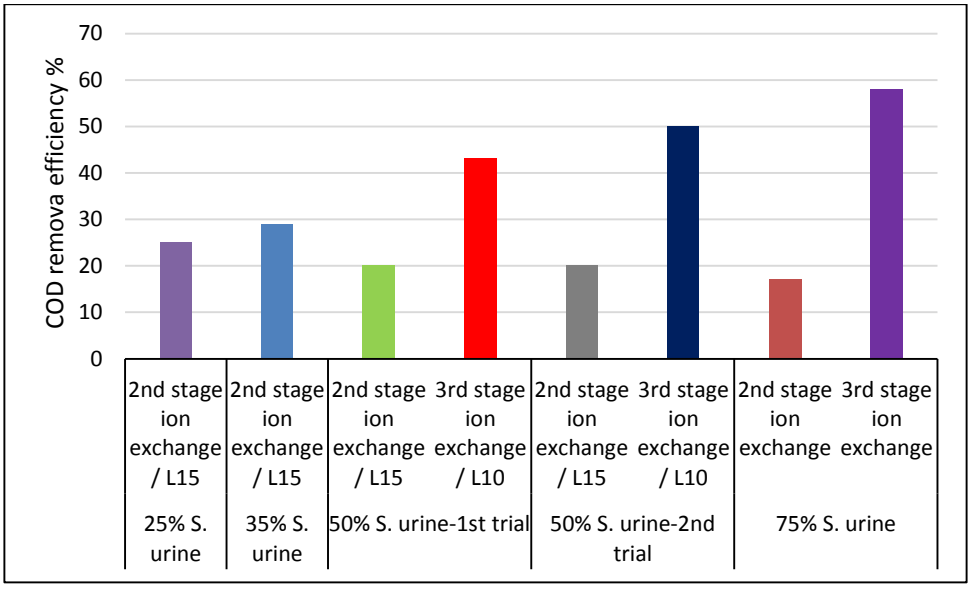

Figure 5.65: Stage wise COD removal for anaerobic effleunt from configuaration (b).

For 100% stored urine stage, two different paths of removal were applied, one staring with 10 mg NH_4^+/ g clinoptilolite initial loading then followed by 5 mg NH_4^+/ g clinoptilolite, the other path is starting with 15 mg NH_4^+/ g clinoptilolite and then followed by 5 mg NH_4^+/ g clinoptilolite. The results revealed that using a lower initial loading sequence will result in lower ammonium concentration at the end of the 3rd stage. For a sequence of 10 and 5 mg NH_4^+/ g clinoptilolite initial loading, ammonium concertation reduced from 1110 mg/l to 90 mg/l at the end of the 3rd stage ion exchange showing a total removal efficiency of 92%. The sequence of 15 and 5 mg NH_4^+/ g clinoptilolite initial loading, ammonium concentration reduced by 92 % at the end of the 3rd stage ion exchange with ammonium concertation of 80 mg/l. Figures 5.65 – 5.68 shows the ammonium removal of 100% stored urine stage with multiple stages of ion exchange. Regarding COD removal, both of the sequences used for 100% stored urine stage showed similar removal efficiencies at the end of the 3rd stage ion exchange with 75% removal efficiency and a concentration about 230 mg/l, Figure 5.69 – 5.72 shows the COD concentration changes and removal efficiencies during multiple stages of ion exchange for the effluent resulted from anaerobic process of 100% stored urine w/o nutrients.

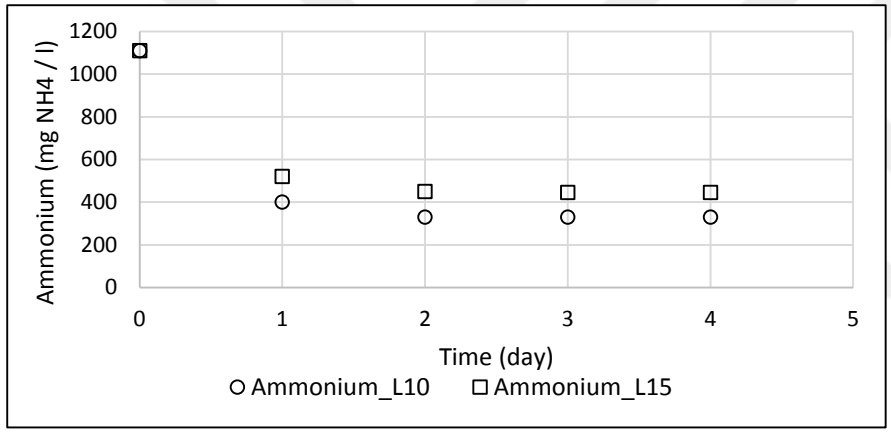

Figure 5.66: Ammonium cocncetration at the 2nd stage ion exchange.

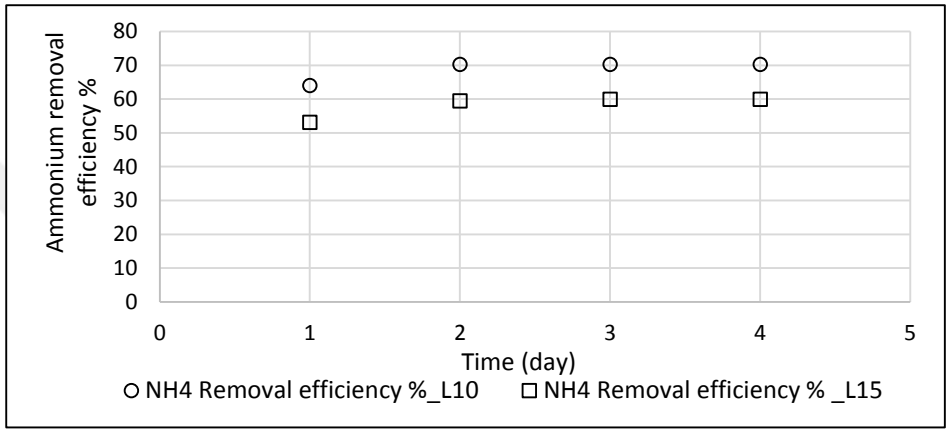

Figure 5.67: Ammonium removal effficiency athe the 2nd stage ion exchange.

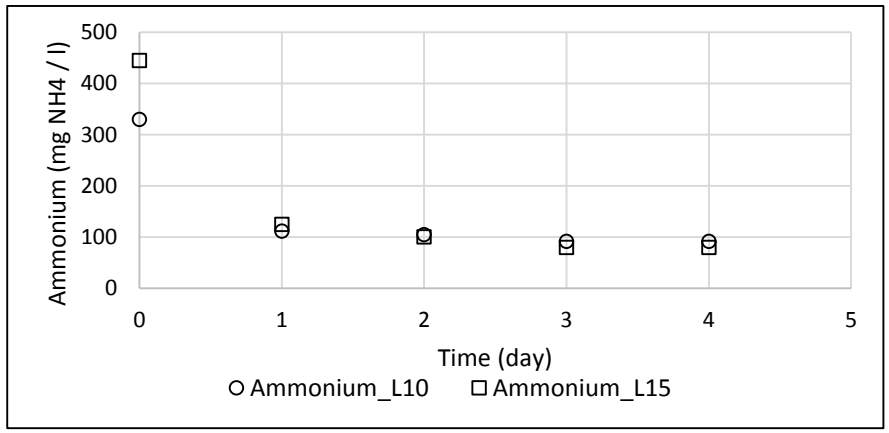

Figure 5.68: Ammonium cocncetration at the 3rd stage ion exchange.

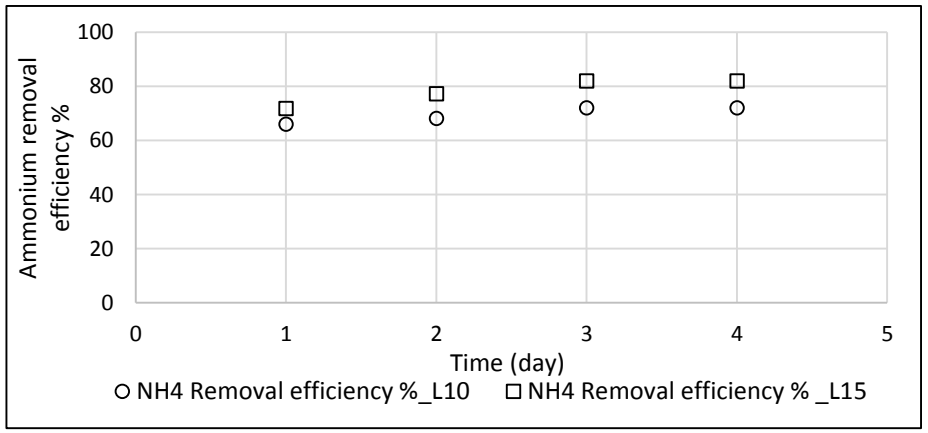

Figure 5.69: Ammonium removal effficiency athe the 3rd stage ion exchange.

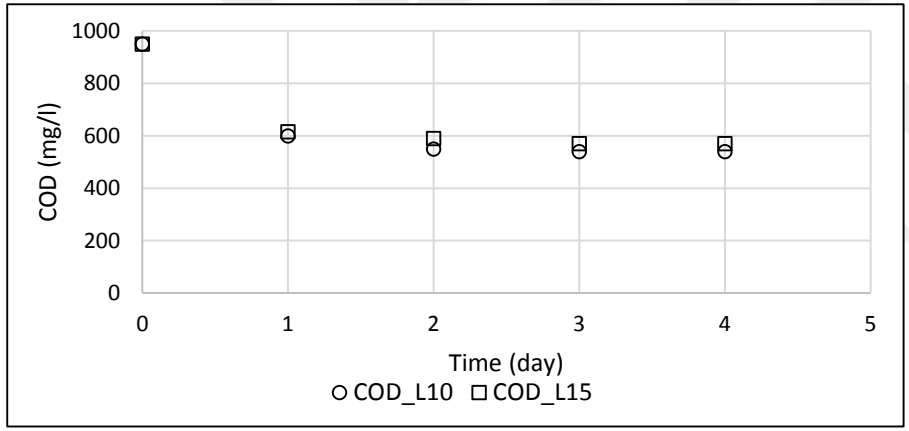

Figure 5.70 : COD cocncetration at the 2nd stage ion exchange.

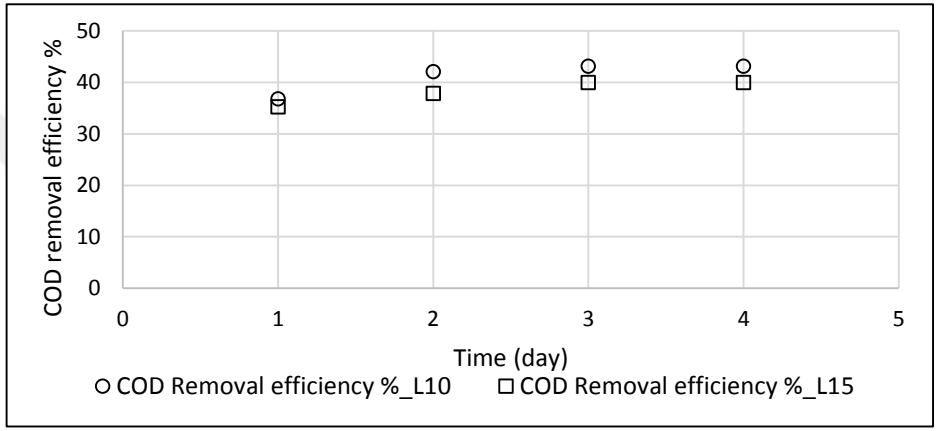

Figure 5.71 : COD removal effficiency athe the 2nd stage ion exchange.

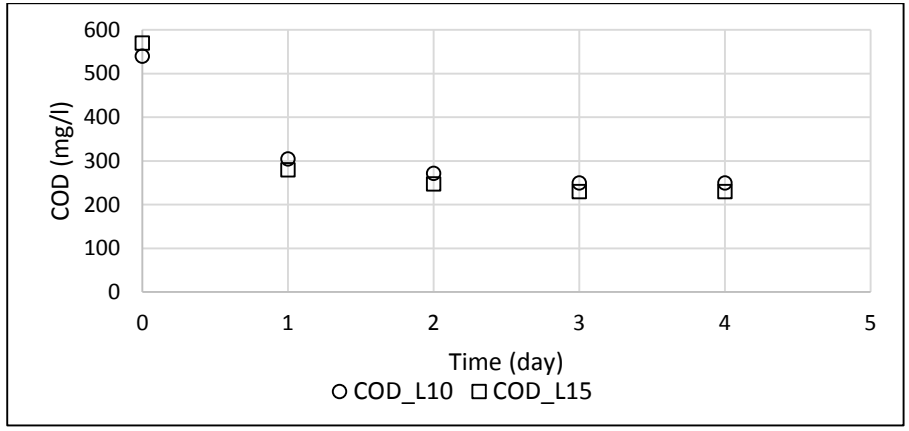

Figure 5.72 : COD cocncetration at the 3rd stage ion exchange.

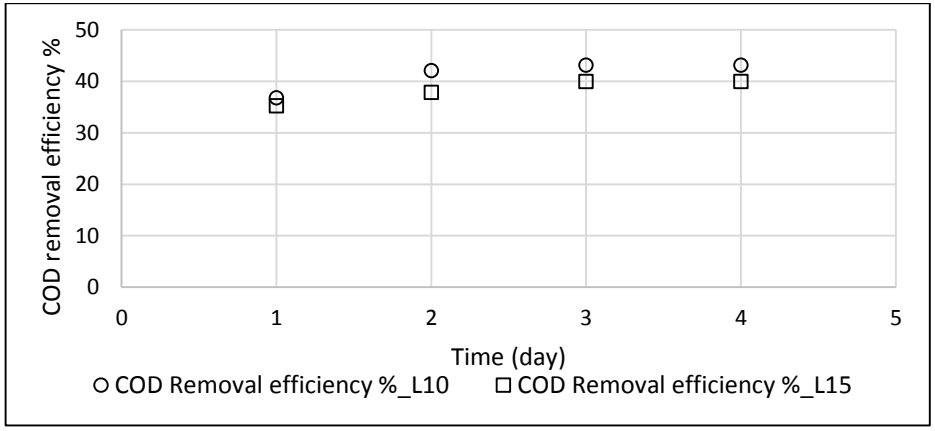

Figure 5.73: COD removal effficiency athe the 3rd stage ion exchange.

Regarding phosphorus removal in configuration (c), the 2nd stage of ion exchnage was enough to remove all the phosphorus in the liquid phase as shown in Figure 5.73. All the stages were showing the same removal efficiency with almost 100% removal which is confirming the previos observation by (Allar and Beler Baykal, 2015).

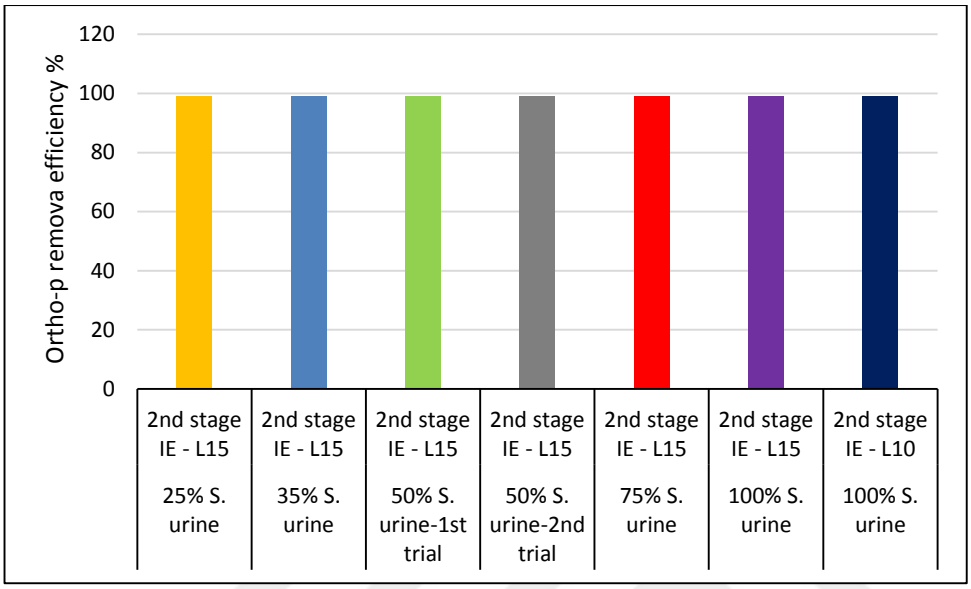

Figure 5.74 : Phosphorus removal for anaerobic effleunt from configuaration (b).

Table 5.7 shows the summary of final effluent concentrations for ammonium, COD and phosphorus obtained by applying stage wise operation of ion exchnage process in configuration (c). These effluents are more or less similar to low streangth domestc wastewater (Metcalf & Eddy, 2003).

Table 5.7 : Summary of the effluent charactiristics at the end of configuration (c).

Parameter	Unit	25% stored urine	35% stored urine	50% stored urine-1st trial	50% stored urine2nd trial	75% stored urine	100% stored urine
Ammonium	mg/l	85	100	70	52	50	80 - 90
COD	mg/l	165	165	112	120	130	230
Phosphorus	mg/l	0.5	0.5	0.4	0.4	0.4	0.4

Configuration (c) with ion exchange using stage wise operation following anaerobic process seems very effective in terms of improving the quality of the effluent of the EGSB reactor for environment protection. Ammonium, COD and phosphorus were reduced considerably and that the effluent of this configuration could be discharged to the sewer system.

5.6. Salinity Effect on Removal of Organic Matter

The effect of salinity on the anaerobic process with human urine was discused previously in this chapter. In order to understand the effect of different salinity levels on organic matter removal using anaerobic processing, an experiment was conducted with a synthetic solution that simulates stored human urine after nutrient removal with an initial loading of 15 mg NH4+/g clinoptilolite. Although it is well understood that real urine has other components in competition in sorption processes synthetic urine was used to mantain controlled conditions to observe the effect of salinity only, specifictly keeping a constant COD and variable levels of salinity. The characterization of this synthetic solution shown in Table 5.8.

Table 5.8: Characteristics of synthetic urine and stored urine.

Parameter	Unit	Synthetic urine	Stored Urine
pH	-	7.5	7.5
E. conductivity	µS/cm	32000 – 10000	32000
Total COD	mg/l	2700	3900-2200
Soluble COD	mg/l	2700	3870-2175
Ammonium	mg NH_4^+-N/l	985	1000
TKN	mg NH_3-N/l	-	-
Ortho-p	mg PO_4^{3-}-P/l	33	5
TP	mg PO_4^{3-}-P /l	-	-
Potassium	mg K^+/l	385	400

Synthetic urine composition was presented previously in Chapter 4, and Table 4.2 provides the chemical composition of this solution. COD of the synthetic urine was kept constant at all times during the experiments of the salinity effect on organic matter removal with 2700 mg COD/l. Ammonium, ortho-p, potassium were at similar concentrations in real stored urine after nutrients had been removed. The salinity of this synthetic solution was changed according to the concentrations used in the investigation of organic matter removal from liquid residue. The salinity of synthetic urine was prepared to mimic the salinity of 100, 75, 50 and 25% stored urine with a range of 32000 – 10000 µS/cm. The COD concentrations, removal efficiencies and electrical conductivity levels of synthetic urine trials are shown in Figure 5.75, 5.76 and 5.77.

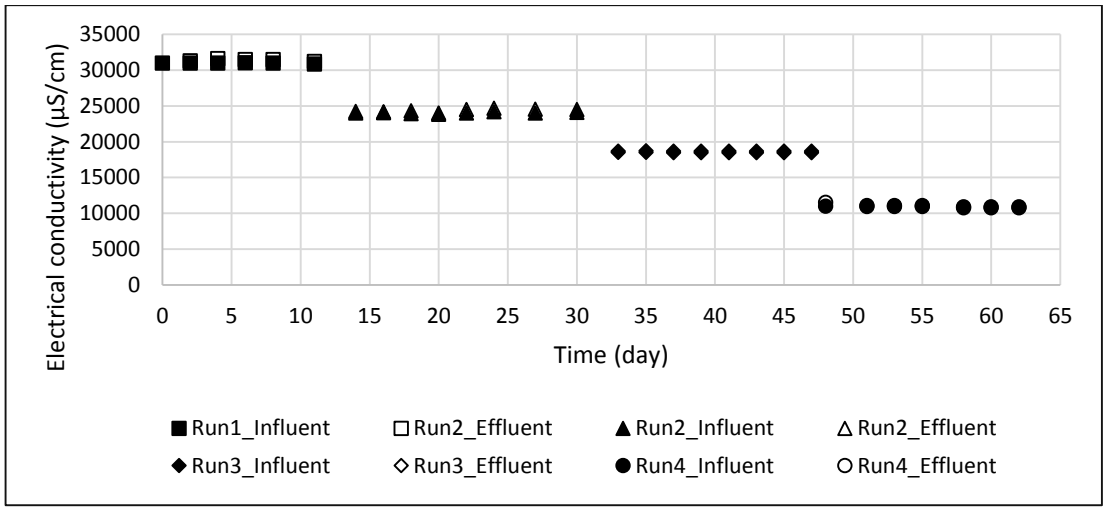

Figure 5.75: Electrical conductivity of synthetic urine at different operation stage.

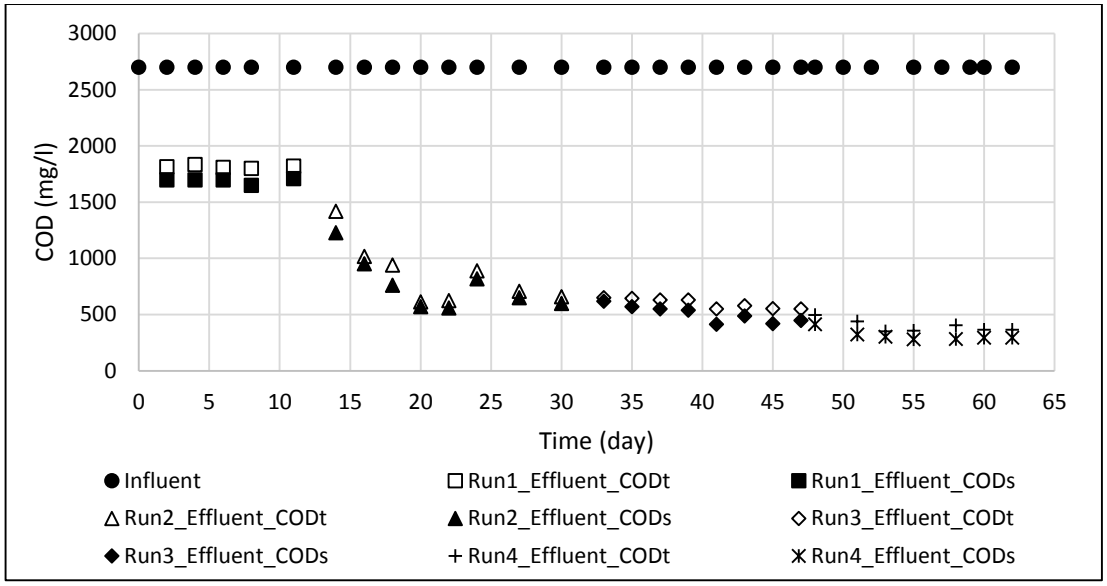

Figure 5.76: COD concentration of 100, 75, 50 and 25% of synthetic urine stages.

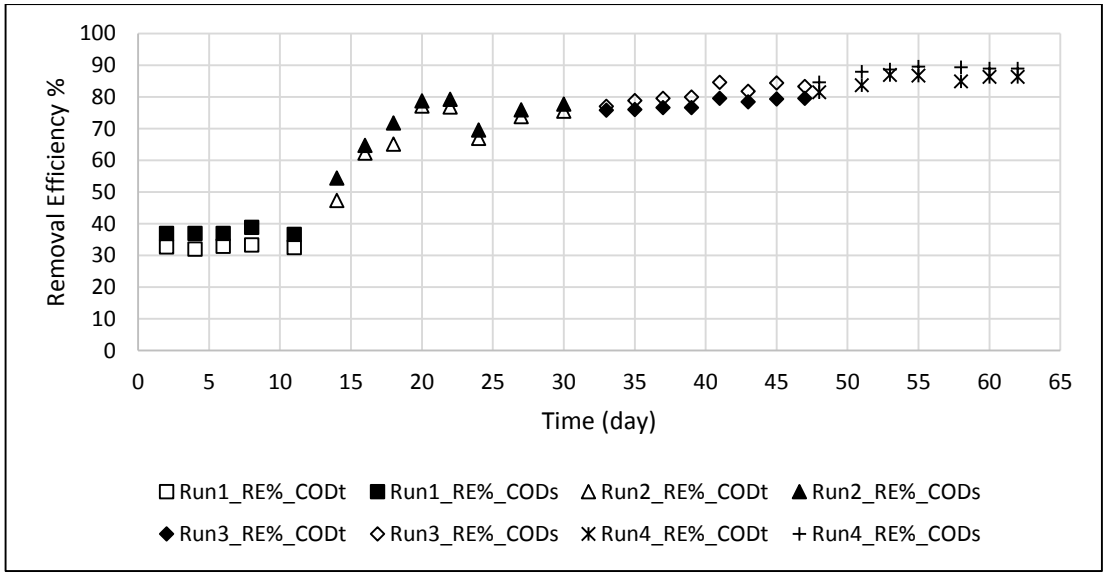

Figure 5.77: COD removal efficiency of 100, 75, 50 and 25% of synthetic urine.

The effect of salinity was observed to be very significant during this experiment. At a high salinity level of 32000 µS/cm which simulates a salinity level of 100% stored urine, COD removal efficiency was at its lowest percenatage with 40% only. After a stable performance with 40% COD removal efficiency, the influent was shifted to a salinity level which corresponds to 75% stored urine in the feed. Electrical conductivity at this stage was 24000 µS/cm. At this stage removal efficiency started to increase gradually till it was stabilized at an average of 75%. This stage indicates the recovery of the anaerobic granular sludge from the high salinity of the previous stage. Anaerobic granular sludge improved its performance within about one week. Although Ogata et al. (2016) reported a salinity threshold inhibition of 35000 µS/cm, the results of this experiment showd that the threshold may fall in range of 24000 - 32000 µS/cm. After a stable performance of the EGSB reactor with 75% removal efficiency at 24000 µS/cm, the salinity level was reduced to 18000 µS/cm which corresponds to 50% stored urine. The removal efficiency at this level of salinity showed better results as it was increased to an average of 81%. Salinity level then reduced after a stable COD removal efficiency was observed with 50% salinity to a level of salinity that of which matches that one of 25% stored urine. The COD removal efficiency was increased to an average of 90%. The electrical conductivity at this stage was around 10500 µS/cm, which is the electrical conductivity of the synthetic urine without any addition of NaCl. All in all, in this experiment it was observed that the removal effciency was affected greatly at 32000 µS/cm and in which COD removal efficiency was around 40% only then increased to reach 90% when the salinity level was at the lowest value in this experiment which was 10500 µS/cm.

5.7. Nutrient Recovery

The nutrient recovery experiment were performed through desorption by contacting the nutrient enriched clinoptilolite with tap water. Nutrient enriched clinoptilolite was produced in this work which was processed with single stage ion exchange in configuration (b) using stored urine from batch 2. Table 4.9 in Chapter 4, illustrated the characteristics of nutrient enriched clinoptilolite used in nutrient recovery experiment. A continuous feeding regime was applied with two different contact times 5 and 300 min were selected as a low and high contact time. The selected contact times were calculated by Allar, (2015) to simulate the two actual irrigation types.

Ammonium, phosphorus, potassium and COD were monitored beside pH and electrical conductivity of the water coming out from the recovery columns.

For 5 min contact time, Figure 5.78 and 5.79 illustrate the pH and electrical conductivity of the tap water enriched with nutrients after passing through the nutrient enriched clinoptilolite columns. Results of pH showed a pH of 8.3 then stabilized at a value of 7.7. The electrical conductivity at the beginning had a value around 1800 µS/cm then with time the electrical conductivity stabilized at a level similar to electrical conductivity of the tap water used for recovery which was around 450 . Both pH and electrical conductivity are important parameters for irrigational water, both pH and electrical conductivity were below the max limit of electrical conductivity of water to be used for irrigation purposes which around 3000 µS/cm (FAO, 1988; Allar, 2015).

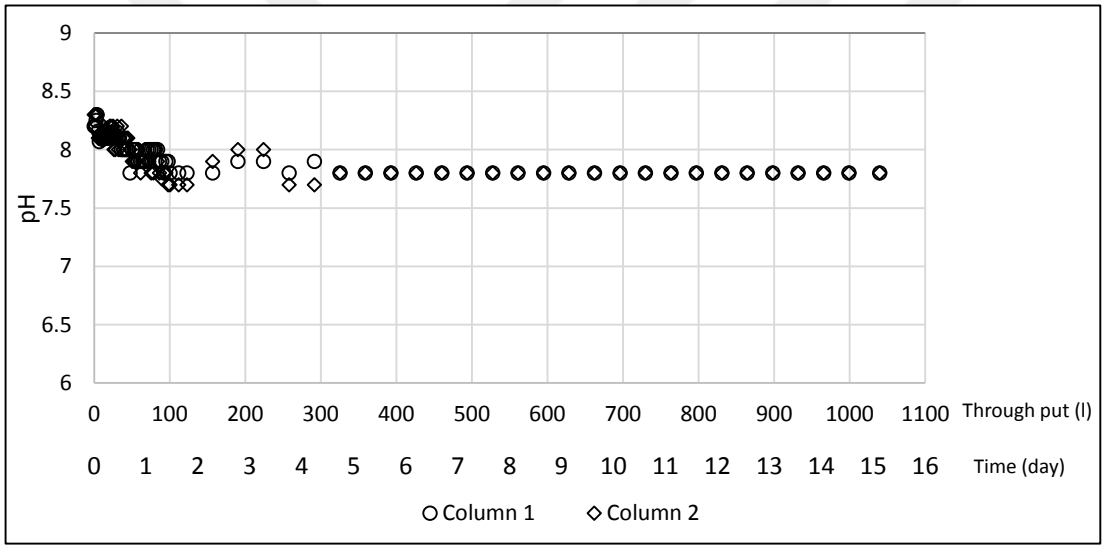

Figure 5.78 : pH of 5 min contact time recovery run.

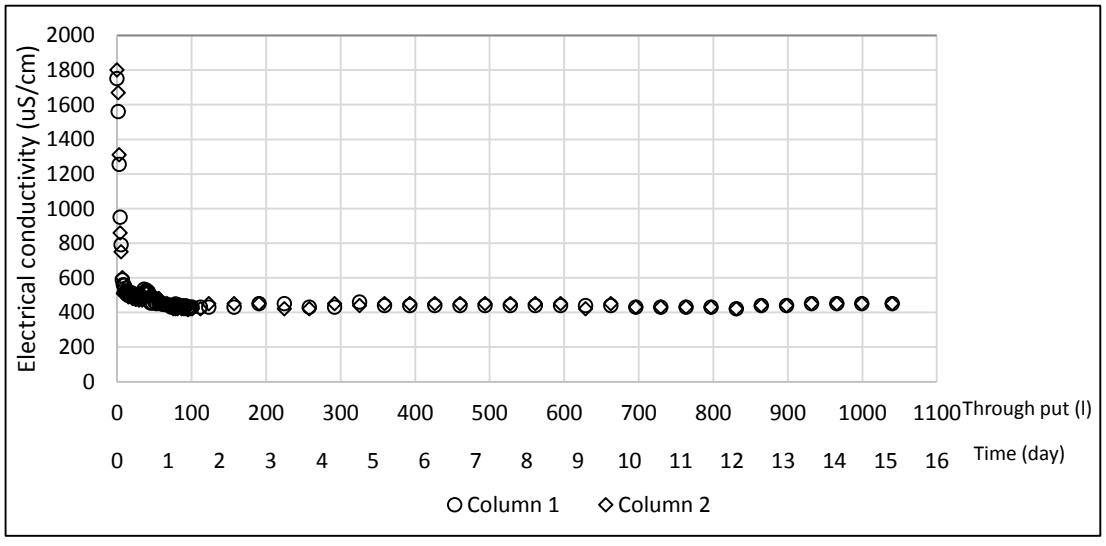

Figure 5.79 : Electrcial conductivity of 5 min contact time recovery run.

The amount of ammonium released form the clinoptilolite surface was monitored, and the recovery results started at a concentration of 16 mg/l then stabilized wich is in line with guidlines(FAO, 1988; Atıksu Arıtma Tesisleri Teknik Usuller, 2010). Nutrient enriched clinoptilolite at recovery experiments act as a slow release fertilizer due to the fact that irriagating plants will be carryed out for specific amount of time through the day not over 24 hours, thus the nutrients will be released over a longer time from nutrient enriched clinoptilolite surface. The release of ammonium with 5 min contact time was carried until no release at all was observed from clinoptilolite surface. The recovery of ammonium lasted for 15 days under contact time of 5 min consuming around 1100 l of tap water, which is shorter compared to a previous study which used the same conditions with ammonium recovery lasting for almost 25 days (Allar, 2015). The percentage of ammonium recovered was almost 100% as can be observed from Figure 5.80, which is in line with previous studies (Kocaturk and Beler Baykal, 2012; Allar, 2015).

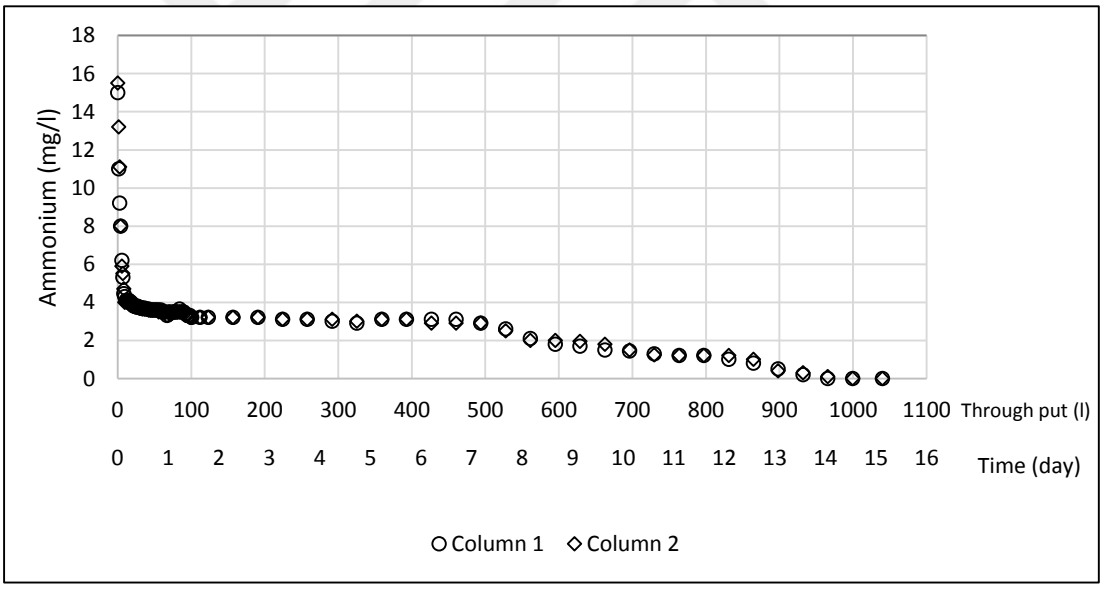

Figure 5.80 : Ammonium recovery with 5 min contact time recovery run.

The phosphorus release was much faster than the ammonium, and in a short period of time about 5 days almost 90% of the phosphorus was released from the clinoptilolite surface. Figure 5.81 illustrates the release of phosphorus with 5 min contact time. This percent of recovery was in line with other studies which used 5 min contact time for recovery (Kocaturk and Beler Baykal, 2012; Allar, 2015).

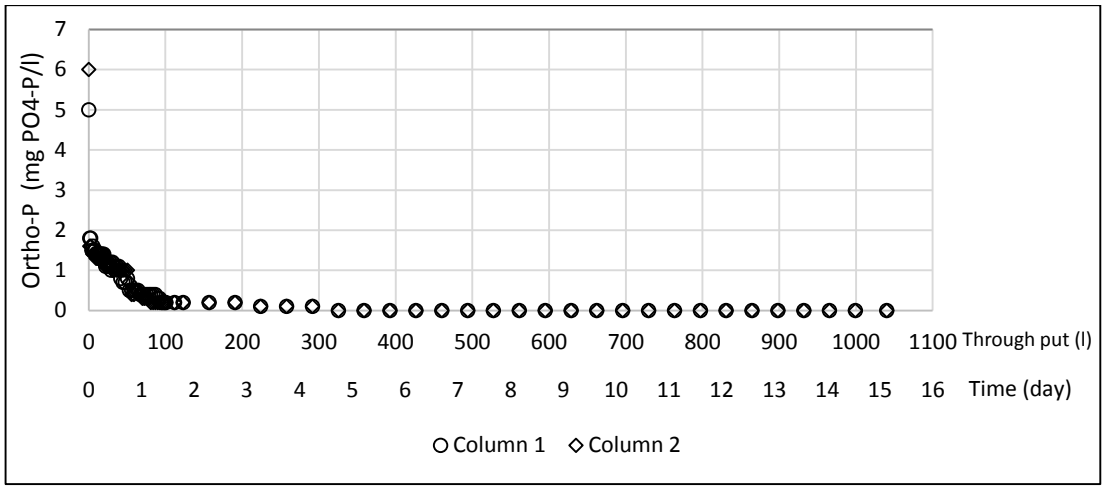

Figure 5.81: Phosphorus recovery with 5 min contact time recovery run.

Regarding potassium, the results revealed that about 15% only of potassium was released from clinoptilolite surface as shown in Figure 5.82. The release of potassium in other studies was indicated as no release at all (kocaturk and Beler Baykal, 2012; Allar, 2015), however this work obtained a release but at a very low percentage. The problem with no or very small amount of potassium recovery from clinoptilolite surface is due to the presence of potassium in tap water which simulates irrigation water clinoptilolite selictivity for potassium ions.

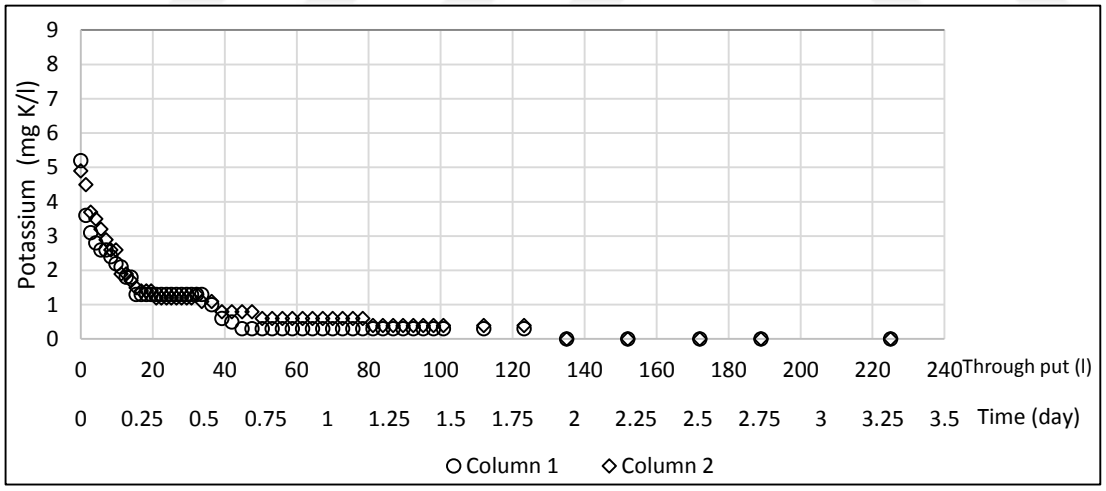

Figure 5.82 : Potassium recovery with 5 min contact time recovery run.

It was observed in this work section 5.4, COD was removed by 25 – 35% from the liquid phase in configuration (b) with single stage ion exchange process. No information about the release of COD was encounterd in previous work. The results of recovery with 5 min contact time revealed that the COD release was very small that dropped to 0 after few litters of tap water contacted the clinoptilolite surface which indicates negligibale release of COD as shown in Figure 5.83.

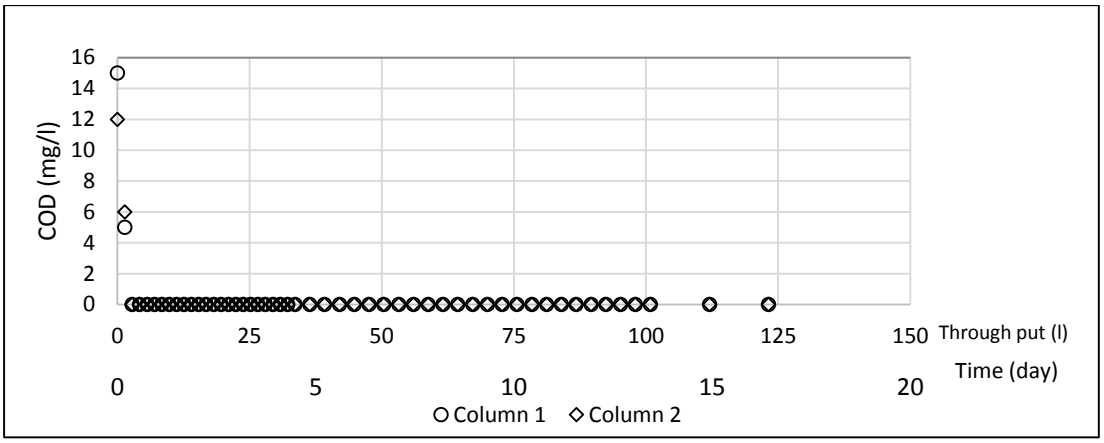

Figure 5.83 : COD release with 5 min contact time recovery run.

Recovery experiments carried out at 300 min of contact time that carried out in a smaller flow rate. 300 min contact time was selected to simulate a very slow actual irrigation type (Allar, 2015). The results revealed that a much slower release of nutrient can be obtained with high contact time. Ammonium was released with 90% till about 120 days of operation showing the slow release fertilizer action that can be observed with clinoptilolite as presented in Figure 5.84. Phosphorus was released with 98% within 18 days of operation and potassium was released with 8% only within 22 days as illustrated in Figure 5.85 and 5.86.

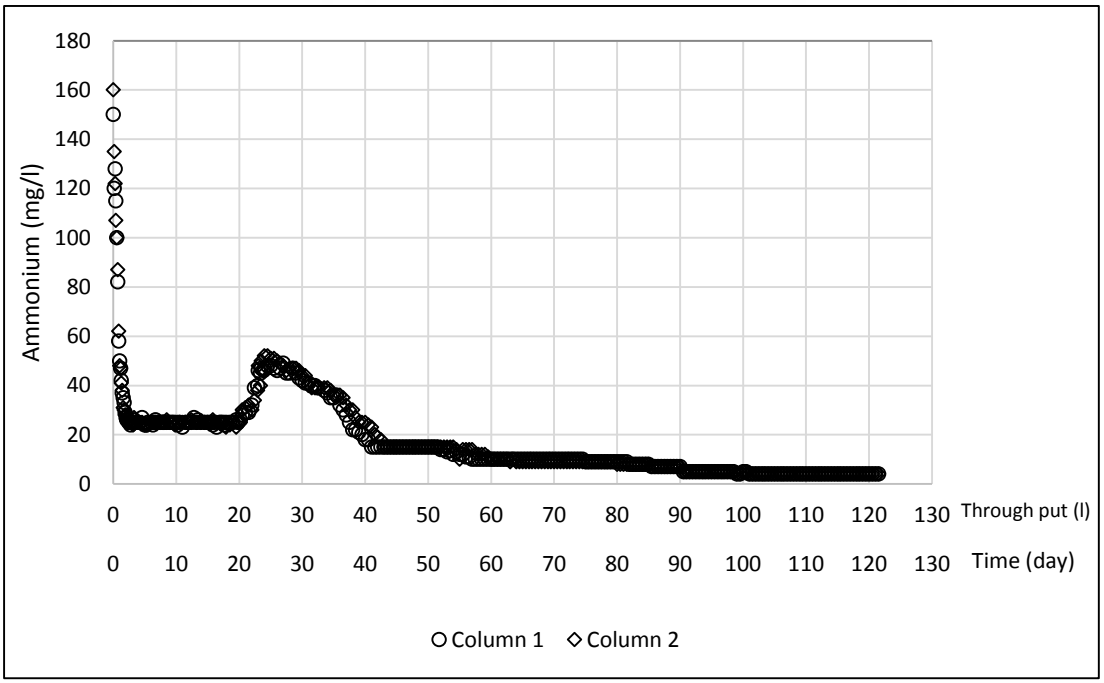

Figure 5.84 : Ammonium recovery with 300 min contact time recovery run.

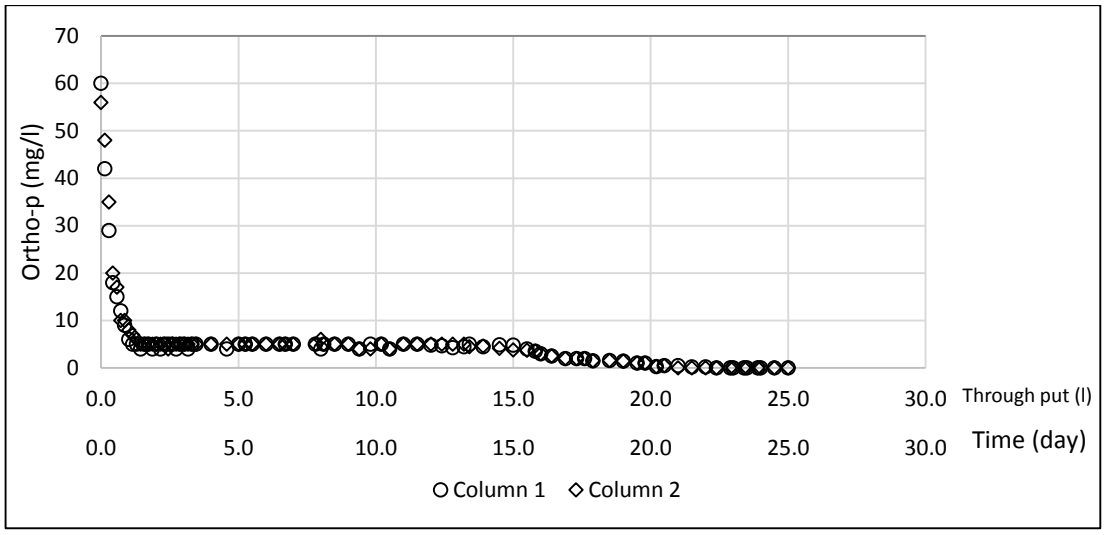

Figure 5.85 : Phosphorus recovery with 300 min contact time recovery run.

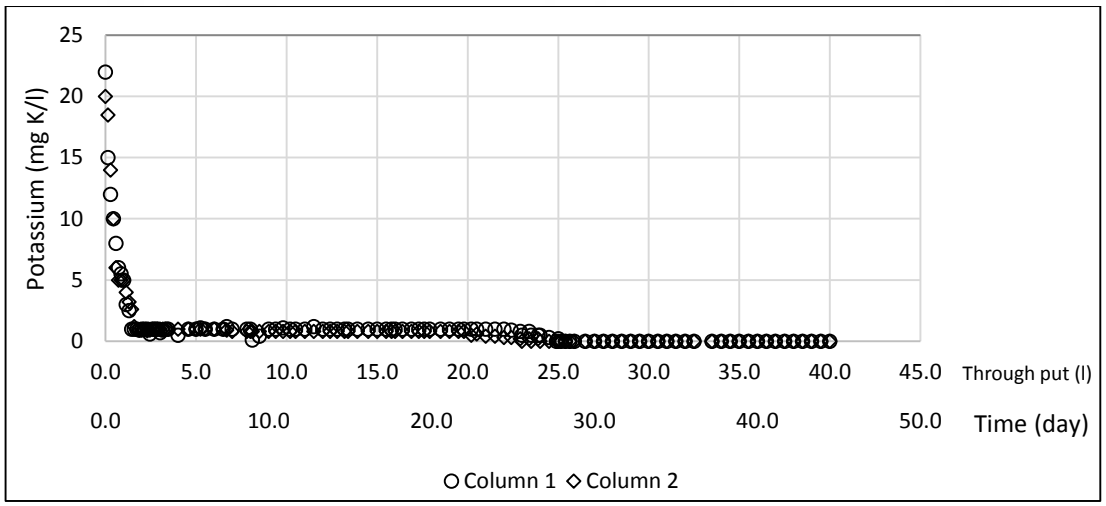

Figure 5.86 : Potassium recovery with 300 min contact time recovery run

The results of COD release from clinoptilolite with 300 min contact time revealed that the release was very small that dropped to 0 after few letters of tap water contacted the clinoptilolite surface as shown in Figure 5.87 as was the case for 5 min contact time.

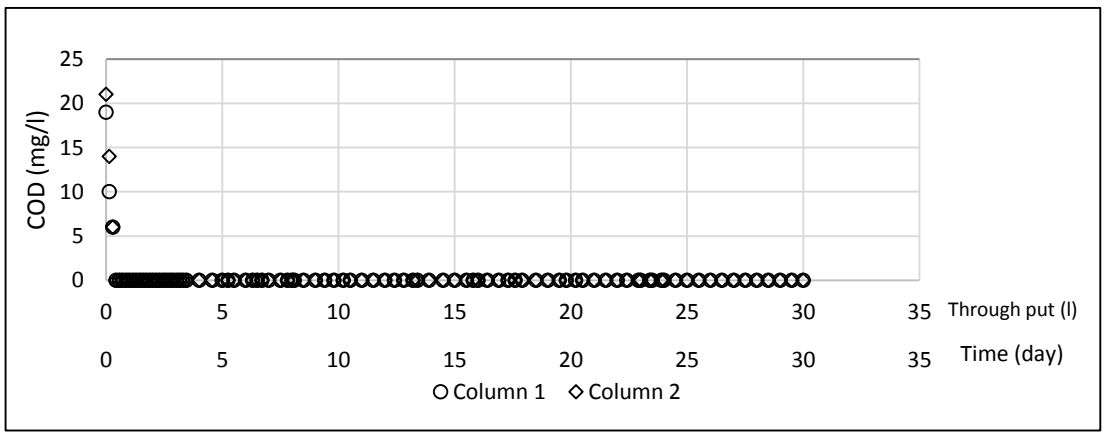

Figure 5.87 : COD release with 300 min contact time recovery run.

The pH and connectivity of this recovery run was similar to that one of 5 min contact time. Figure 5.88 and 5.89 the pH and electrical conductivity of the tap water enriched with nutrients after passing through the nutrient enriched clinoptilolite columns. Results of pH showed a pH of 8.3 then stabilized at a value of 7.7. The electrical conductivity at the beginning had a value around 1800 µS/cm then with time the electrical conductivity stabilized at a level similar to electrical conductivity of the tap water used for recovery which was around 450 . Both pH and electrical conductivity are important parameters for irrigational water, both pH and electrical conductivity were below the max limit of electrical conductivity of water to be used for irrigation purposes which around 3000 µS/cm (FAO, 1988; Allar, 2015).

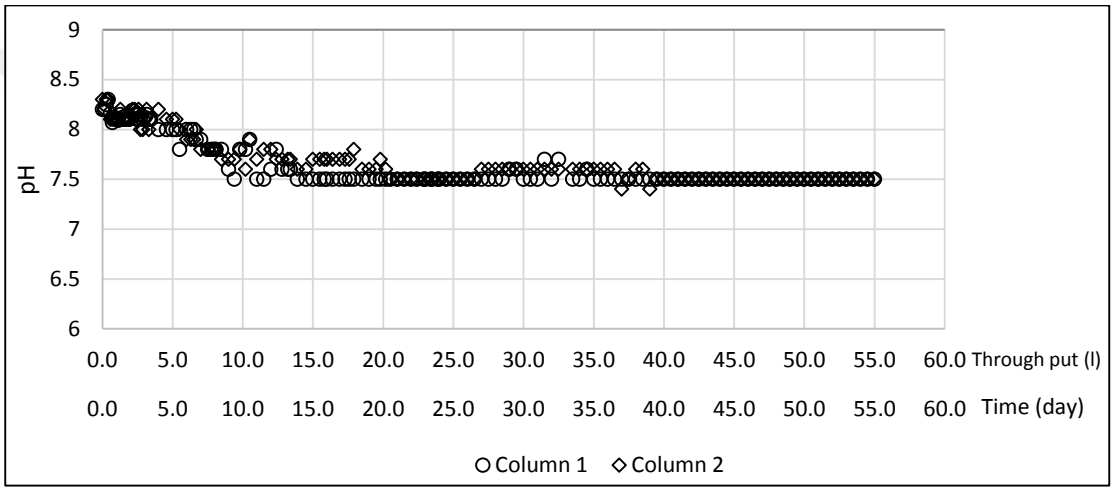

Figure 5.88 : pH of 300 min contact time recovery run.

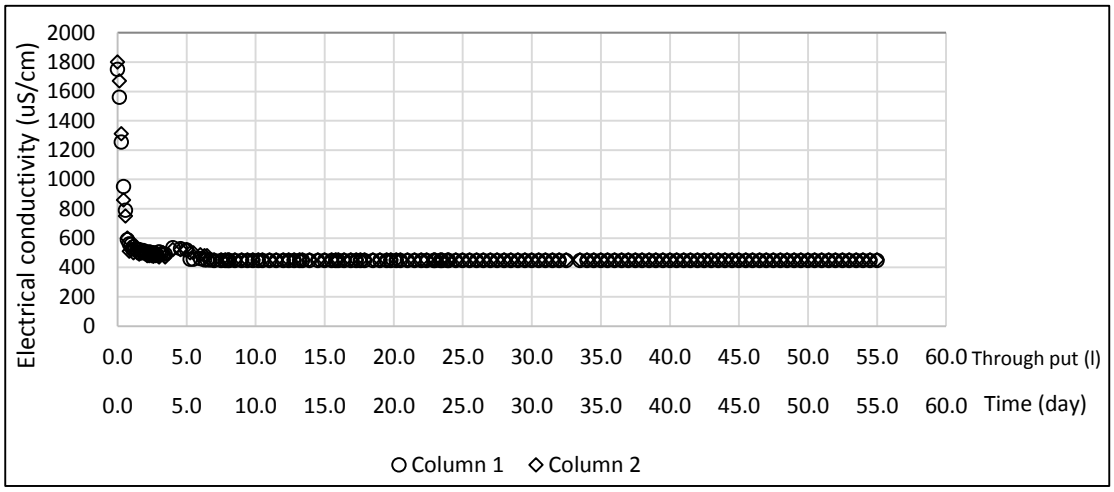

Figure 5.89 : Electrcial conductivity of 300 min contact time recovery run.

Table 5.9 summarizes the recovery experiment with continuous mode operation performed with two different contact times.

Table 5.9: Summary table for nutrient recovery with continous mode under two different contact times.

Parameter	Nitrogen		Phosphorus		Potassium	
Contact time (min)	5	300	5	300	5	300
Actual loading (mg/g clinoptilolite)	12.0	12.0	0.58	0.58	2.27	2.27
Amount of nutrient recovered (mg/g clinoptilolite)	12.0	10.8	0.52	0.57	0.34	0.18
% Recovery	100	90	90	98	15	8
Recovery duration (day)	15	120	5	18	1.5	22

Because potassium is an important fertilizer component, although it was removed secssufly with 70% almost no recovery was observed using tap water which had 3.0 mg K^+/l. Obviously there is room for the relaese of potassium from nutrient enriched clinoptilolite with water of lower potassium concentrations. In an attempt to investigate further possible recovery of potassium batch experiments with 4 types of water, tap, rain, drinking and deionized water were performed. The aim of this batch experiment is to understand if using water with no potassium or a smaller concentration compared to that of tap water will help to recover more potassium.

The characteristics of the four types of liquid phase i.e. tab, rain, drinking and deionized water are shown in Chapter 4, Table 4.10. All the water types have no phosphorus and almost no ammonium. Tap water has the highest potassium concentration and electrical conductivity among the other types of water, while deionized water has no potassium at all and ignorable electrical conductivity level. Clinoptilolite which has not undergone any recovery and clinoptilolite which had undergone recovery at 5 min contact time were used as the solid phase in this experiment. The results are illustrated in Figure 5.90 and 5.91 for both samples of clinoptilolite.

The results showed that the release of potassium was much higher when deionized water was used with 50% of clinoptilolite which had not undergone recovery and 32% recovery with clinoptilolite in which nutrients had undergone recovery of 5 min contact time. The recovery results with rain water showed a higher release than tap and drinking

water due to the very small concentration of potassium. The release percentage was 31% for clinoptilolite in which nutrients had not undergone recovery and 26% for clinoptilolite had undergone recovery of 5 min contact time. Tap and drinking water had a smaller release due to the presence of potassium in both of them, 8% and 17% of potassium was released by tap and drinking water respectively from clinoptilolite surface in which had not undergone recovery. In case of clinoptilolite in which had undergone recovery of 5 min contact time, the percentages of release were much smaller, 6% by using tap water and about 12% by drinking water. These results give an indication that in case of the clinoptilolite was distributed on the soil and subjected to irrigation from a water that does not contain or has very small potassium concentration, for instant rain water, the release will be much higher compared to a case of tap water used for irrigation. Table 5.10 shows

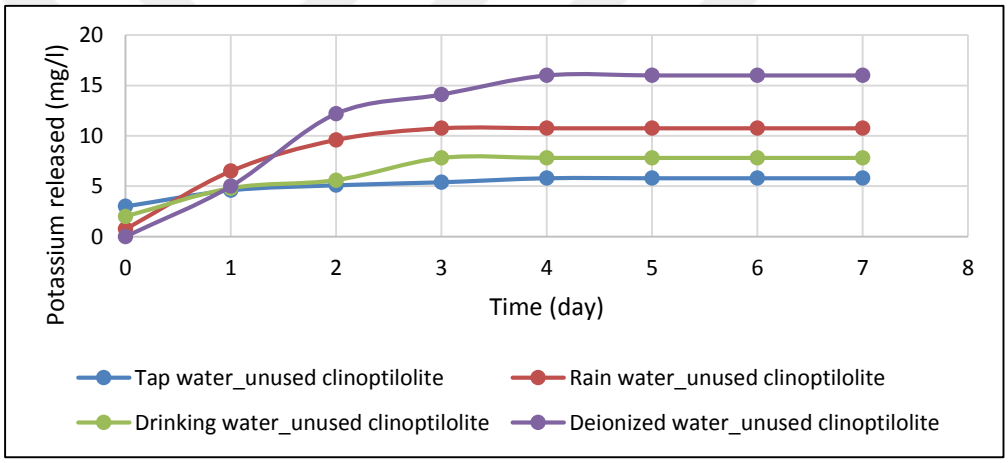

Figure 5.90 : Potassium release in batch experiment with clinoptilolite that nutiernt had not been recoverd from its surface.

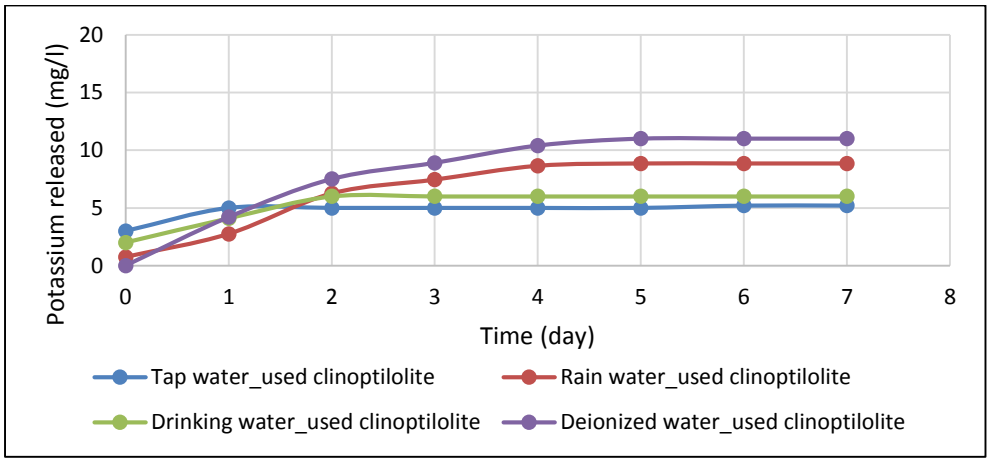

Figure 5.91 : Potassium release in batch experiment with clinoptilolite that nutiernt hasd been recoverdd from its surface.

Table 5.10 : Summary of potassium release in batch experiment.

Clinoptilolite sample	No recovery of any type				Undergone recovery of 5 min contact time			
Type of water	Tab	Drinking	Rain	Deionized	Tab	Drinking	Rain	Deionized
Actual loading (mg/g clinop.)	2.27	2.27	2.27	2.27	1.93	1.93	1.93	1.93
Amount of nutrient recovered (mg/g clinop.)	1.18	0.39	0.70	1.14	0.12	0.23	0.50	0.62
% Recovery	8	17	31	50	6	12	26	32
Recovery duration (day)	7	7	7	7	7	7	7	7

5.8. Plant Experiment

In the final stage of the experimental study, the effectiveness of nutrient enriched clinoptilolite (NEC) that was produced from urine in this work was compared to commercially available synthetic fertilizer using pot trials. Pepper and tomato seedlings were used in this comparison as described in chapter 4. Nitrogen supports the green structure of plants and hence the plant's height, while phosphorus supports flower formation and fruit structures (Razaq et al, 2017). Therefore, the comparison results between fertilizers were interpreted according to the changes in plant height and the number of flowers observed. Figure 5.92 and 5.93 show the changes observed in plant height for pepper and tomato.

It was observed that both fertilizers have a different growth characteristic. Regarding pepper pots receiving NEC, had grown to about 25cm in plant height after 2 months. On the other hand, the pepper pots in which synthetic fertilizer was used had an increase in height less than that one for the NEC pots. The change in height of tomato plants in which NEC was about double that of the synthetic fertilizer. After two months the height tomato with NEC was around 45 cm while it was 35 cm planted with synthetic fertilizer. Figure 5.94 and 5.95 show the differences among the control, clinoptilolite and synthetic fertilizer pots for both pepper and tomato.

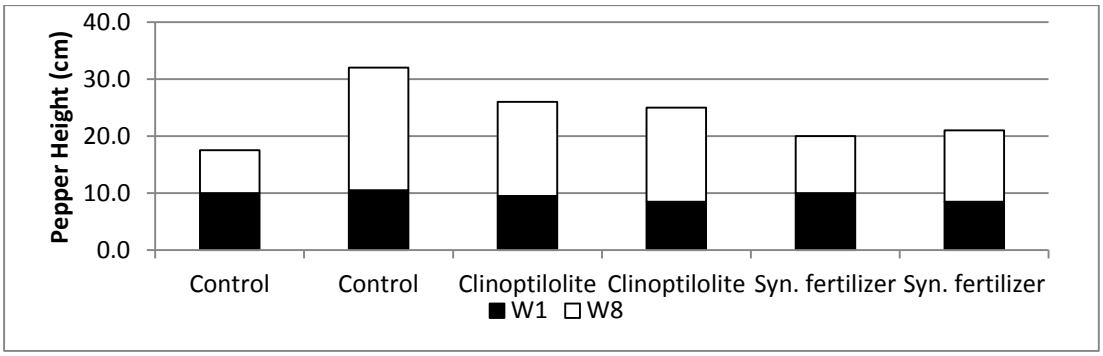

Figure 5.92: Changes in pepper plant height over time intervals.

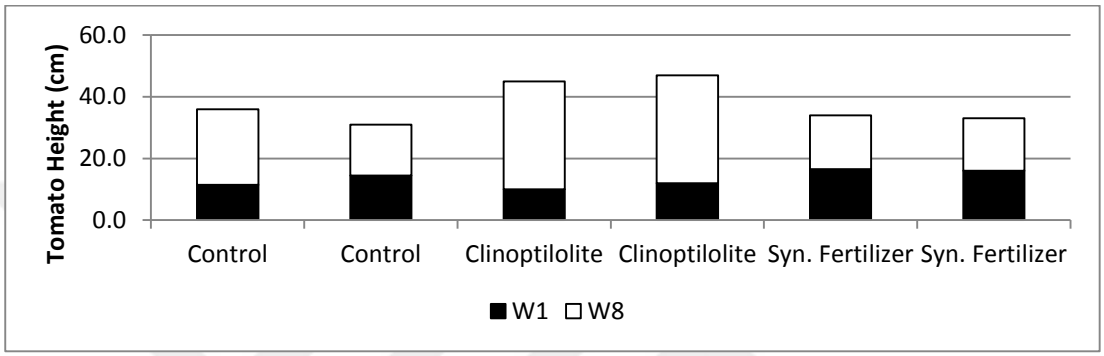

Figure 5.93: Changes in tomato plant height over time intervals.

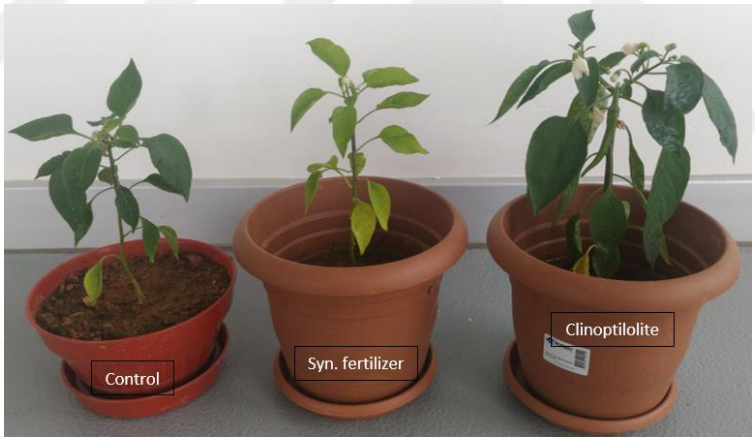

Figure 5.94 : Difference in pepper plants stucture.

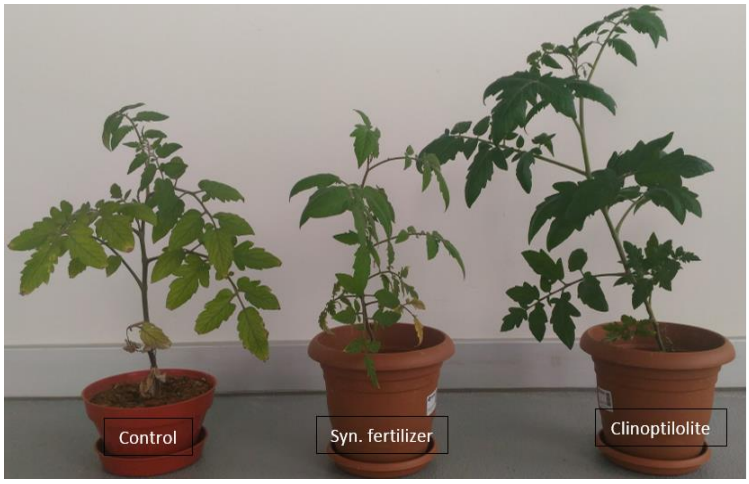

Figure 5.95 : Difference in tomato plants stucture.

Regarding the number of flowers, it can be observed from Figure 5.96 and 5.97 that pots of pepper and tomato in which NEC was used showed a higher number of flowers compared to that one of the synthetic fertilizer. In case of pepper, the formation of the fruit pepper took place after the flowers. The flower bloomed first, then dropped its leaves and in the last stage began to develop as pepper. Figure 5.98 shows an example of pepper fruit that was produced from the pot in which NEC was used.

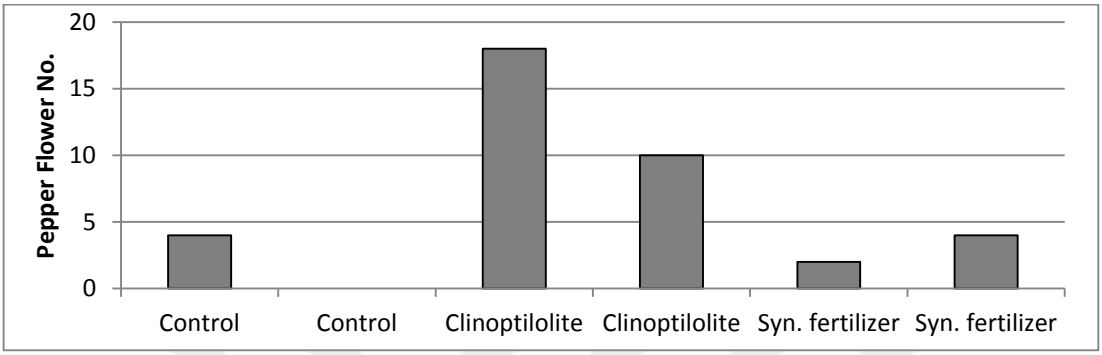

Figure 5.96: Number of pepper flowers after two months.

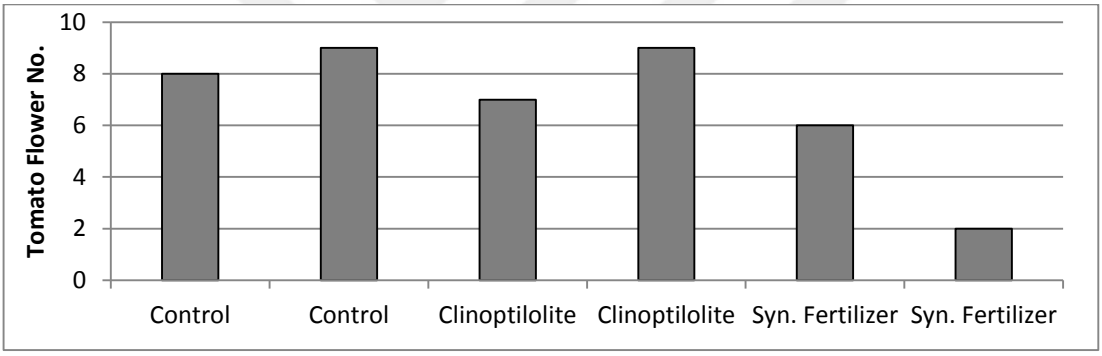

Figure 5.97: Number of tomato flowers after two months.

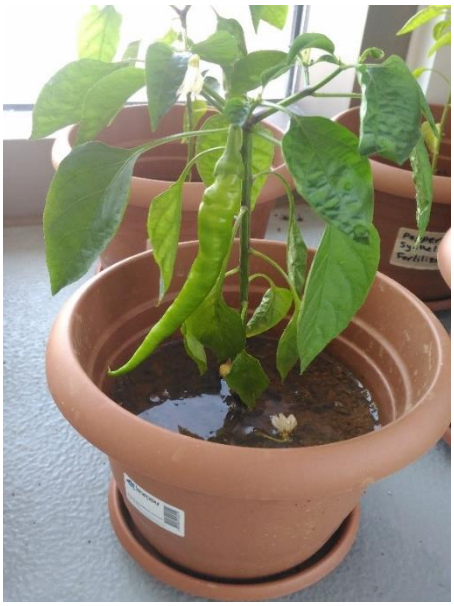

Figure 5.98 : Pepper fruit produced by using nutrient enriched clinoptilolited.

All in all, the pot trials with pepper and tomato reveald that potential of NEC is considrable and all the pots in which NEC was used were shoing a better results in terms of plant height and flower formation compareed to that one of senthetic fertilizer. Regarding the control pots in which no fertilizer of any type was used, in terms of plant height, the results were more or less similar to those of the NEC. On the other hand, in pepper controll pots the flower formation was very small in number compared to NEC pots and synthetic fertiliz pots. In tomato control pots, flower formation was almost similar to NEC pots.

6. CONCLUSION AND RECOMMENDATION

This work aimed to investigate various combinations/configurations of ion exchnage/adsorption and anaerobic processing for nutrient recovery from source separated human urine, especially removal of organic matter in the liquid residue of ion exchange process. EGSB reactor with anaerobic granular sludge from a confectionery wastewater treatment plant was adapted to treat highly saline human urine. Three different configurations were investigated in this work. The suggested configurations were based on a combination between ion exchange and anaerobic processes. The following points present the conclusion and recommendation of this work:

- COD removal efficiency at the adaptation stage was found to be reasonably good at low concentrations of fresh urine in the feeding, specifically with 25%, while at higher percentages COD removal efficiency reduced for example 40% removal efficiency was observed with 65%.
- The reduction of the COD removal efficiency was attributed to the increasing level of ammonium that exceeded the recommend threshold level by the literature at 65% concentration.
- Ammonium release was observed but not at appreciable amount and the percentage that was released at most 6% with 25% fresh urine concentration in the feeding olution.
- Due to the reduction of COD removal efficiency and the low ammonium release from anaerobic process, use of configuration (a) (Anaerobic process followed by Ion exchnage process) was not recommended.
- Regarding storage, nitrogen, phosphorus and potassium changes were in line with previous studies. COD concentrations were observed to be changing during long storage periods which were beyond the time required for completion of hydrolysis. The reduction at the end of 4 months was around 60 – 65%. This observation was not reported in the literature by any of the research conducted on stored human urine.

- In case the anaerobic process is intended for removal of organic matter from the residue of the ion exchange process, it is recommends that stored urine must be processes once the hydrolysis is accomplished, in order to avoid the reduction in COD concentration during long time storage.
- Configuration (b) used for removal of nutrients in a single stage ion exchange process followed by anaerobic process for organic matter removal. The results of nutrient removal runs by single ion exchange process stage using fixed bed clinoptilolite columns were in line with the removal efficiencies reported in the literature. Ammonium was removed by 80%, phosphorus by almost 99% and potassium by 70%.
- COD removal was observed during ion exchange process. The removal efficiencies ranged between 25% and 35%. This observation was not reported in any of references reviewed.
- The observations had shown that stored urine after processing with single stage ion exchnage should be used for adaptation instead of fresh urine due to high ammonium concentrations in fresh urine.
- The new adaptation with stored urine, showed better results regarding COD removal efficiencies. Removal efficiencies were ranged from 60 – 85% during this adaptation
- The best obtained removal efficiency was with 50% of stored urine in the feeding, as 85% removal efficiency was observed. 100% of stored urine in which nutrients had been removed did not reveal a good performance as the removal efficiency was 60%. The reason was attributed to the effect of salinity as it was approaching the threshold of inhibition for anaerobic processes in terms of electrical conductivity.
- The quality of the effluent of all the anaerobic stages in configuration (b) revealed that effluent quality control is needed environmental protection before discharge.
- Upon the last observation from configuration (b), this work recommends another stage of ion exchange process to be employed in a manner of stage wise operation.

- The stress of nitrogen and COD in the effluent of anaerobic process were considerably reduced to a level that the remnant can be discharged to the sewer by the addition of another ion exchange stage with stage wise operation.
- In general, the threats imposed by nutrients and organic matter in source separated human urine can be eliminated by employing a combination of ion exchange and anaerobic processes. The best fit of these two processes is obtained to be ion exchange followed by anaerobic process followed by stage wise ion exchange.
- Salinity was observed to play an important role in the performance of anaerobic processes treating source separated human urine, thus this work recommends to use the urine with 50 to 75% in the influent.
- The role of salnity was obtained to be signeficant and the threshold that obtained to be negatively effect the COD removal was around 32000 µS/cm in this specific work.
- The use of nutrient enriched clinoptilolite as an alternative natural fertilizer was observed to be significant as it was reveald by the results of plant experiments. Beetter results in terms of height, streanght, plant texture and potential fruit production was observed with nutrient enriched clinoptilolite compared to that one of synthetic fertilizer.
- Further studies should concentrate more upon the best fit of operational conduction for both ion exchange and anaerobic processes. Regarding ion exchange, focus on working with different initial loadings that possibly will affect COD removal through ion exchange. For anaerobic process working with different HRTs and OLRs should be investigated, and more research should concentrate upon the inhibition of ammonium and salinity from human urine combined with COD concentrations.
- biogas production and energy recovery from source separated human urine should be investigated.
- Another point to be investigated is the reasons behind COD reduction during long storage and weather a long storage period will be enough to eliminate organic matter threat in this wastewater stream.

REFERENCES

Ahring, B. K., and Westermann, P. (1985). Sensitivity of thermophilic methanogenic bacteria to heavy metals. *Current Microbiology, 12*(5), 273-276.

Ahring, B.K., Alatriste-Mondragon, F., Westermann, P., and Mah, R.A. (1991). Effects of cations on Methanosarcinathermophila TM-1 growing on moderate concentrations of acetate: production of single cells. *Applied microbiology and biotechnology, 35*(5), 686–689.

Allar, A. D. (2015). Processing alternatives of urine with clinoptilolite for indirect use of human urine as fertilizer (PhD thesis). Istanbul Technical University, Graduate school of science and engineering technology, Turkey (in Turkish with an extended summary in English).

Allar, A. D., and Beler-Baykal, B. (2013). Phosphorus recovery from source separated human urine upon processing with clinoptilolite. *Proceedings of the Water Environment Federation,* 2013(4), 117-124.

Allar, A. D., and Beler Baykal, B. (2015). Stagewise processing of yellow water using clinoptilolite for nitrogen and phosphorus recovery and higher residual quality. *Water Science and Technology, 71*(12), 1869-1874.

Allar-Emek, A. D., and Beler-Baykal, B. (2017). Continuous versus batch contacting for nutrient recovery from human urine upon processing with clinoptilolite I: surface capacities and operation times. *Desalination Water Treatment, 93*, 361-367.

Allar-Emek, A., Yıldız-Dogan, N., Beler-Baykal, B. (2016). Public perception and acceptance of fertilizers from human urine among Turkish citizens holding university degrees. *Proceedings of the 8th International Conference on Environmental Science and Technology*, Houston, TX, USA.

Ammary, B. Y. (2004). Nutrients requirements in biological industrial wastewater treatment. *African Journal of Biotechnology, 3*(4), 236-238.

Antonini, S., Paris, S., Eichert, T., and Clemens, J. (2011). Nitrogen and phosphorus recovery from human urine by struvite precipitation and air stripping in Vietnam. *CLEAN–Soil, Air, Water, 39*(12), 1099-1104.

Atıksu Arıtma Tesisi Teknik Usuller Tebliği. (2010). *T. C. Resmi Gazete*, 27527, 20 Mart 2010.

Baere, L.A., Devocht, M., van Assche, P., and Verstraete, W. (1984). Influence of high NaCl and NH4Cl salt levels on methanogenic associations. *Water Research. 18,* 543–548.

Başakçilardan-Kabakci, S., İpekoğlu, A. N., and Talinli, I. (2007). Recovery of ammonia from human urine by stripping and absorption. *Environmental Engineering Science, 24*(5), 615-624.

Beal, C., Gardner, T., Ahmed, W., Walton, C., and Hamlyn-Harris, D. (2007). Closing the nutrient loop: a urine-separation and reuse trial in the Currumbin ecovillage, QLD. *Innovation and Technology for On-site Systems: Proceedings of On-site 2007 Conference,* Armidale, Australia.

Beler-Baykal, B. (2015). Stream segregation in household use: a review of grey water as an alternative source of water and yellow water as an alternative source of fertilizers. *Water Quality, Exposure and Health,7*(1), 27-37.

Beler-Baykal, B., Allar, A. D., and Bayram, S. (2011). Nitrogen recovery from source-separated human urine using clinoptilolite and preliminary results of its use as fertilizer. *Water Science and Technology, 63*(4), 811-817.

Beler-Baykal, B., Bayram, S., Akkaymak, E., and Cinar, S. (2004). Removal of ammonium from human urine through ion exchange with clinoptilolite and its recovery for further reuse. *Water Science and Technology, 50*(6), 149-156.

Beler Baykal, B., and Doğan, G., (2016). Two Stage Processing Options for Enhancing Total Nutrient Recovery from Source Separated Human Urine to be Used as Fertilizer. *WEF / IWA Nutrient Removal and Recovery NRR*, Denver, USA.

Beler-Baykal, B., Oldenburg, M., and Sekoulov, I. (1996). The use of ion exchange in ammonia removal under constant and variable loads. *Environmental technology, 17*(7), 717-726.

Borja, R., Sanche´z, E., and Weiland, P. (1996). Influence of ammonia concentration on thermophilic anaerobic digestion of cattle manure in upflow anaerobic sludge blanket (UASB) reactors. *Process Biochemistry, 31* (5), 477–483.

Breck, D. W. (1974). *Zeolite Molecular Sieves*. New York : John Wiley & Sons.

Bujoczek, G., Oleszkiewicz, J., Sparling, R., and Cenkowski, S. (2000). High solid anaerobic digestion of chicken manure. *Journal of Agricultural Engineering Research 76*(1), 51–60.

Chen, J. L., Ortiz, R., Steele, T. W., and Stuckey, D. C. (2014). Toxicants inhibiting anaerobic digestion: a review. *Biotechnology advances, 32*(8), 1523-1534.

Chen, W.H., Han, S.K., and Sung, S. (2003). Sodium inhibition of thermophilic methanogens. *Journal of Environmental Engineering, 129*(6), 506–512.

Chen, Y., Cheng, J. J., and Creamer, K. S. (2008). Inhibition of anaerobic digestion process: a review. *Bioresource technology, 99*(10), 4044-4064.

Colleran, E., Finnegan, S., and Lens, P. (1995). Anaerobic treatment of sulphate-containing waste streams. *Antonie van Leeuwenhoek, 67*(1), 29–46.

Cheremisinoff, N. P. (1997). *Biotechnology for waste and wastewater treatment.* Burlington : Elsevier.

Connaughton, S., Collins, G., and O'Flaherty, V. (2006). Psychrophilic and Mesophilic Anaerobic Digestion of Brewery Effluent: A Comparative Study. *Water research, 40*(13), 2503-2510.

Cooney, E. L., Booker, N. A., Shallcross, D. C., and Stevens, G. W. (1999). Ammonia removal from wastewaters using natural Australian zeolite. I. Characterization of the zeolite. *Separation science and technology, 34*(12), 2307-2327.

De Feo, G. Antoniou, G. Franz Fardin, H. El-Gohary, F. Yun Zheng, X. Reklaityte,I., Butler, D., Yannopoulos, S., and Angelakis, A. N. (2014). Historical Development of Sewers Worldwide. *Sustainability 6*(6), 3936-3974.

De Lemos Chernicharo, C. A. (2007). *Anaerobic reactors.* London; New York : IWA publishing.

de Man, A. W. A., Grin, P. C., Roersma, R. E., GroUe, K. C. F. and Lettinga, G. (1986). Anaerobic treatment of municipal wastewater at low temperatures. Anaerobic treatment. *Proceedings of EWPCA Water Treatment Conference Anaerobic treatment, a grown-up technology*, Amsterdam, The Netherlands.

Dinsdale, R. M., Hawkes, F. R., and Hawkes, D. L. (2000). Anaerobic Digestion of Short Chain Organic Acids in an Expended Granular Sludge Bed Reactor. *Water Research, 34*(9), 2433-2438.

Dogan G. (2015). A comparative investigation on the production of fertilizer from the urine (master's thesis). Istanbul Technical University, Graduate school of science and engineering technology, Turkey (in Turkish with an extended summary in English).

Draaijer, H., Maas, J. A. W., Schaapman, J. E., and Khan, A. (1992). Performance of the 5 MLD UASB reactor for sewage treatment at Kanpur, India. *Water Science and Technology, 25*(7), 123-133.

Enright, A. M., McHugh, S., Collins, G., and O'Flaherty, V. (2005). Low-temperature Anaerobic Biological Treatment of Solvent-containing Pharmaceutical Wastewater. *Water Research, 39*(19), 4587-4596.

Esrey, S. A., Andersson, I., Hillers, A., and Sawyer, R. (2001). *Closing the loop: ecological sanitation for food security*. Swedish International Development Cooperation Agency.

Etter, B., Tilley, E., Khadka, R., and Udert, K. M. (2011). Low-cost struvite production using source-separated urine in Nepal. *Water research, 45*(2), 852-862.

Feijoo, G., Soto, M., Mende´z, R., and Lema, J. M. (1995). Sodium inhibition in the anaerobic digestion process: antagonism and adaptation phenomena. *Enzyme and Microbial Technology, 17(*2), 180–188.

Feilden, N. E. H. (1983). The theory and practice of anaerobic digestion reactor design. *Process biochemistry, 18*(5), 34-37.

Fernandez, N., and Forster, C. F. (1994). The anaerobic digestion of simulated coffee waste using thermophilic and mesophilic upflow filters. *Process safety and environmental protection, 72*(1), 15-20.

Fittschen, I., and Hahn, H. H. (1998). Characterization of the municipal wastewaterpart human urine and a preliminary comparison with liquid cattle excretion. *Water Science and Technology*, *38*(6), 9-16.

Flanigen, E. M. (2001). Zeolites and Molecular Sieves. An Historical Perspective. In P. A. Jacobs, E. M. Flanigen, J. C. Jansen Herman van Bekkum (Eds.), *Introduction to Zeolite Science and Practice* (2nd ed., Vol. 137, pp. 11-35). Amsterdam : Elsevier.

Food and Agriculture Organizatıon of The United Nations (FAO) (1988). *Irrigation water management: Irrigation methods*. Training Manual No 5, Roma, Italya.

Gallert, C., Bauer, S., and Winter, J. (1998). Effect of ammonia on the anaerobic degradation of protein by a mesophilic and thermophilic biowaste population. *Applied Microbiology and Biotechnology*, *50*(4), 495-501

Gallert, C., and Winter, J. (1997). Mesophilic and thermophilic anaerobic digestion of source-sorted organic waste: effect of ammonia on glucose degradation and methane production. *Applied microbiology and biotechnology*, *48*(3), 405-410.

Ganrot, Zs., Slivka, A. and Dave, G. (2008). Nutrient recovery from human urine using pretreated zeolite and struvite precipitation in combination with freesing-thawing and plant availability tests on common wheat. *Clean, 36*(1), 45-52.

Giresunlu, E., and Beler-Baykal, B. (2014). A preliminary investigation on pathogenic indicators in segregated domestic wastewater streams. *IWA 12th specialized conference on small water and wastewater systems & 4th specialized conference on resources oriented sanitation*, Muscat, Sultanate of Oman.

Grady, H. A., Maree, J. P., and Mnqanqeni, S. (2000). Comparsion between sucrose, ethanol and methanol as carbon and energy sources for biological sulphate reduction. *Water science and technology 41*(12), 247 – 253.

GTZ (Deutsche Gesellschaft fu¨ r Technische Zusammenarbeit) (2002). Ecosan—recycling beats disposal. Eschborn (Germany)7 GTZ.

GTZ (2005). Technical Data Sheets for Ecosan Components.

Gujer, W., and Zehnder, A. J. (1983). Conversion processes in anaerobic digestion. *Water science and technology*, *15*(8-9), 127-167.

Harada, H., Shimizu, Y., Miyagoshi, Y., Matsui, S., Matsuda, T., and Nagasaka, T. (2006). Predicting struvite formation for phosphorus recovery from human urine using an equilibrium model. *Water science and technology*, *54*(8), 247-255.

Harada, H., Uemura, S., and Monomoi, K. (1994). Interactions between sulphate-reducing bacteria and methane-producing bacteria in UASB reactors fed with low strength wastes containing different levels of sulphate. *Water Research, 28*(2), 355–367.

Harper, S. R., and Pohland, F. G. (1986). Recent developments in hydrogen management during anaerobic biological wastewater treatment. *Biotechnology and bioengineering*, *28*(4), 585-602.

Hedström, A. and Amofah, L.R. (2008). Adsorption and desorption of ammonium by clinoptilolite adsorbent in municipal wastewater treatment systems. *Journal of Environmental Engineering and Science, 7*(1), 53-61.

Heinonen-Tanski, H., and van Wijk-Sijbesma, C. (2005). Human excreta for plant production. *Bioresource technology, 96*(4), 403-411.

Henze, M., and Harremoës, P. (1983). Anaerobic treatment of wastewater in fixed film reactors–a literature review. *Water science and technology, 15*(8-9), 1-101.

Henze, M., van Loosdrecht, M. C., Ekama, G. A., and Brdjanovic, D. (2008). *Biological wastewater treatment*. London : IWA publishing.

Hejnfelt A., and Angelidaki I., (2009). Anaerobic Digestion of Slaughterhouse By-products. *Biomass and Bioenergy 33*(8), 1046–1054.

Hoglund, C. (2001). *Evaluation of microbial health risks associated with the reuse of source-separated human urine* (PhD thesis). KTH Royal Institute of Technology, Stockholm, Sweden.

Hulshoff Pol, L. W. (1989). *The phenomenon of granulation of anaerobic sludge* (PhD thesis). Wageningen Agricultural University, Wageningen, The Netherlands.

Hwu, C. S., Lier, J. B., and Lettinga, G. (1998). Physicochemical and Biological Performance of Expended Granular Sludge Bed Reactors Treating Long-chain Fatty Acids. *Process Biochemistry, 33*(1), 75-81.

Ishii, S. K., and Boyer, T. H. (2015). Life cycle comparison of centralized wastewater treatment and urine source separation with struvite precipitation: Focus on urine nutrient management. *Water research, 79*, 88-103.

Jackson-Moss, C.A., Duncan, J.R., and Cooper, D.R. (1989). The effect of calcium on anaerobic digestion. *Biotechnology Letters, 11*(3), 219-224.

Jagtap, N., and Boyer, T. H. (2018). Integrated, multi-process approach to total nutrient recovery from stored urine. *Environmental Science: Water Research & Technology, 4*(10), 1639-1650.

Jeremiah Wendt. (2011). Ammonia Removal and pH adjustment in Aerated Lagoons, WWOA 45th Annual Conference, October 6th 2011.

Jianlong, W. and Jing, K. (2005) The Characteristics of Anaerobic Ammonium Oxidation (ANAMMOX) by Granular Sludge from an EGSB Reactor. *Process Biochemistry, 40*(5), 1973-1978.

Jonsson, H., Stintzing, A. R., Vinnerås, B., and Salomon, E. (2004). Guidelines on the use of urine and faeces in crop production. EcoSanRes Programme.

Kabdaslı, I., Tunay, O., Islek, C., Erdinc, E., Huskalar, S., and Tatlı, M. B. (2006a). Nitrogen recovery by urea hydrolysis and struvite precipitation from anthropogenic urine. *Water Science and Technology, 53*(12), 305-312.

Kabdasli, I., Tuenay, O., Tatli, B. M., and Topcuoglu, S. (2006b). Nitrogen recovery by struvite precipitation from anthropogenic nutrient solution. *Fresenius Environmental Bulletin, 15*(9), 1146-1149.

Karri S., Sierra-Alvarez R., and Field J. A. (2006). Toxicity of copper to acetoclastic and hydrogenotrophic activities of methanogens and sulfate reducers in anaerobic sludge. *Chemosphere, 62*(1), 121–127.

Kato, M. T. (1994) The anaerobic treatment of lowstrength soluble wastewaters. PhD thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Kato, M. T., Field, J. A., Kleerebezem, R. and Lettinga, G. (1994). Treatment of low strength soluble wastewater in UASB reactors. *Journal of Fermentation and Bioengineering, 77(6),* 679-686

Khanal, S. K. (2011). Anaerobic biotechnology for bioenergy production: principles and applications. John Wiley & Sons.

Kocaturk, N.P. (2010). Recovery of nutrients with separated urine from clinoptilolite and examination of applicability in agriculture. (master's thesis). Istanbul Technical University, Graduate school of science and engineering technology, Turkey (in Turkish with an extended summary in English).

Kocaturk, N.P. and Beler Baykal, B. (2012). Recovery of plant nutrients from dilute solutions of human urine and preliminary investigations on pot trials. *Clean – Soil, Air, Water, 40 (5),* 538-544.

Kongshaug, G. (1998). Energy Consumption and Greenhouse Gas Emissions in Fertilizer Production. *IFA Technical Conference*, Marrakech, Morocco.

Koster, I.W. and Lettinga, G. (1988). Anaerobic digestion at extreme ammonia concentrations. *Biological Wastes 25(1)*, 51–59.

Kvarnström, E., Emilsson, K., Stintzing, A. R., Johansson, M., Jönsson, H., af Petersens, E., and Ridderstolpe, P. (2006). Urine diversion: one step towards sustainable sanitation. EcoSanRes Programme.

Kpata-Konan N. E., Gnagne T., Konan Koffi F., Bony Kotchi Y., Kouamé Kouamé M., Kouamé Yao F., and Tano Kablan. (2013).Improving Anaerobic Biodigestion of Manioc Wastewater with Human Urine as Co-substrate. *International Journal of Innovation and Applied Studies, 2(3),* 335-343.

Lamichhane, K. and Babcock, R. (2012). An economic appraisal of using source separation of human urine to contain and treat endocrine disrupters in the USA. *Journal of Environmental Monitoring, 14(10),* 2557-2565.

Larsen, T. A., and Gujer, W. (1996). Separate management of anthropogenic nutrient solutions (human urine). *Water Science and Technology, 34(3-4),* 87-94.

Lavagnolo M. C., Girotto F., Hirata O., and Cossu R. (2017). Lab-scale Co-digestion of Kitchen Waste and Brown Water for a Preliminary Performance Evaluation of a Decentralized Waste and Wastewater Management. *Waste Management 66*, 155–160.

Lefebvre, O., Quentin, S., Torrijos, M., Godon, J. J., Delgenes, J. P., and Moletta,R. (2007). Impact of increasing NaCl concentrations on the performance and community composition of two anaerobic reactors. *Applied microbiology and biotechnology, 75(1),* 61-69.

Lettinga, G., Field, J., Van Lier, J., Zeeman, G., and Pol, L. H. (1997). Advanced anaerobic wastewater treatment in the near future. *Water Science and Technology, 35(10),* 5-12.

Lettinga, G., Rebac, S., and Zeeman, G. (2001). Challenge of psychrophilic anaerobic wastewater treatment. *TRENDS in Biotechnology, 19(9),* 363-370.

Lettinga, G. A. F. M., Van Velsen, A. F. M., Hobma, S. D., De Zeeuw, W., and Klapwijk, A. (1980). Use of the upflow sludge blanket (USB) reactor concept for biological wastewater treatment, especially for anaerobic treatment. *Biotechnology and bioengineering, 22(4),* 699-734.

Li C, Fang HHP. (2007). Inhibition of heavy metals on fermentative hydrogen production by granular sludge. *Chemosphere, 67*:668–73.

Lienert, J., and Larsen, T. A. (2006). Considering user attitude in early development of environmentally friendly technology: A case study of NoMix toilets. *Environmental Science and Technolgy, 40*, 4838-4844.

Lind, B. B., Ban, Z., and Bydén, S. (2000). Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. *Bioresource Technology, 73(2),* 169-174.

Lim, S. J. (2009). Comparisons Between the UASB and the EGSB Reactor. Iowa State University, 17.

Malina, Jr., and Frederick, G. Pohland. (1992). *Design of Anaerobic Processes for the Treatment of Industrial and Municipal Wastes*. Florida : CRC Press-Water Quality Management Library.

Mansouri, N., Rikhtegar, N., Panahi, H. A., Atabi, F., and Shahraki, B. K. (2013). Porosity, characterization and structural properties of natural zeolite-clinoptilolite-as a sorbent. *Environment Protection Engineering, 39(1).*

Maurer, M., Pronk, W., and Larsen, T. A. (2006). Treatment processes for source-separated urine. *Water research, 40(17),* 3151-3166.

McCarty, P.L. (1964). Anaerobic waste treatment fundamentals, Part III. Toxic materials and their control. *Public Works, 95*, 91–94.

McCarty, P. L. (2001). The development of anaerobic treatment and its future. *Water Science and Technology, 44(8),* 149-156.

McCarty P. L., and McKinney R. E. (1961). Salt toxicity in anaerobic treatment. *Journal of Water Pollution Control Federation, 33*, 399–415

Mende´z, R., Lema, J.M., and Soto, M., (1995). Treatment of seafood-processing wastewaters in mesophilic and thermophilic anaerobic filters. *Water Environment Research. 67 (1),* 33–45.

Metcalf & Eddy, 2003. *Wastewater Engineering: Treatment and Reuse*. Boston: McGraw-Hill.

National Intelligence Council(US) (Ed.). 2013. Global trends 2030: alternative worlds. Central Intelligence Agency.

Nunez, L.A. and Martinez, B. (1999) Anaerobic Treatment of Slaughterhouse Wastewater in an Expended Granular Sludge Bed (EGSB) Reactor. *Water Science and Technology., 40(8),* 99-106..

O'Neal, J. A., and Boyer, T. H. (2013). Phosphate recovery using hybrid anion exchange: Applications to source-separated urine and combined wastewater streams. *Water research, 47(14),* 5003-5017.

O'Neal, J. A., and Boyer, T. H. (2015). Phosphorus recovery from urine and anaerobic digester filtrate: comparison of adsorption–precipitation with direct precipitation. *Environmental Science: Water Research & Technology, 1(4),* 481-492.

Ogata, Y., Ishigaki, T., Nakagawa, M. and Yamada, M. (2016). Effect of Increasing Salinity on Biogas Production in Waste Landfills with Leachate Recirculation: a Lab-scale Model Study. *Biotechnology Reports, 10,* 111-116.

Omil, F., Mende´z, R., and Lema, J. M. (1995). Characterization of biomass from a pilot plant digester treating saline wastewater. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental and Clean Technology*, *63*(4), 384-392.

Otterpohl, R., Braun, U., and Oldenburg M. (2003). Innovative technologies for decentralization water wastewater and biowaste management in urban and peri-urban areas. *Water Science and Technology 48*(11), 23-31.

Ozaydin, S., Kocer, G., and Hepbasli, A. (2006). Natural zeolites in energy applications. *Energy Sources, Part A, 28*(15), 1425-1431.

Ozgun, H., Karagul, N., Dereli, R. K., Ersahin, M. E., Coskuner, T., Ciftci, D. I., and Altinbas, M., (2012) Confectionery Industry: A Case Study on Treatability-based Effluent Characterization and Treatment System Performance. *Water Science and Technology, 66,* 15- 2.

Polat, E., Karaca, M., Demir, H., and Onus, A. N. (2004). Use of natural zeolite (clinoptilolite) in agriculture. *Journal of fruit and ornamental plant research, 12*(1), 183-189.

Pradhan, S. K., Holopainen, J. K., and Heinonen-Tanski, H. (2009). Stored human urine supplemented with wood ash as fertilizer in tomato (Solanum lycopersicum) cultivation and its impacts on fruit yield and quality. *Journal of agricultural and food chemistry, 57*(16), 7612-7617.

Razaq, M., Zhang, P., & Shen, H. L. (2017). Influence of nitrogen and phosphorous on the growth and root morphology of Acer mono. *PloS one, 12*(2).

Rebac, S., van Lier, J. B., Lens, P., Stams, A. J. M., Dekkers, F., Swinkels, K. T. M., and Lettinga, G. (1999). Psychrophilic Anaerobic Treatment of Low Strength Wastewaters. *Water Science and Technology, 39*(5), 203-210.

Rehakova, M., Čuvanová, S., Dzivak, M., Rimár, J., and Gaval'Ova, Z. (2004). Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type. *Current Opinion in Solid State and Materials Science, 8*(6), 397-404.

Ritter (2016),MILLIGASCOUNTER Manual, V3.4 Rev. 2016-Jun-02.

Rose, C., Parker, A., Jefferson, B., and Cartmell, E. (2015). The characterization of feces and urine: a review of the literature to inform advanced treatment technology. *Critical reviews in environmental science and technology, 45*(17), 1827-1879.

Rota Madencilik (2018). Clinoptilolite product information sheet.

Sadeghbeigi, R. (2012). Fluid catalytic cracking handbook: An expert guide to the practical operation, design, and optimization of FCC units. Elsevier.

Sangeetha, C., and Baskar, P. (2016). Zeolite and its potential uses in agriculture: A critical review. *Agricultural Reviews, 37*(2).

Saleh, M. M., and Mahmood, U. F. (2004). Anaerobic digestion technology for industrial wastewater treatment. *Proceedings of the Eighth International Water Technology Conference, IWTC,* Alexandria, Egypt.

Savenije H. H.G., and Hoekstra A. Y. (2009). *Water Resources Management Volume 1*, EOLSS Publications.

Sawyer, C. N., McCarty, P. L., and Parkin, G. F. (1978). *Chemistry for environmental engineers*. New York: Mc Graw-Hill Book Company.

Schellinkhout, A., and Collazos, C. J. (1992). Full-scale application of the UASB technology for sewage treatment. *Water Science and Technology, 25*(7), 159-166.

Schmidt, J.E., and Ahring, B.K., (1993). Effects of magnesium on thermophilic acetate-degrading granules in upflow anaerobic sludge blanket (UASB) reactors. *Enzyme and microbial technology. 15*(4), 304–310.

Scully C, Collins G, and O'Flaherty V. (2006). Anaerobic biological treatment of phenol at 9.5 and 15 _C in an expanded granular sludge bed (EGSB)-based bioreactor. *Water Research, 40*(20):3737-3744.

Seghezzo, L., Zeeman, G., van Lier, J. B., Hamelers, H. V. M., and Lettinga, G. (1998). A review: the anaerobic treatment of sewage in UASB and EGSB reactors. *Bioresource technology, 65*(3), 175-190.

Simha, P., and Ganesapillai, M. (2017). Ecological Sanitation and nutrient recovery from human urine: How far have we come? A review. *Sustainable Environment Research, 27*(3), 107-116.

Speece, R. E. (1983). Anaerobic biotechnology for industrial wastewater treatment. *Environmental Science &Ttechnology, 17*(9), 416A-427A.

Speece, R. E. (1996). *Anaerobic biotechnology for industrial wastewater treatment*. Archae Press, Nashvillee, TN, USA.

Standard Methods for the Examination of Water and Wastewater (2005). American Public Health Association, American Water Works Association, Water Environment Fedration; 21. Baski; Port City Press, Baltimore, Maryland.

Tchobanoglous, G., Burton, F. L., and Stensel, H. D. (1991). *Wastewater engineering: Treatment and Reuse*. New York, NY : McGraw-Hill, - McGraw-Hill series in civil and environmental engineering.

Tettenborn, F., Behrendth, J. and Otterpohl, R. (2007). Resource recovery and removal of pharmaceutical residues Treatment of separate collected urine. Final report for task 7 of the demonstration Project "Sanitation Concepts for Separate Treatment of Urine, Faeces and Greywater (SCST)", Institute of Wastewater Management and Water Protection, Hamburg University of Technology.

Tsitsishvili, G. V., Andronikashvili, T. G., Kirov, G. N. and Filizova, L. D. (1992). *Natural zeolites*, New York : Ellis Horwood Ltd.

Tunay, O., Kabdasli, I., and Tatli, M. B. (2009). Nitrogen removal and recovery from human urine by struvite precipitation. *International Journal of Environment and Waste Management, 3*(3-4), 382-392.

Udert, K. M., Larsen, T. A., Biebow, M., and Gujer, W. 2003. Urea hydrolysis and precipitation dynamics in a urine-collecting system. *Water research, 37*(11), 2571-2582.

Udert, K.M., Larsen, T.A. and Gujer, W. (2006). Fate of major compounds in source-separated urine. *Water Science and Technology*, *54* (11-12), 413-420.

United Nations. (2007). World population prospects: the 2006 revision. New York, NY: United Nations Population Division.

U.S. Geological Survey, Mineral Commodity Summaries, January 2011. (https://minerals.usgs.gov/minerals/pubs/commodity/zeolites/mcs-2011-zeoli.pdf), access date 18/04/2019.

Van Haandel, A. C., and Lettinga, G. (1994). *Anaerobic sewage treatment: a practical guide for regions with a hot climate*. John Wiley & Sons.

van Langerak, E. P. A., Gonzales-Gil, G., van Aelst, A., van Lier, J. B., Hamelers, H. V. M., and Lettinga, G., (1998). Effects of high calcium concentrations on the development of methanogenic sludge in upflow anaerobic sludge bed (UASB) reactors. *Water Research. 32* (4), 1255–1263.

van Lier, J. B., Mahmoud, N., and Zeeman, G. (2008). Anaerobic wastewater treatment. biological wastewater treatment, principles, modelling and design. in M. Henze, , M. C. van Loosdrecht, , G. A. Ekama, , D. Brdjanovic (Eds), *Biological Wastewater Treatment*. (pp 415-456)London: IWA publishing. .

Vinnerås, B., Nordin, A., Niwagaba, C., and Nyberg, K. (2008). Inactivation of bacteria and viruses in human urine depending on temperature and dilution rate. *Water Research, 42*(15), 4067-4074.

Weber, W.J. (1972). *Physicochemical Processes for Water Quality Control*, New York : Wiley Interscience,.

Werner, C., Fall, P. A., Schlick, J., and Mang, H. P. (2003). Reasons for and principles of ecological sanitation. *IWA 2nd international symposium on ecological sanitation*, Lubeck, Germany.

Wilsenach, J. A., Schuurbiers, C. A. H., and Van Loosdrecht, M. C. M. (2007). Phosphate and potassium recovery from source separated urine through struvite precipitation. *Water research, 41*(2), 458-466.

Yamaguchi T., Harada H., Hisano T., Yamazaki S., and Tseng I.C. (1999). Process behavior of UASB reactor treating a wastewater containing high strength sulfate. *Water Research, 33*(14), 3182-3190.

Yang, B., Wang, M., Wang, J., Song, X., Wang, Y., Xu, H., and Bai, **J.** (2018). Mechanism of high contaminant removal performance in the expanded granular sludge blanket (EGSB) reactor involved with granular activated carbon for low-strength wastewater treatment. *Chemical Engineering Journal, 334*, 1176-1185.

Yoochatchaval, W., Ohashi, A., Harada,H., Yamaguchi, T., and Syutsubo. K., (2008). Characteristics of Granular Sludge in an EGSB Reactor for Treating Low Strength Wastewater. *International Journal of Environmental Research, 2*(4).

Yu, H. Q., Tay, J. H., and Fang, H. H. P. (2001). The roles of calcium in sludge granulation during UASB reactor start-up. *Water Research 35(*4), 1052–1060.

Yurtoglu, A. (2007). Effects of mineral clinical properties of Turkish clinoptilolites on ammonium removal capacity by ion exchange method. (master's thesis). Istanbul Technical University, Graduate school of science and engineering technology, Turkey (in Turkish with an extended summary in English).

Zayed G, and Winter J. (2000). Inhibition of methane production from whey by heavy metals protective effect of sulfide. *Applied microbiology and biotechnology, 53*(6), 726-731.

Zeeman, G., Wiegant, W. M., Koster-Treffers, M. E., and Lettinga, G. (1985). The influence of the total ammonia concentration on the thermophilic digestion of cow manure. Agric. *Wastes 14*, 19–35.

URL 1: https://www.alexandriava.gov/tes/info/default.aspx?id=97881, date retrieved 05/03/2019.

URL 2: https://www.mountprospect.org/departments/public-works/flood-relief-leeve-37/understanding-mount-prospect-sewer-systems/separate-sanitary-and-storm-sewer-system, date retrieved 05/03/2019.

CURRICULUM VITAE

Name Surname **: Mustafa Taher**

Place and Date of Birth **: Iraq – Baghdad 25-04-1990**

E-Mail **: mustafan90@gmail.com**

EDUCATION **:**

- **B.Sc.** **:** 2012, Salahaddin University, Engineering Faculty, Civil Engineering Department

PROFESSIONAL EXPERIENCE AND REWARDS:

- 2018 – 2019 Research assistant in Lipid Production with Yarrowia Lipolytica fed by waste / wastewater streams project, Istanbul Technical University, Istanbul, Turkey
- 2017 Research assistant in National Research Center on Membrane Technologies (MEM-TEK), Istanbul, Turkey
- 2012 – 2013 Site Engineer at CYC Construction Company, Erbil, Iraq
- 2013 – 2015 Wireline Engineer at Schlumberger, Erbil, Iraq

PUBLICATIONS, PRESENTATIONS:

- Taher, M. N., Basar, A., Abdelrahman, A. M., & Beler-Baykal, B. (2018, July). Yellow Water to Aid Food Security—Perceptions/Acceptance of Consumers toward Urine Based Fertilizer. In Multidisciplinary Digital Publishing Institute Proceedings (Vol. 2, No. 11, p. 606).
- Taher, M.N., J. Awayes, S. Cavkas, B. Beler-Baykal. (2018, October). Public Attitude for Acceptance of Grey Water Reuse in Istanbul and the Impact of Informing Potential Consumers. 4th International Conference on Recycling and Reuse. Istanbul, Turkey. 24-26 October 2018.

- Taher, M.N., M. Altinbas, B. Beler-Baykal. (2018, October). Preliminary Results for Start-up and Adaptation of an EGSB Reactor for Valorization and Treatment of Fresh Urine. 4th International Conference on Recycling and Reuse. Istanbul, Turkey. 24-26 October 2018.
- Taher, M.N., M. Altinbas, B. Beler-Baykal. (2018, November). A suggestion on nutrient removal/recovery from source separated human urine using clinoptilolite combined with anaerobic processing. WaterEnergyNEXUS Conference. Saleerno, Italy. 14-17 November 2018.
- Taher, M. N, Sadrzadeh F., Altinbas, M., Beler-Baykal, B. (2019, June). Recovering nutrients from two waste streams to be used further as fertilizer. 10th IWA Ineternational Symposium on Waste Management Problems in Agro-Industries. Rhodes Island, Greece. 19-21 June 2019.