COMBINED BIOLOGICAL REMOVAL OF PESTICIDES AND NITRATES IN DRINKING WATERS

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of
Dokuz Eylül University
In Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in Environmental Engineering, Environmental Technologies

by
Şükrü ASLAN

September 2002
İZMİR

Ph.D. THESIS EXAMINATION RESULT FORM

We certify that we have read the thesis, entitled **"COMBINED BIOLOGICAL REMOVAL OF PESTICIDES AND NITRATES IN DRINKING WATERS "** completed by **Şükrü ASLAN** under supervision of **Prof. Dr. Ayşen TÜRKMAN** and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Ayşen TÜRKMAN
(Supervisor)

Prof. Dr. Füsun ŞENGÜL
(Thesis Committee Member)

Prof. Dr. Nilgün HARMANCIOĞLU
(Thesis Committee Member)

Prof. Dr. Necdet ALPASLAN
(Jury Member)

Assoc.Prof.Dr. Cumali KINACI
(Jury Member)

Approved by the
Graduate School of Natural and Applied Sciences

Prof.Dr. Cahit HELVACI
(Director)

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my advisor, Prof. Dr. Ayşen TÜRKMAN, for providing excellent guidance and constant encouragement throughout the preparation of this work. Her contribution to the achievements of this work was significant.

I would like to extend special thanks to my dissertation committee members, Prof. Dr. Füsun ŞENGÜL and Prof. Dr. Nilgün HARMANCIOĞLU, for their academic support and encouragement through my Ph.D. program.

I would like to thank TARİŞ Research-Development Center and Prof. Dr. Tamerkan ÖZGEN, Dean of Faculty of Science; Chairperson Prof. Dr. Levent ARTOK and Research Scientist Oya ALTUNGOZ from Department of Chemistry at Izmir Institute of Technology for the use of Gas Chromatograph for some part of pesticides analysis.

I would like to thank also Prof Dr. Mehmet SAGLAM, Prof. Dr. Mithat YUKSEL at Ege University Department of Chemical Engineering, Dr. Hasan ERTAS at Ege University Department of Chemistry, Dr. Thomas GREMM at Engler-Bunte Institute at University of Karlsruhe, and Dr.-Ing. Wolf-Rüdiger MULLER at University of Stuttgart Institute for Sanitary Engineering, Water Quality and Solid Waste Management, for their academic support.

I would like to thank for financial supporting to Cumhuriyet University-AIF (Research Foundation of CU) and INCO-DC, Contract No: ERBIC 18 CT 970167.

Finally, I would like to thank my parents for their encouragements, and my wife, Züleyha ASLAN, for her patience and understanding.

Şükrü ASLAN

ABSTRACT

In this thesis, biodenitrification in drinking water has been studied to remove pesticides and nitrates, which create problems especially in rural areas with heavy agricultural activities.

Evaluation of pesticides use in Turkey has led to a preliminary selection of three pesticides, which are trifluralin, fenitrothion, and endosulfan (α+β) as relevant substances for this study. This selection was based on the quantity of use in the vicinity of İzmir region and persistency of the pesticides.

In this thesis, various natural organic solid subtrates (NOSS) were evaluated in order to determine suitable carbon source for biological reactor. Thus, poplar, hornbeam and pine shaving waste materials and wheat straw were selected as a carbon source for biological denitrification. After determining the dissolved organic carbon (DOC) contents of these materials by batch studies, biological denitrification experiments were carried out in a batch unit with the NOSS for about three months. The overall amount of nitrate removed during the batch study amounted to about 30 mg, 40 mg, 60 mg and 185 mg in 250 mL for poplar, hornbeam, pine shaving and wheat straw, respectively. Since the highest elimination of nitrate was observed with the wheat straw, it was selected as a carbon source and support medium for biodenitrification continuous reactor while medium solution was spiked with the selected pesticides. During the continuous experimental study; between 95.4-99.8, 84.4-99.4, and 83.7-97.4 % the removal efficiencies were obtained for trifluralin, fenitrothion and endosulfan (α+β), respectively.

Adsorption experiments of the pesticides were conducted with poplar, pine shaving and wheat straw. In order to compare the pesticides removal efficiency of the NOSS, experiments were performed with the activated carbon under the same

conditions. The sequence of the adsorption affinity for the pesticides were similar for activated carbon and other adsorbents (Trifluralin > Endosulfan > Fenitrothion).

Biological nitrate and pesticides elimination studies were also performed by using liquid organic substances. In this study, acetic acid and ethanol were applied and compared as to the biological elimination of the nitrate and carbon. Considering the results of the batch experiments; ethanol was selected as a carbon source and optimum ethanol to nitrate-nitrogen (C/N) ratio as 1.5 and pH of the feeding solution as 7.5 for continuous experiment.

The biological denitrification study was carried on with the addition of pesticides after determining effects of the hydraulic residence time on the system performance. In this experiment, using plastic coil materials to support particles in continuous reactor, removal efficiency of the pesticides during biodenitrification was determined. Although no significant improvement in nitrate and organic carbon eliminations were observed at θ_h=12 hours, 100% of pesticides elimination was obtained. Higher than 95, 91, and 95 % removal efficiencies were observed for trifluralin, fenitrothion, and endosulfan (α+β), respectively when θ_h was lower than 12 hours. Although the high pesticides removal efficiencies were obtained using packed column biological denitrification reactor, effluent water could not be used for drinking purpose, because of the total pesticides concentrations when the θ_h was lower than 12 hours. Effluent pesticides concentrations increased with decreasing hydraulic residence times. Pesticides were removed between 20-55% by using slow sand filter for various θ_h values.

ÖZET

Bu çalışmada yoğun tarımsal faaliyetlerin uygulandığı bölgelerde karşılaşılan içme suyunda nitrat ve pestisit sorununa çözüm getirmek amacıyla farklı koşullarda biyodenitrifikasyon denemeleri yapılmıştır.

Çalışılacak tarım ilaçlarının seçiminde, İzmir yöresinde kullanımı, çevresel ortamda kalıcılığı, yeraltı ve yüzeysel su kaynaklarını kirletme potansiyelleri değerlendirilmiştir. Bu değerlendirme sonucunda, trifluralin, fenitrothion ve endosulfan (α+β) deneysel çalışmada temel tarım ilaçları olarak seçilmiştir.

Biyolojik nitrat giderimi çalışmasında en uygun karbon kaynağını belirlemek amacıyla, farklı doğal organik maddeler kullanılmıştır. Çalışma kapsamında kavak, çam ve gürgen talaşı ile saman biyolojik nitrat giderimi çalışmasında karbon kaynağı olarak seçilmiştir. Biyolojik denitrifikasyon çalışması kesikli ünitelerde 3 ay süresince çalışılmıştır. Bu çalışma sonucunda sırasıyla 30, 40, 60 ve 185 mg toplam nitrat giderimi kavak, gürgen, çam talaşı ve saman için elde edilmiştir. Bu çalışma sonucunda en uygun karbon kaynağı olarak saman sürekli çalışma için seçilmiştir. Sürekli çalışmada saman karbon kaynağı ve mikrobiyal büyüme için tutunma yüzeyi olarak kullanılmış, ham suya nitrat ve seçilen tarım ilaçları trifluralin, fenitrothion, endosulfan (α+β) eklenerek, bu pestisitlerin biyolojik giderimi değerlendirilmiştir. Sürekli çalışmada trifluralin, fenitrothion ve endosulfan (α+β) için sırasıyla % 95-99, 84-99 ve 84-97 giderme verimleri elde edilmiştir.

Tarım ilaçlarının kavak, çam ve samana adsorpsiyon çalışması yapılmış ve çalışma benzer koşullarda, aktif karbon ile tekrarlanarak kıyaslama yapılmıştır. Adsorbsiyon çalışması sonucunda pestisitlerin adsorbsiyon sıralaması Trifluralin > Endosulfan > Fenitrothion olarak belirlenmiştir.

Biyolojik nitrat ve tarım ilacı arıtım çalışmasına, sıvı karbon kaynağı kullanılarak devam edilmiştir. Bu çalışmada öncelikli olarak en uygun sıvı karbon kaynağını

belirlemek amacıyla, kesikli deney çalışmalarında asetik asit ve etanol kullanılmıştır. Çalışmalar sonucunda, etanol uygun karbon kaynağı olarak belirlenmiştir. Kesikli deney çalışmaları ile en uygun işletme koşulları belirlenmiş ve C/N oranı 1.5 ve optimum pH değeri 7.5 olarak seçilmiştir.

Plastik dolgu malzemesinin tutunma yüzeyi olarak kullanıldığı sürekli sistemde, farklı hidrolik alıkonma zamanlarında, nitrat ve tarım ilacı giderme verimleri incelenmiştir. Bu çalışma neticesinde 12 saat hidrolik alıkonma zamanı için çıkış suyunda pestisit tesbit edilememiştir. Alıkonma süresinin 12 saatten daha düşük olması durumunda % 90'ın üzerinde pestisit giderimi elde edilmesine rağmen çıkış suyu standart değerlerini sağlayamamaktadır. Hidrolik alıkonma süresi düşürülünce çıkış suyu pestisit konsantrasyonunun artış gösterdiği belirlenmiştir. Yavaş kum filtresi kullanılarak farklı yüzeysel hidrolik yüklemelerde % 20-55 oranında pestisit giderimi elde edilmiştir.

CONTENTS

Chapter three

NITRATE and PESTICIDE TREATMENT in DRINKING WATER

Chapter four

SELECTED PESTICIDES

Chapter five

MATERIALS and METHODS

Chapter Six

RESULTS and DISCUSSION

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE
INTRODUCTION

1.1 Introduction

Water is fundamental importance for life on earth. The whole mechanism of metabolism, the synthesis and structure of colloidal cellular constituents, the solution and transport of nutrients inside cells and interactions with environment are closely related to the specific characteristics of water. About 2.66% of the total global water resources (groundwater, lakes and rivers, polar ice and glaciers) are fresh water but only a small fraction (~0.6%) is available as drinking water (Shirimali and Singh, 2001).

As water requirements have increased with time, countries have progressively increased its supply by steadily increasing the extent of utilization of their available resources. Because demands for all types of traditional water use increase, the signs of conflict between the various beneficiaries are becoming increasingly evident in most parts of the world.

As human activities have increased, so have the effluent discharges to the environment, which have contaminated with many currently used sources of surface and groundwater. The degree of contamination may vary from place to place, but the problem is serious in most parts of the world. Among the many contaminants are untreated or partially treated sewage, and all types of industrial effluents and agricultural chemicals.

Groundwater is the source for drinking water for human around the world, especially for rural areas. Groundwater also may not meet the standards because it contains dissolved constituents coming from natural sources and organic liquids, dissolved organic and inorganic constituents, or pathogens that comes from an

anthropogenic source. In such cases the groundwater is contaminated by the acts of humans.

A wide variety of materials have been identified as contaminants found in groundwater. These include synthetic organic chemicals, hydrocarbons, inorganic cations, inorganic anions, and radionuclides. Although most attention has focused on waste materials as a carbon source for groundwater contamination, there are numerous sources that are not associated with solid or liquid wastes.

Continual deep cultivation coupled with the extensive use of fertilizers and pesticides have made as agriculture a major source of groundwater pollution. Pesticides applied to the soil may migrate through the soil to the water table. Pesticides in use today are usually biodegradable to some extent. However, their breakdown products can also be found in groundwater. Farmers and homeowners alike apply fertilizers containing nitrogen, phosphorus and potassium. Phosphorous is not very mobile in soil and thus does not pose a significant threat to groundwater. The rate of potassium application is generally low and, although it is mobile, the literature does not indicate that potassium from fertilizers is a major factor causing groundwater problem. However, nitrogen from fertilizers can be a major cause of groundwater contamination.

The increasing importance of environmental aspects in agriculture involves the production of chemicals that will assure the best crop production. These products must be highly effective but not toxic to humans, easily decomposed and at low environmental impact. In environmental field partial degradation with parallel and subsequent microbial degradation happens and might produce undesirable toxic substances (Mansour, 1993 and Mansour et al., 1993).

Most of the applied load of pesticides is dispersed in the environment, not reaching the target pests. In this way, pesticides enters into the aquatic ecosystems from agricultural runoff or leaching and, as a consequence, have become some of the most frequently occurring organic pollutants in aquatic ecosystem (Rioboo, et al., 2001).

Nitrate and pesticides concentrations in groundwater supplies in many areas are becoming a serious environmental problem worldwide. Because ingestion of high levels of nitrate and pesticides may cause negative effects on human health, efficient and economic removal processes are needed.

1.2 Objectives and Scope

Major objectives of this thesis can be summarized as follows:

1. To investigate selected pesticide adsorption capacities of the natural organic solid substrates.
2. To investigate suitable carbon and solid substances using natural organic solid substrates for using in the biological denitrification reactor.
3. To investigate pesticides and nitrate elimination in the biological denitrification batch unit.
4. To investigate nitrification and pesticides elimination of the wheat straw as a carbon source and solid medium in the denitrification reactor.
5. To investigate sand filter effects on the system performance considering nitrate and pesticides elimination.
6. To investigate suitable liquid carbon sources for biological denitrification using acetic acid and ethanol considering optimum C/N ratios.
7. To determine optimum pH in order to improve nitrate and pesticide elimination in the biological denitrification using ethanol.
8. To investigate temperature affects on the denitrifying microorganisms.
9. To evaluate pesticides and nitrate elimination performance of the continuous reactor at various hydraulic residence time.
10. To evaluate nitrate, nitrite, and pesticides elimination and MLSS removal capacity of the sand filter.

In the first part of the thesis, pesticides adsorption capacities of the natural organic solid substrates like poplar, pine, and wheat straw were evaluated and compared with the activated carbon at the batch experiments under the same conditions.

In the second part of the thesis, batch experiments were performed with various substances like poplar, hornbeam, pine shaving, and wheat straw to select suitable carbon source for biodenitrification reactor. As a result of the batch studies, wheat straw was selected as a carbon source and support particles for biological denitrification reactor for further studies because the highest nitrate removal was observed with the wheat straw.

In the third part of the thesis, firstly, batch experiments were carried out to investigate optimum carbon and nitrate ratio for acetic acid and ethanol and to define the most suitable carbon source in these chemicals for biological denitrification experiment. As a result of the batch experiments ethanol was selected as a carbon source for continuous study. Considering the results of the batch studies, continuous experiments were carried out for optimum carbon/nitrogen ratio and pH. Biological denitrification studies were performed at various hydraulic residence times using pure and tap waters, which were spiked with selected pesticides. The sand filter was placed at the end of the biological denitrification unit.

CHAPTER TWO

WATER POLLUTION by AGRICULTURAL ACTIVITIES

2.1 Introduction

Water pollution by pesticides and nitrate from routine agricultural practices is a common and growing problem in the major agricultural areas of the world (Hallberg, 1987). Since the last decades, concern about the contamination of water sources has risen due to the increasing nitrate and number of pesticides detected. In regions where pesticide contamination is a problem, nitrate concentrations are often high. Based on the results of the survey (EPA, 1990), EPA estimates that about 52.1% of the 94.600 community water system wells in the United States contain nitrate; about 10.4% contain one or more pesticides, and about 7.1 % may contain both. Of the approximately 10.5 million rural domestic wells, EPA estimates that about 57.0% contain nitrate, contain one or more pesticides, and about 3.3% contain both. EPA estimates that less than one percent (0.6%) of rural domestic wells containing pesticides, or approximately 60.900 wells, contain at least one pesticide over a Maximum Contaminant Level (MCL) or Lifetime Health Advisory Level (HAL). Efforts are being made to implement best agricultural practices in order to control the use of synthetic chemicals in agriculture but in the mean time, nitrate and pesticide must be treated when the concentration exceeds the maximum contaminant level in water resources.

2.2 Water Pollution by Nitrate

Nitrate concentrations in surface water and especially in groundwater have increased in many locations in the world. Man-made or man caused sources of nitrogen introduction into the subsurface environment include agricultural fertilizers, septic tank system, and animal waste disposal. Rural areas characterized by heavily

agricultural activities are the most susceptible locations to groundwater nitrate contamination. One of the agricultural activities contributing to the nitrate contamination problem is livestock. The other problem is the overapplication of nitrogen based fertilizers. This is the largest source and the primary concern of nitrate contamination in groundwater.

Many farmers apply nitrogen as fertilizers or manures to their crops. Nitrogen applied through fertilizers or manure is converted to plant-available-nitrate by bacteria living in the soil. The growing plants consume part of these nitrates. Growing bacteria also consume nitrates. When sufficient decomposable organic matter is present, soil bacteria can remove a significant amount of nitrate-nitrogen through a process called immobilization. Nitrate-nitrogen becomes a part of soil organic matter through this process of immobilization. Another group of bacteria use nitrates as a substitute for oxygen when oxygen is limited. These bacteria convert nitrate-nitrogen to gases such as nitrogen, nitrous oxide, and nitrogen dioxide. This conversion of nitrate-nitrogen to gaseous form is known as denitrification. Nitrate-nitrogen not taken up by crops or immobilized by bacteria into soil organic matter or converted to atmospheric gases by denitrification can leach out of the root zone and possibly end up in groundwater. Nitrate is highly water-soluble and therefore tends to migrate from soil into groundwater (Thompson, 2001).

Nitrate is found in most of the natural waters at moderate concentration but is also often enriched to the contaminant levels in the groundwater resources mainly from the excessive use of fertilizers and uncontrolled on land discharged of raw and treated wastewater. This leads to an increasingly important problem, limiting the direct use of the groundwater resources for human consumption in several parts of the world including Saudi Arabia, India, China, Japan, USA and UK. Several parts of Europe also have similar problems (Shrimali and Singh, 2001) including Turkey (Aslan et al., 2001).

A high nitrate is a major contributing factor in the problem of eutrophication of water bodies. In drinking water, among many suspected health risks ranging from hypertrophy of the thyroid to 15 different types of cancers, birth defects and hypertension in adults; methaemoglobinaemia in infants has the most convincing

evidence (Mirvish, 1991; Morales Suarez Varela et al., 1995; Fan and Steinberg, 1996). Infants less than six months of age are considered the most susceptible. Blue-baby syndrome called methemoglobinemia is a condition in which nitrite reacts with haemoglobin to form methaemoglobin, which impairs the oxygen carrying capacity of the blood. Nitrites also have been found to react with amines and amides to form nitrosoamines and nitrosoamides, which are known carcinogens in many organs of rodents. Specifically, nitrosamines induce tumours of the liver, kidney, oesophagus, oral and naval cavities, lung, trachea, urinary bladder, pancreas and thyroid in rodents. Nitrosamides induce tumours of the stomach, intestine, brain, nervous system, bone and skin, acute leukaemia and T and B cell lymphoma. There is no other group of carcinogens that can produce such as a wide variety of tumours. However, it appears that the association of nitrates in water with the formation of the nitroso compound causing human gastric tract cancer has not been expressly verified. The USEPA has not classified the carcinogenity of nitrate and nitrite cause of inadequate evidence based on long-term case study (Dahab and Kalagari, 1996).

Due to the potential health risks, European community and the USA have regulated that maximum levels of nitrate in drinking water should not exceed 50 mg/L as NO^{-}_{3} or 10 mg/L as NO^{-}_{3}-N, respectively, and 45 mg NO^{-}_{3}/L has been recommended in water consumption in Turkish Drinking Water Standards (TDWS, 1997).

A survey carried out during 1976-1993 in Hungary reported over 1700 causes of methaemoglobinaemia in babies including 28 fatal cases. The yearly number of cases dropped from about 300 to 20-30 as a result of supplying babies with imported bottled water and establishing new water works (Csandy and Straub, 1995).

2.3 Water Pollution by Pesticides

The development and use of pesticides have played an important role in the increase of agricultural productivity. The majority of such substances are applied directly to soil or sprayed over crop fields and hence released directly to the environment. For that, pesticides can enter as contaminants into natural waters either directly in applications or indirectly from drainage of agricultural lands. The amount

and kind of pesticides in water of a given area depends largely on the intensity of production and kind of crops. However, the transport of pesticides out of their area of application results in the presence and accumulation of these compounds in many parts of the hydrosphere. For example, atmospheric precipitation is an important route of transport of pesticides, resulting in contamination of environmental waters far away from agricultural areas. Substantial amounts of pesticides have been found in ice and water of polar regions, lakes, seawater, rainwater or potable water (Vidal, et al., 2000).

Pesticides are ubiquitous water and soil pollutants by virtue of their extensive use. In recent years, many studies have shown fresh surface, drinking and groundwater to frequently contain pesticides at high concentrations (Steen et al., 1997). Continuous use of chemical inputs such as pesticides has resulted in damage to the environment, caused human ill health, negatively impacted on agricultural production and reduced agricultural sustainability (Pimentel et. al. 1992; Pimentel and Greiner, 1997). Fauna and flora have been adversely affected (Pimentel and Greiner, 1997). Numerous short- and long-term human health effects have been recorded (Wilson, 1998). The decimation of beneficial agricultural predators of pests has led to the proliferation of several pests and disease (Pimentel and Greiner, 1997). Despite all these impacts and cost, farmers continue to use pesticides in most countries at an increasing rate, while biological methods of pest control have become limited (Wilson and Tisdell, 2001).

According to the Aspelin (1997) the worldwide consumption of pesticides has reached 2.6 million metric tons of this 85% is used in agriculture. Developing countries use about 20 % of the pesticides in the world. The fact that the higher proportion of human pesticide poisonings and deaths occurs in those countries reflects the existing conditions of inadequate occupational and safety standards, insufficient enforcement of standards, poor labelling of pesticides, lack of safe handling and application, poorly implemented controls, illiteracy and insufficient, knowledge of pesticide hazard by users (Pimentel, 1996).

The insecticides used in developing countries often consist of organochlorines, organophosphates and carbamates. Although organophosphate and carbamate insecticides are less persistent than organochlorides, they are potentially more toxic

to farmers and field workers, especially if they are misused (Wilson and Tisdell, 2001).

It is well known that most of the applied pesticides are subject to many transport and conversion processes. Thus, they do not remain at their target site but often enter aquatic environments via soil percolation, air-drift or surface run-off, etc., affecting abundance and diversity of non-target species, producing complex effects on the ecosystems and altering tropic interactions (Rand et al., 1995).

Many pesticides eventually end up in groundwater and their residues or transformation products may remain for years. Rivers and streams are receptors of toxic wastes generated on land. Pesticides impair beneficial uses of these waters and their biological resources. Organochloride pesticides are a group of organic compounds, which have been found in aquatic systems worldwide (Rovedatti et al., 2001).

Since the last decades, concern about the contamination of water sources has risen due to the increasing number of pesticides detected. In recent years, many studies have shown fresh surface, drinking and groundwaters to frequently contain pesticides at high concentrations. Pesticides are primarily moved from agricultural fields to surface waters in surface runoff. The amount lost from fields and transported to surface waters depends on several factors, including soil characteristics, topography, weather, agricultural practices, and chemical and environmental properties of individual pesticides (Columé et al., 2001). Regulations for drinking water are required in order to limit human risks and environmental pollution. Turkish Drinking Water Standards (TDWS, 1997) and WHO (1986) limits pesticides in drinking water as 0.1 μg/L for a single pesticide and 0.5 μg/L for the sum of all pesticides. In some countries common pesticides are limited. For example in USA.

Some of the pesticides like DDT, monocrotophos, parathion, methamidophos are already banned or severely restricted, but are still used illegally because they are no longer under patent protection and hence are cheaper than newly invented pesticides (Wilson and Tisdell, 2001).

The use of pesticides has not only influenced the level of agricultural production and its sustainability but has also affected the health of users, those living near farms and consumers of food products. Deaths from exposure to pesticides are not uncommon (Wilson and Tisdell, 2001).

2.4 Groundwater Pollution by Nitrate and Pesticides in Turkey

Population increase, industrialization and rapid urbanization have caused many environmental problems in Turkey. There are many studies indicating groundwater contamination by nitrogen and pesticides.

Seepage from cesspools causes ammonium, nitrate, nitrite and microorganisms pollution problems in groundwater. There are many cases of this type of pollution, an important example being Eskisehir City. In Eskisehir groundwater, ortophsophate and NH_3 values have been determined to vary between 0.04-0.39 mg/L and 0.0-0.72 mg/L respectively as a result of seepage from cesspools (Özcelik and Sarıiz, 2001).

Kaçaroglu and Günay (1997) studied nitrate pollution in Eskişehir City also. In this study about four hundred groundwater samples were taken from the 51 wells between July and August 1988. According to this study, 34.2% of all samples exceeded the upper limit of TDWS with respect to nitrate.

The settlement in Antalya itself is an important source of pollution. The liquid wastes are directly injected into the travertine plateau through drill-holes. There is no sewage system in the city. Water quality analyses show that groundwater has been and is being contaminated by sewage discharge, industrial works, and other activities that create an over-expanding impact to the only available aquifer. The existence of nitrate is a clear evidence of pollution, and this contamination is confirmed by the presence of coliform bacteria, which is accounted above 240/100 mL in some wells. NH_3 concentration was above 0.3 mg/L in all of the samples (Karagüzel and Scholz, 1999).

An abundant source of groundwater can be found in aquifers under the plains where the urban areas are located. An example of groundwater pollution from city sewerage system can be given from Isparta City. The Isparta Plain is an important

groundwater basin with a recharge area of approximately 276 km^3 in the southeast corner of Turkey (Karagüzel and Irlayıcı, 1998). Results of well water analysis indicate that NH^+_4 values range between zero and 0.29 mg/L, NO^-_2 values between zero and 0.05 mg/L and NO^-_3 values between 0.55 and 48 mg/L. High values were obtained in samples within the proximity of city sewerage system.

Another example for the groundwater pollution is Yozgat City. The high nitrate, nitrite and organic matter contents are correlated with sewerage system of the city (Çelik and Arıgün 2001).

In Izmir City, some of the apartment blocks have their own wells, which draw water from shallow aquifer (20-30 m). The analyses indicate coliform bacteria and nitrite pollution in these waters (Türkman, 1986).

In a study conducted in Bornova, it has been determined that well waters near a waste disposal site contained the following pollutants: microorganisms, organic matter, dissolved solids, ammonium and nitrate (Avcı, 1998).

The quality of groundwater was assessed to determine its suitability for domestic and irrigation use for Adana City, which is situated at the southern part of Turkey (Abacı, 1997). Groundwater analysis indicating nitrate concentration above 50 mg/L was correlated with agricultural pollution.

Mutlu et al. (1999) studied about thousand samples taken from Elazığ, Malatya, Tunceli, Bingol cities. According to this study, about 42.5% of the 200 samples, taken in Elazığ city and villages could not be used for drinking water because of the NO^-_2 and NH^+_4 concentrations. Also some of the samples taken from Bingöl, Malatya and Tunceli cities contained NO^-_2 and NH^+_4, which are not at acceptable levels in drinking water.

Aslan et al. (2001) studied nitrate pollution in Urla and Menemen region, where agricultural activities are densely applied. It was observed that nitrate concentration in the groundwater exceeded TDWS in the 30% of the 30 samples.

In some cases wells are closed due to the contamination problem. Two wells have been closed in Develi village in Izmir because of nitrate and coliform bacteria contamination in groundwater.

In Izmir, about 1000 tons of pesticides are applied per a year. The largest contribution is by organophosphorus insecticides (88%) and the remaining is carbamates and chlorinated hydrocarbons. In a study conducted in some wells in the Izmir region, pesticides pollution in groundwater has been detected for aldrin, lindane, heptachlor epoxide, dieldrin and heptachlor (Türkman et al., 2001).

Geyikçi and Büyükgüngör (2002) studied organochlorinated pesticides, benzene hexachloride (BHC) and its isomers, whose uses have been banned since 1985. In groundwater and surface water in the Middle North of the Black Sea region, it has been detected that in some of the samples, the BHC concentration exceeded the permissible level of TDWS.

CHAPTER THREE

NITRATE and PESTICIDE TREATMENT in DRINKING WATER

3.1 Introduction

Standard water treatment practices do not affect nitrate and pesticide concentrations in the water significantly. Nitrates from water can be removed by specialized water treatment technologies, such as ion exchange, biochemical denitrification, and reverse osmosis. Incorporation of these technologies for removal of nitrates into a water treatment system could substantially increase the cost of water treatment. Thus, once an aquifer is contaminated with nitrate, it will cost a large amount of money to use that aquifer as a source of drinking water.

Nitrate and pesticides concentrations in groundwater supplies in many areas are becoming a serious environmental problem worldwide. Because ingestion of high levels of nitrate and pesticides may cause negative effects on human health, efficient and economic removal processes are needed.

3.2. Nitrate Removal Methods

The conventional processes like coagulation, filtration, chlorination, UV, and ozone treatment, applied for water potability is not useful for the elimination of nitrate ion from the water. Therefore, other methods have to be applied. The techniques capable of nitrate elimination are ion exchange, reverse osmosis and electrodialysis. The ion exchange process removes not only nitrate but also sulphates from the water under treatment. This results in the production of brine solution from the resin regeneration process, rich in these two anions that have to be eliminated before its discharge. Reverse osmosis offers an alternative to the above treatment

technique and its advantage lies in ability separate and concentrate the compounds contained in water without modifying their molecular structure. However, the utility of these processes has been limited as they are relatively expensive and merely displace nitrate into concentrated waste brine that may pose a disposal problem. Thus, there is considerable interest in developing alternative treatment techniques to remove nitrate from the contaminated streams in a cost-effective method (Shirimali and Singh, 2001).

Among the various methods for nitrate removal from drinking water supplies, biological processes have been shown to be more efficient and convenient (Green, et. al., 1994; Volokita et al., 1996a; Mohsani-Bandpi et al., 1999). Biological denitrification is the only process that directly targets nitrate and does not shift the concentration of other ions.

The majority of microbial denitrification treatment relies on heterotrophic bacteria, which require an organic carbon source; but drinking water has low carbon content. Therefore an external carbon has to be supplied for microbial growth. Several types of organic compounds have been used as the carbon source in water denitrification processes. Generally, liquid carbon sources are added into the raw water or microorganisms are obtained organic matter from the solid substances, which are used support particles also.

Though methanol assures the highest denitrification rate, it can constitute certain risk if the treated water is used for drinking purpose. Gomez et al. (2000) used methanol, ethanol and sucrose as source of carbon for microorganisms to remove nitrate from groundwater, which contain 50-70 mg NO^{-}_{3}/L. The concentration was adjusted to 100 mg/L by adding $NaNO_3$. To remove nitrate completely various C/N ratios were tested considering the nature of the carbonaceous compounds. The highest C/N ratio was obtained for sucrose (C/N=2.5) and the minimum for ethanol and methanol (C/N=1.08 and C/N=1.1, respectively). Experiments with ethanol and methanol showed lower nitrite concentrations in the effluent. For sucrose dosages that brought in a yield among 45-85% of nitrogen removal, up to 5.5±0.5 mg/l in nitrite concentration was detected.

Methanol was also used as a carbon source for well water treatment at various loading rates using membrane bioreactor. It was concluded that the process was most effective during the stable phase of the apparatus's operation at a loading of 0.4 Kg-NO^{-}_3/m^3. day with hydraulic retention time of 5.3 hour. Removal of nitrates amounted to 88.8 % (Wasik, et al., 2001a).

Dahab and Sirigina (1994) evaluated fixed film biological denitrification and GAC-sand filter system. In this study, ethanol and methanol were used as a carbon source. The results indicated that the change of the carbon source did not appear to cause any noticeable impacts on the nitrate elimination. Significant water quality improvement was observed using the GAC-sand filter unit considering the turbidity, COD, and TSS.

Gomez et al., (2002), studied the effect of dissolved oxygen (DO) on the biological denitrification using three carbon sources; sucrose, ethanol, and methanol. Negative linear correlation between DO and nitrogen removal yields was shown when ethanol was used as carbon source, similar to methanol and sucrose assays. Nitrogen removal was almost constant for DO concentration below 4.5 mg/L.

Green et al. (1994a), used ethanol as the carbon source for denitrifying bacteria in the fluidized bed reactors to remove high concentrations of nitrates at very high nitrate loading rates with corresponding short retention times. Higher than 97% of nitrate removal yield was observed at retention times of three to five minutes while nitrite concentrations were less than 1 mg/L. At a retention time of 1.5 minutes, nitrate concentrations varied between 1 to 46,6 mg/L and nitrite concentrations varied between zero to 3.8 mg/L. It was explained that the main reason for the deterioration in the effluent quality at the shorter retention times (<3 minutes) was an insufficient frequency of biomass removal. The increase in biofilm thickness caused mass transfer limitation and also a drastic increase in bed expansion, resulting in bioparticles washout from the reactor.

Green et al., (1994b) used ethanol also in upflow sludge blanket reactor to remove nitrate from groundwater and mixture water including groundwater and surface water contain hardness up to 450 mg/L as $CaCO_3$. When water containing higher hardness

was used (380-450 mg/L as $CaCO_3$) at the retention time of 8 min, nitrate concentrations in the treated water were lower than 10 mg/L, nitrite and ethanol concentrations were close to zero, depending on the C/N ratio. It was concluded that this type of reactor was found to be strongly affected by the hardness of the water as a result of changes in the mineral fraction of the granules. The formation of well settling biomass granules in the denitrifying UASB reactor was found to be strongly influenced by its mineral contents. Tarre et al. (1994) explained that biomass granules having an ash fraction of 25% or more exhibited low SVI values, while those having a mineral content of about 10 to 15% exhibited higher SVI values accompanied by poor reactor performance.

Mohsani-Bandpi et al. (1999) investigated the ability to remove nitrate from groundwater using acetic acid as a carbon source in the RBC. The nitrate removal rate was found to be dependent on the influent acetic acid loading rate. The main disadvantage of acetic acid as compared with other carbon sources was its high consumption ratio and high cost. Balszczyk et al. (1981) pointed out that using acetic acid could have a significant effect on the production of nitrite in the reactor.

Teixeira and Oliveira (2001) investigated the effect of disk submergence on denitrification in a closed RBC using $C_6H_5NO_3O_7x2H_2O$ as carbon source. The results indicated that the RBC with a completely submerged biofilm was more efficient than were partially immersed disks but had longer delay in start-up.

Soares and Abeliovich (1998) studied in up-flow biological denitrification reactor with wheat straw that served as the sole carbon source and support particles. The highest nitrate elimination was observed in fresh reactors during the first week of operation and the efficiency of the process declined thereafter. Colour and soluble organic carbon released from the wheat straw were removed by using powdered activated carbon. At the end of the study, 40% of the initial weight was lost and 11 g of wheat straw were consumed per g of N eliminated.

Volokita et al., (1996a,b) studied in denitrification column packed with shredded newspaper and unprocessed cotton, separately. Complete removal of nitrate was readily achieved without accumulation of nitrite for both of the column. It was

concluded that the cellulose-dependent denitrification was affected by changes in the temperature. In the packed columns, nitrate removal rate at 14 ^{0}C was approximately one-third and half of the rates observed at 32 ^{0}C for shredded newspaper and unprocessed cotton, respectively.

Yatong (1996) used volatile fatty acid (VFA) as a carbon source in the suspended sludge system. It was explained that mixed VFA C-source had higher denitrification rate than single VFA. It was suggested to apply immobilized denitrification bacteria system or to use attached sludge denitrification system in order to reduce carbon consumption in denitrification system, reduce cost of performance,

Use of sulphur as the reactor packing material was reported in autotrophic denitrification process in biological contact beds (Lee et al., 2001; Koenig and Liu, 2001; Sorokin et al., 2001; Soares, 2002). For the influent concentration of 25 NO^-_3-N mg/l, removal of nitrate up to 98% was achieved by using sulphur or limestone filter columns in presence of large amounts of *Thiobacillus denitrificans* (Shrimali and Singh, 2001). Denitrification at extremely high pH up to 10.5 by the *Thioalkalivibrio denitrificans* strain ALJD was studied by Sorokin et al. (2001). In aerobic thiosulfate-limited chemostats Thioalkalivibrio strain ALJD was able to grow between pH values of 7.5 and 10.5 with an optimum at pH 9.0.

Liu and Koenig (2002) used limestone for pH control and elemental sulphur as the electron donor in autotrophic denitrification, *Thiobacillus denitrificans*. They reported that the use of limestone supplies effective buffering capacity if the initial alkalinity was insufficient for complete denitrification.

Combination of biological denitrification and microfiltration membrane has also widely studied for denitrification process. Barreiros et al. (1998), evaluated the performance of a membrane bioreactor with cell recycle to be used for drinking water denitrification when operated with a high nitrate load and low hydraulic retention time using acetate (CH_3COOK). High nitrate and nitrite removal was observed for all the operational conditions applied. However, at the same nitrate loading rate, nitrite accumulation increases for operation with a lower hydraulic retention time. This was explained by the fact that for lower hydraulic retention time,

nitrite produced was washout faster and consequently nitrite accumulation in the bioreactor was lower than for higher hydraulic retention time. Wasik et al., (2001b) observed that increasing nitrate loading rate resulted in increase in the concentration of nitrates and nitrites in the culture effluent. A nitrate removal efficiency of approximately 90 % or a flux of 4 g NO^-_3-N/m^2/d of membrane area was achieved with an influent concentration of 20 mg NO^-_3-N /L (Mansell and Schroeder, 1999).

Nuhoğlu et al (2002) explained that a membrane bioreactor system was able to produce a drinking water with NO^-_3-N concentration of less than 4 ppm from water with NO^-_3-N contamination level of 367 ppm. It was found that the membrane limiting permeates flux increased with increasing MLSS concentration.

Biological denitrification was investigated using natural gas methane as a carbon source. Methane would be an inexpensive and readily available alternative reducing agent since it is produced at some landfill sites and during sludge digestion at many wastewater treatment plants (Rajapakse and Scutt, 1999). Methanotrophic bacteria can use methane as sole carbon and energy sources under aerobic conditions. Energy is set free by the oxidation of methane to carbon dioxide. The first step, the oxidation of methane to methanol, is catalysed by dehydrogenases (Eisentraeger et al., 2001). Methanogenic bacteria use ammonia, nitrate and in some cases nitrite as nitrogen sources. Most of them are able to fix nitrogen. The uptake of gaseous nitrogen monoxide has been proved by Kraemer et al (1990).

Rajapakse and Scutt (1999) used three types of plastic beds in biological denitrification using methane as a carbon source also. Among these beds, IP-spaces produced the highest nitrate removal yield (up to 93% at 0.6 m/h).

In-situ denitrification study was performed using methane as a carbon source. Eisentraeger et al. (2001) reported that no methane oxidation occurred in the absence of oxygen and a denitrification of groundwater occurs if aerobic methanotrophic and anaerobic denitrifying bacteria can interact in heterogeneous system.

Yu and Smith (2000) developed a two-stage bioreactor to link dechlorination of haloganated methane compounds to the anaerobic process of methanogenesis and

denitrification. In the denitrifying bioreactor, the residual carbon tetrachloride was completely removed and the dichloromethane removal efficiency was more than 95%. After acclimation, the denitrifying bioreactor removed more than 95% of the dichloromethane from the influent.

Spence et al. (2001) evaluated phenol degradation and denitrification in a contaminated aquifer. Prior to nitrate addition no p-cresol degradation was observed. Degradation proceeded rapidly in the nitrate bearing with the 40 mg/L of nitrate initially present. The nitrate reducing bacteria could rapidly degrade 200 mg/L of p-cresol with the simultaneous degradation of trace phenol.

Boley et al. (2000) studied biological denitrification using biodegradable polymers as solid substrates and biofilm carrier. They concluded that the denitrification process based on the use of solid substrates could not yet compete in its performance with the classical treatment units for biological nitrate removal with liquid substrates like ethanol, methanol, and acetic acid.

Lin and Wu (1996) studied removal of ammonia, nitrite and nitrate from aqueous solution using combined process, ozonation and ion exchange. Ozonation was found to be able to completely convert nitrite to nitrate. However its capability of ammonia removal was much limited. The anionic and cationic ion exchange resins were able to efficiently remove nitrate and residual ammonia. It was observed that the combined process was capable of efficiently maintaining the nitrogenous compounds in the aqueous solution at very low concentration levels.

Fonseca et al. (2000) developed a novel ion-exchange membrane bioreactor to treat drinking water. The treated water obtained was free of inorganic nutrients and ethanol the carbon source was selected for the biological process and the surface denitrification rate achieved was 7 g N/ m^2.d.

The nitrate in water reduced iron, aluminium and stainless steel and in the process it was converted into nitrite, ammonia and then into nitrogen. Nitrate in the water was reduced using a Pd/Cu-GFC catalyst (Matatov-Meytal et al., 2001). The maximal initial removal activity was found for a catalyst with Pd/(Pd+Cu) ratio of

0.81. The selectivity to nitrogen declined at high conversions of nitrate and high pH. It was concluded that the Pd-GFC catalyst was active for nitrite reduction, while to ensure the reduction of nitrates in the presence of a second metal, namely copper, was necessary.

3.3. Pesticides Treatment Methods

A considerable amount of study has been published on pesticides removal, but most of them concern higher pesticides concentrations than those usually found in drinking water, and it is not always possible to assess the effectiveness of such processes in reducing pesticides concentrations to less than 0.1 μg/L. Foster et al., (1991) explained that both types of surface-water treatment, chemical coagulation and slow sand filtration were effective in removing only low solubility pesticides such as the organochlorine compounds, except where pesticides are complexed with humic materials. Chlorination was reported as being effective in breaking down the phenylamide herbicides and organophosphorus insecticides. Common wastewater treatment methods, like activated carbon sorption, mean expensive investment and operating costs (Bras et al., 1999).

The drinking water containing micropollutants like odor and pesticides are generally treated with AC adsorption as the last process, but suffers from the problems of the regeneration or disposal of used carbon and the cost of construction and maintenance (Yang et al., 1993). The granular activated carbon adsorption has been identified as an effective, dependable, and economically viable method for the removal of a micropollutants for water (Pirbazari et al., 1992).

Advanced oxidation processes are one of the most attractive emerging treatment technologies that can discharge multiple purposes in drinking water treatment applications. The most favourable methods of advanced oxidation are ozone, ozone/hydrogen peroxide, ultraviolet (UV) radiation, or UV/hydrogen peroxide. (Badriyha, 1996).

The oxidations of organochloride compounds were carried out using ozone (O_3) and O_3 in the presence of hydrogen peroxide (H_2O_2). It was concluded that the

O_3/H_2O_2 system appears to be more efficient than the O_3/high-pH system to remove chlorobenzeneoic compounds. Tetradifon and dichlorobenzophenone were totally oxidized by O_3/H_2O_2 and O_3/high-pH (Ormad et al., 1997).

Activated carbon fibers (ACF) were used to remove pesticides in waters. Atrazine solutions were prepared with pretreated groundwater. Gullon and Font (2002) explained that minicolumn tests showed that the performance of highly activated carbon fibers was around 7 times better than the commercial GAC.

Although the mechanism is poorly understood, it is well established that microbes can concentrate chlorinated hydrocarbon insecticides from water. Accumulation of lindane by cells of the yeast Saccharomyces cerevisiae and by 13 bacterial species obtained by some researchers. Removal of lindane from water by magnetite plus adsorbed microbial cells which Saccharomyces cerevisiae, streptomyces venezuelae, phodopseudomonas sphaeroides, and chlorella vulgaris, was worked by Mac Rae (1985).

Nanofiltration is a process in which pesticides; hardness and nitrates can be simultaneously removed or partly removed. The removal of nitrate, hardness, and four pesticides atrazine, simazine, diuron, and isoproturon with various membranes was studied by Van der Bruggen et al. (2002). The results showed that pesticide rejections were satisfactory; hardness was also very efficiently removed, whereas only small fraction of nitrate was removed for most membranes, except for one where a 76% removal of nitrate was obtained. It was concluded that removal of pesticides was efficient when the right membrane was selected.

Bras et al. (1999) used pine bark to remove organochlorine pesticides from water solution. The yield of removal from synthetic water solutions ranging from 1 to 10 μg/L was 97% on average for some selected pesticides. Lindane could not be efficiently adsorbed by this method. Its smallest log K_{ow} explained its poorer capacity of adsorption. They resulted that the increase in the adsorbent amount did not significantly improve the removal.

Bending et al. (2002) obtained greatest biological degradation of pesticides using white rot fungi, *Coriolus versicolor, Hypholoma fasciculare and Streum hirsutum.* It was concluded that white rot fungi have the capacity to degrade contrasting groups of pesticides and selected white rot fungi could prove valuable in on-farm pesticides bioremediation systems. Zouari et al. (2002) investigated 4-chlorophenol degradation by suspended and immobilized *Phanerochaete chrysosporium.* The best results were achieved when experiment was carried out in a rotating biological conductor.

Brereton et al. (1999) studied sorption of pesticides to novel materials: snail pedal mucus and blackfly silk produced by macro invertebrates that exist in high densities in rivers and streams. Experimental results indicated that mucus and silk produced by invertebrates has a high affinity for selected pesticides, capable of sorbing such compounds to a far greater than soils or sediments alone and much closer in magnitude to the sorption found for organic colloids in fresh water.

Van der Hoek et al. (1999) studied pesticides and organic matter removal in water treatment plants that are using surface water as raw water source. In order to reduce the organic carbon content in the finished water, and to remove organic micropollutants, pesticides, plants are equipped with a biological activated carbon filtration. All the assayed pesticides were completely removed in the carbon filters (>99%).

Biological denitrification and trace pesticides removal in a combined biofilm–electrode reactor (BER)/adsorption was investigated by Feleke and Sakakibara (2001). Experimental results showed that complete and stable denitrification was achieved in BER without accumulation of nitrite and nitrous oxide. Pesticide, isoprothiolane was removed, with an efficiency of 97 %, by adsorption onto either granular activated carbon or silicone resin.

An entrapment of mixed microbial cells process was used to remove pesticides, ethylene dibromide (EDB), trichlopropane (TCP), which were used as secondary substrate, and in the groundwater (Yang et al., 1993). The system was able to remove ore than 90% of EDB (influent concentration of 300 μg/L) at more than 30 minutes of hydraulic retention time. TCP (influent concentration of 2.81 μg/L) could not be

detected in the effluent at the same hydraulic retention time. The system was able to remove more than 99% of nitrate influent concentration of NO_3-N ranging from 50 to 850 mg/L at a hydraulic retention time of more than 2 hours.

Toller and Flaim (1988) designed a filtering unit using readily available organic media (peat, moss and manure) to filter out a variety of commonly used pesticides from wastewater. On the average, more than 99 % and 60 % removal efficiencies were obtained.

CHAPTER FOUR
SELECTED PESTICIDES

4.1 Introduction

Turkey has very fertile agricultural land and exports many agricultural products. Although it is considered as a country at industrialization stage, agricultural activities are still very important. Of the total groundwater available in Turkey about 40% is used for agricultural purpose. 4 million ha area is irrigated with surface waters and the remaining 570.000 ha (about 13.6%) is irrigated with groundwater (DSI, 2000).

In order to increase the agricultural products, pesticides consumption increases continuously. Total pesticides consumption in 1996 (as active material) is approximately 14.000 tons. Recently, pesticides consumption in Turkey is 736 gr/ha. This value is lower than many countries such as Japan, USA, Germany, Switzerland and Poland (Delen, et al., 1998). For example it is about $1/29^{th}$ of Holland, $1/13^{th}$ of Italy, $1/10^{th}$ of Greece and $1/6^{th}$ of USA (Gokce, 2001).

The pesticides use is not equally distributed among all the agricultural areas in Turkey. A dense pesticide application can be seen in some areas, while in some other areas almost no application is observed. Uncontrolled use of agricultural chemicals in intensive agricultural areas of Turkey causes serious soil, surface, and groundwater pollution problems. If the pesticides are classified according to their volatilization, mobility, and persistence characteristics and groundwater pollution potential, it indicates that nearly 65% of the pesticides commonly used in Turkey have a high pollution potential (Türkman, 1998). Because low quality pesticides, whose production stage does not include proper treatment methods, are cheaper than others, they are used more commonly and their concentration increases in the environment.

4.2 Selected Pesticides

4.2.1 Endosulfan

Endosulfan (Figure 4.1) (chemical name, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9,-methano-2,4,3, benzo(e)dioxathiepin-3-oxide) is a chlorinated insecticide and acaricide of the cyclodiene subgroup which acts as a poison to wide variety of insects and mites on contact (Figure 4.1). The EPA has classified endosulfan as toxicity class I- highly toxic. Although it may also be used as a wood preservative, it is used primarily on a wide variety of food crops, including tea, coffee, fruits, and vegetables, as well as on rice, cereals, maize, sorghum, or other grains. Technical preparation of endosulfan contains approximately 70% endosulfan α and 30% endosulfan β (Goebel et al., 1982; Kamrin, 1997). Endosulfan is highly to moderately toxic to bird species and is very highly toxic to some fish species (Quest et al., 1989).

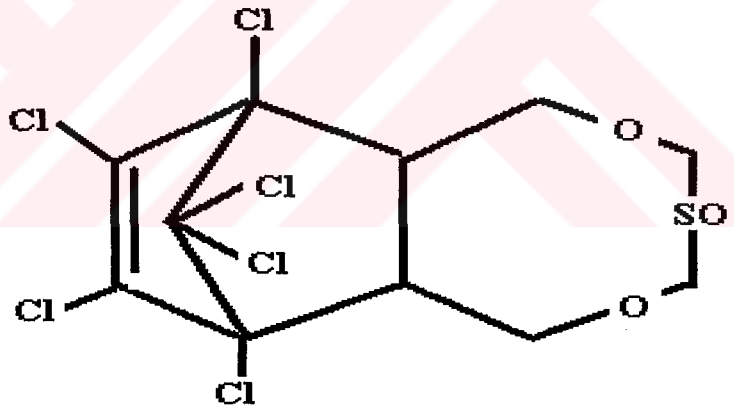


Figure 4.1 Chemical structure of endosulfan

In river water at room temperature and exposed to light, both isomers disappeared in 4 week. A breakdown product first appeared within the first week. The breakdown in water is faster (5 weeks) under neutral conditions than at more acidic conditions or alkaline conditions (5 months) (Lu, 1995).

Ground-based sprayers apply endosulfan, usually two or three times annually during the growing season. This practice creates a potential for endosulfan to

contaminate non-target aquatic areas by drift deposition, runoff, and leaching. This potential is increased by the persistence of endosulfan in the environment. Endosulfan contamination has been detected in soils, water, air and food products because of its abundant usage and potential for environmental transport.

Endosulfan is moderately persistent in the soil environment; with a reported average field half-life of 50 days (Wauchope et al., 1992), but it is known to persist in soils for up to 2 years or more (Wan et al., 1995). The two isomers have different degradation times in soil. The half-life for the alpha-isomer is 35 days and 150 days for the beta-isomer under neutral conditions. These two isomers will persist longer under more acidic conditions. Endosulfan mineralization in soil by fungi and bacteria was studied by Kidd and James (1991) and in liquid culture by Awasthi et al, (2000).

Endosulfan does not easily dissolve in water and has a very low solubility. It has a moderate capacity to adhere or adsorb to soils. Transport of these pesticides is most likely to occur if endosulfan is adsorbed to soil particles in surface runoff (Ouest et al, 1989 and Wauchope et al., 1992). It is not likely to be very mobile or to pose a threat to groundwater (Lu, 1995). It has, however, been detected in some wells in İzmir Region (INCO-DC Project, 1997), in Bulgarian Danube Plain well water (Balinova and Mondesky, 1999) and in California well water (Howard, 1991).

4.2.2 Fenitrothion

Fenitrothion (Figure 4.2) (0,0- Dimethyl 0-4-nitro-m-tolylphosphorothioate) is a contact insecticide and selective acaricide of low ovicidal properties (Spencer, 1981). It belongs to the organophosphate family of insecticides. The EPA has classified fenitrothion as toxicity class 2- moderatly toxic. It is considered a cholinesterase inhibitor (Kidd and James, 1991). Fenitrothion is effective against a wide range of pests, i.e. penetrating, chewing and sucking insect pests (coffee leaf miners, locusts, rice stem borers, wheat bugs, flour beetles, grain beetles, grain weevils) on cereals, cotton, orchard fruits, rice, vegetables, and forests. It may also be used as a fly, mosquito, and cockroach residual contact spray for farms and public health programs (Thomson, 1982). Fenitrothion, whose use has been banned in some countries, is also effective against household insects and the entire nuisance insects listed by the

World Health Organization. Its effectiveness as a vector control agent for malaria is confirmed by the World Health Organization (Worthing, 1987). Fenitrothion is non-systemic and non-persistent (Briggs, 1992). Although acute toxicity was not reported, small amount of fenitrothion and its metabolities (less than 0.3 μg/g body weight) were found to accumulate in tiger shrimps after 24 h exposure to concentration of 0.5 μg/L in water (Karamfilow et al., 1996). Fenitrothion is also used in the post-harvest treatment of stored grain.

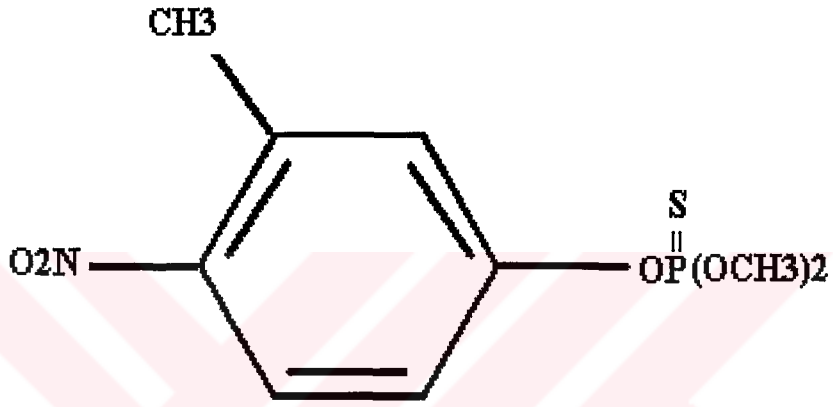


Figure 4.2 Chemical structure of fenitrothion

The persistence of fenitrothion was affected mainly by water quality (river water or sea water) and sunlight (exposed or unexposed), but also partially by temperature; it was not affected by the presence of suspended solid or vaporization.

Several studies were performed to elucidate the mechanism of the apparent rapid disappearance of fenitrothion from the water phase after the field spraying of fenitrothion formulation. The processes most likely to explain the phenomena include sorption by the sediments, photolysis, microbial degradation, hydrolysis, and volatilization. Marshall and Roberts (1977) discounted volatilization as a major pathway for the disappearance on the basis of the calculated half-life of 93 days obtained in a 1m water column, designed as a simple model for small, well-mixed lentic systems with compartments representing the major pools, i.e., the water, the hydrosol, and the suspended solids, which include both biotic and abiotic material.

Maguire (1992) studied volatilization of fenitrothion from the surface and subsurface water. According to the study, fenitrothion sprayed on the surface of water and injected into the subsurface and over all the experiments, an average of 65 ± 18% and 51% of the fenitrothion lost from surface and subsurface water, respectively.

Laboratory experiments demonstrated that volatilization of fenitrothion from true solutions (5 mg/litre) in distilled water followed first-order kinetics and that the half-life of disappearance at 20 °C was estimated to be 64 ± 5 days (Maguire and Hale, 1980).

The photostability of fenitrothion in water is dependent on both pH and energy of UVR or sunlight (Miyamoto, 1977). Fenitrothion rapidly decomposed in distilled water under sunlight and in pH 7 and pH 9 solutions at ambient temperatures, but was considerably more stable at pH 3. The half-life of fenitrothion was 10, 50, 20, and 6 h, respectively, in distilled water and in solutions at pH 3, pH 7, and pH 9. Fenitrothion decomposed nearly 8 times faster at pH 9 than at pH 3. The half-lives of fenitrothion within the pH range of 5-9 (normally found in natural water) were about 200-630 days at 15 °C, 17-61 days at 30 °C, and 4-8 days at 45 °C. Fenitrothion was less stable at pH 9 with a half-life of 100-101 days, compared with those of 180-186 days and 191-200 days at pH 7 and pH 5, respectively.

In aquatic environments, fenitrothion residues disappeared rapidly by dilution and by physicochemical and microbial degradation to low levels, 0.03 µg/liter (Sundaram, 1973) within a period of 40 days. Levels of less than 1.0 µg/liter were found 2-8 days after spraying at 140-280 g a.i./ha (Morin et al., 1986)

Fenitrothion is used as insecticide at golf courses and was detected at high frequency in the drainage at concentrations from nanograms per litre to micrograms per litre levels (Suzuki et al., 1998)

When fenitrothion was applied to thin-layer plates with a 2 mm thickness of 7 different types of soil and exposed to sunlight, it took 50-150 days for the 90% disappearance of fenitrothion from the soils (Miyamoto, 1977).

In the 1980 spray programme in Canada, fenitrothion was detected occasionally in air, the maximum concentration being 12 ng/m^3, when the compound was sprayed at 140-280 g/ha (Mallet, 1980).

Three types of algae, *Chlorella vulgaris, Nitzschia closterium*, and *Anabaena flos-aquae,* also rapidly absorbed fenitrothion with maximum bioaccumulation ratios of 44, 105, and 53, respectively (Kikuchi et al., 1984). Only A. flos-aquae (blue-green algae) actively degraded fenitrothion. When transferred to a fenitrothion-free medium, these algae released fenitrothion, as well as its metabolites, with half-lives of the compounds of less than 1 day, except in the case of A. flos-aquae when the half-life was 2.6 days. Bioaccumulation ratios for fenitrothion in 2 species of blue-green algae (Anabaena sp. and Aulosira fertilissima) were reported to be 42-347 and 136-784, respectively, when exposed to 1, 5, or 10 mg/litre solution (Lal et al., 1987).

4.2.3 Trifluralin

Trifluralin (Figure 4.3) (a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) is a selective, pre-emergence dinitroaniline herbicide used to control many annual grasses and broadleaf weeds in a large variety of tree fruit, nut, vegetable, and grain crops, including soybeans, sunflowers, cotton, and alfalfa. Pre-emergence herbicides are applied before weed seedlings sprout (Kamrin, 1997). Trifluralin is acting as a cell division inhibitor and represent a diverse selection of molecular structures and environmental contaminants that might become bioaccumulated and/or detoxified by benthic invertebrates (Guerrero et al., 2002).

The EPA has classified trifluralin as toxicity class 3.5 (between slightly – practically non-toxic). Trifluralin is practically non-toxic to birds (Hudson et al., 1984), but it is very highly toxic to fish and other aquatic organisms (Johnson and Finley, 1984). The compound shows a moderate tendency to accumulate in aquatic organisms.

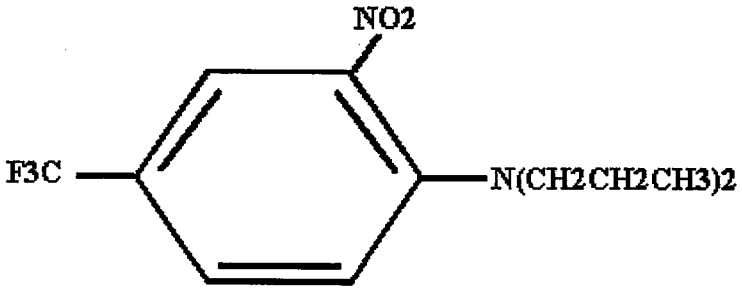


Figure 4.3 Chemical structure of trifluralin

Trifluralin is of moderate to high persistence in the soil environment, depending on conditions. It is subject to degradation by soil microorganisms. Trifluralin remaining on the soil surface after application may be decomposed by UV light or may volatilise. Reported half-lives of it in the soil vary from 45 to 60 days (Wauchope et al., 1992) to 6 to 8 months (Kidd and James, 1991). After 6 months to 1 year, 80 to 90 % of its activity will be gone (U.S., 1995). It is strongly adsorbed on soils and nearly insoluble in water (Wauchope et al., 1992). Because adsorption is highest in soils high in organic matter or clay content and adsorbed herbicide is inactive, higher application rates may be required for effective weed control on such soils (U.S., 1995).

Trifluralin is nearly insoluble in water (Kidd and James, 1991). It will probably be found adsorbed to soil sediments and particulates in the water column.

Wotzka et al (1992) studied on pesticides includes trifluralin that was not frequently detected in the rain because they are incorporated into the soil and generally have shorter soil half-lives. However trifluralin was detected in the rainwater higher than 0.1 μg/L at the four sites in Europe (Trevisan et al., 1993).

CHAPTER FIVE
MATERIALS and METHODS

5.1 Introduction

In this study, pesticides removal experiments during biodenitrification have been performed. Biodenitrification is achieved by NOSS and chemicals. When NOSS is used as carbon source, pesticides are removed from the water by adsorption in addition to cometabolism. Thus, adsorption experiments with different NOSS's have been performed.

Activated carbon and other adsorbent materials are commonly used to remove trace amounts of pollutants from water. These materials have been efficient but are rather expensive. Bearing this in mind, the possibility of using alternative adsorbent materials easily available at a low cost has been studied.

Adsorption experiments of the pesticides were conducted with poplar, pine shaving and wheat straw. In order to compare the pesticides removal efficiency of the NOSS, experiments were performed with the activated carbon under the same conditions.

Processes like activated carbon adsorption, reverse osmosis, electrochemical, ozonation etc. have been employed to remove nitrate and pesticides from drinking water supplies, but these processes are expensive. Removal of these pollutants can be achieved also by using biological processes.

The majority of microbial denitrification treatment relies on heterotrophic bacteria that require an organic carbon. Usually, simple carbon compounds such as ethanol, methanol, acetic acid are used; however cheaper readily available carbon sources are being explored. In order to determine suitable carbon source for

biological reactor, batch experiments were performed with various NOSS. In this study poplar, hornbeam and pine shaving waste materials and wheat straw were selected as a carbon source for biological denitrification. After defining the DOC contents of these materials by batch study, biological denitrification experiments carried on in a batch unit with the NOSS for about two months.

Because the highest elimination of nitrate was observed with the wheat straw, it was selected to use as a carbon source and support particles for biodenitrification continuous reactor while medium solution was spiked with the selected pesticides.

Since drinking water supplies naturally lack organic material, an exogenous carbon source must be added to the water along with other nutrients required by bacteria. In this study, acetic acid and ethanol were performed and compared according to the biological elimination of the nitrate and carbon. As a result of the batch experiments, ethanol was selected for further studies as a carbon source. Batch experiments were operated for various pH to define optimum point for biodenitrification and temperature for determining effects on the nitrate and carbon removal efficiency.

The biological denitrification study was carried on pesticides after determining effects of the hydraulic residence time on the system performance. In this experiment, using plastic coils materials support particles in continuous reactor nitrate elimination was observed and evaluated its removal efficiency performed the biodegradability of the pesticides on denitrification.

During the study, solid phase extraction (SPE) was chosen for sample clean-up/preconcentration and GC with electron capture detector (GC-ECD) has been used, in order to take advantage of the high efficiency of the chromatographic separations and the selectivity of the detection step.

The need to extract large volume of water (up to 2 L) to analyse small amounts of analyte (nanogram-per millilitre levels) in relatively unpolluted water requires using a suitable preconcentration technique. The most widely used sorbents are C_8 and C_{18} chemically bonded to silica, carbon black and polymeric resin (Quintana et al.,

2001). SPE offers advantages such as time saving, solvent reduction, elimination of emulsions, trace enrichment, and a high potential for automation (Balinova, 1996). The most common choices here are SPE (Colume et al., 2001; Feleke and Sakakibara, 2001; Lacorte et al., 1995; Lopez et al., 1998;. Colina et al., 1995; Liska and Bilikova, 1998; Balinova and Mondesky, 1999; Tanabe et al., 1996; Colina et al., 1997; Bras et al., 1999; Quintana et al., 2001; Brereton et al., 1999; Vidal et al., 2000).

Evaluation of pesticides used in Turkey has led to a preliminary selection of pesticides, which are trifluralin, fenitrothion, and endosulfan (α+β or I+II) as relevant substances for this study. This selection was based on the use in Izmir region and persistency of the pesticides.

The characteristics of the selected pesticides are summarized in Table 5.1

Table 5.1 Characteristics of the selected pesticides

Pesticides	Molecular Formula	Molecular Weight (g/mol)	Solubility in Water (mg/L)	Partition coefficient log K_{ow}	Toxicity ♦	Half-Life (d)
Endosulfan	$C_9H_6Cl_6O_3S$	406.95	0.32-0.33 (22°C)	4.74-4.79	1	30-70
Fenitrothion	$C_9H_{12}NO_5PS$	277.2	21 (20°C)	3.43	2	4-20
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	335.3	0.184 (pH 5)	5.27	3.5	57-126

♦1 indicates high toxicity (EPA)

5.2 Adsorption Studies of the Pesticides on Various NOSS and Activated Carbon

5.2.1 Adsorption of the Pesticides on the NOSS

Experiments were conducted with poplar, pine shaving and wheat straw dried at 105±5 ^{0}C until constant weight. After being ground the pine and poplar were sieved in different fractions with 500 μm for poplar and 500 and 2000 μm for pine shaving were selected for the adsorption studies. The straw was cut at average size of 1.32 mm-6.00 mm length, 0.34 mm-4.00 mm thick.

Sorption test performed with vertical fixed bed columns filled with the various NOSS. The column of 11.8 x 84 mm (diameter x height) packed with 500 mg wheat straw and 9.2 x 75 mm, 9.2 x 91 mm and 9.2 x 80 mm packed with 500 mg of the pine shaving size of the 2000 and 500 μm, respectively and 9.5 x 72 mm (diameter x height) packed with poplar shaving. Columns were previously washed with 50 ml of distilled water. Then 200 ml for first study and 500 ml for second study of 10 μg/L standard solution of endosulfan, endosulfan-sulfat, trifluralin and fenitrothion were passed through the columns by 5 ml/min average flow rate.

5.2.2 Adsorption of the Pesticides on the Activated Carbon

500 ml of a spiked pesticide solution was percolated through column of 11.8 x 15 mm packed with 500 mg of the activated carbon with the size of 500 μm at 5 ml/min flow rate.

The experimental conditions and size of the NOSS's are summarized in Table 5.2

Table 5.2 Experimental properties of the NOSS and activated carbon columns

Solid Substrate	Sample Volume (ml)	Adsorbent (mg)	Column Height (mm)	Volume (ml)	Size (μm)
Straw	200	500	84	4.0	1.18-5.80 mm
Pine shaving	500	500	80	5.0	500
Pine shaving	500	500	75	3.0	2000
Poplar shaving	500	500	72	5.0	500
Activated Carbon	500	500	15	2.0	500

5.2.3 Reagents

Pesticides used in this study have the following properties: endosulfan (α+β), purity 99.3%, endosulfan-ether, purity 99.5%, endosulfan-sulphate, purity 99.4%, endosulfan-lacton, purity 99.5%, fenitrothion, purity 98.5%, trifluralin, purity 99.2% from Dr. Ehrenstorfer and internal standard pentachloronitrobenzene from Aldrich,

purity 99%. Acetone and n-hexane (Merck) have been used as solvents. The octadecylsilica (C_{18}) and florisil have been supplied from J.T. Baker.

Stock solutions of each pesticide were prepared in acetone and stored in glass-stoppered bottles at 4 ^{0}C in the dark. Calibration solutions containing selected pesticides were prepared in the various ranges by appropriate dilution of the stock solutions for optimising detector sensitivity and checking the linear responses.

5.2.4 Pesticides Extraction Method for Water

In this method, SPE vacuum manifold from Supelco 12-port model was used. SPE tubes were filled with 1 g C_{18} and florisil was used to remove colours from the extract. C_{18} tubes were assembled the solid phase vacuum manifold for multiple extractions. For conditioning, C_{18} was washed with 30 ml of acetone, 30 ml of pure water containing %1 acetone and then washed with 30 ml pure water. Florisil was conditioned with 20 ml acetone. Using the vacuum source, liquid sample was passed through the C_{18} column at a flow rate of about 5 ml/min. The cartridge (C_{18}) was washed with 10 ml of distilled water. Pesticides were collected on the C_{18} were eluted with 10 ml acetone by using the vacuum. Mixed solvent of the acetone and pesticides were passed through the anhydrous sodium sulphate then evaporated to about 2 ml by a hot air operated at about 40 ^{0}C. The extract was diluted with 8 ml n-hexane and then it was passed through the 1.0 g florisil by means of vacuum control. Finally the extract was evaporated to dryness by the hot air operated at about 40 ^{0}C. The extract was then diluted with 500µl acetone and the internal standard was pentachloronitrobenzene was added for gas chromatographic analysis.

The extraction efficiency of the method for the trifluralin, fenitrothion, endosulfan ($\alpha+\beta$), and endosulfan-sulphate were determined and concentrations of the pesticides were calculated according to these values.

5.2.5 Gas Chromatographic Analyses

Chromatographic separation of the pesticides was performed at a fused silica capillary column (30 m x 0.32 mm i.d.) coated with 5% phenylmethylpolysiloxane film thickness 0.25 µm (Supelco, USA) with a splitless injection volume of 1 µl. The

pesticide analysis was performed with a Unicam 610 Series gas chromatograph equipped with a Ni (63) electron capture detector. Helium of highest quality (5.0) was used as the carrier gas and nitrogen was used as make-up gas at flow rate of 1.5 ml/min, 50 ml/min, respectively. The injector and detector temperatures were 250 and 300 ^{0}C, respectively. The initial oven temperature was kept at 45 ^{0}C for 1 min; then was programmed to 210 ^{0}C at a rate of 15 ^{0}C min/L, then it was raised to 280 ^{0}C at a rate of 10 ^{0}C min/L, held for 3 min and finally at 300 ^{0}C at a rate of 30 min/L held for 1 min. The output from the detector was connected to a recording integrator Unicam 4815. Pesticides concentration is calculated on the basis of peak area measurements.

5.3 Biological Removal of Pesticides and Nitrates from Drinking Water Using Wheat Straw

5.3.1 Experimental Study to Define Dissolved Organic Carbon (DOC) of the Various NOSS

To measure DOC contents of the NOSS, batch experimental studies were performed. In this study, 500 mg NOSS was placed in six various shake flask containing each of them 100 ml distilled water. Solution and 500 mg NOSS was stirred at a speed of 150 rpm for 15, 30, 60, 120, 240, and 360 minutes at the ambient temperature. After mixing, samples were filtered to remove particles and TOC were measured in water.

5.3.2 Biodenitrification Batch Study by Using Various NOSS

500 mg NOSS was placed in 250 ml erlenmeyer flasks containing medium solutions. All flasks were sterilised in an autoclave for half an hour. Microorganisms, which were taken from the biodenitrification reactor in the laboratory, were added to the flasks and cultures were placed on a labquake incubator at 27^{0}C and flasks were shaken manually two times a day. Samples were drawn periodically and assayed for nitrate, nitrite and DOC. After 19 days, when nitrate elimination were not observed any more, 500 mg NOSS were added in order to supply carbon source for microorganisms. Beginning pH was adjusted to 7.5 with NaOH solution. Nitrate and

phosphate were supplemented by addition of an appropriate volume from concentrated stock solution containing 1000 mg/L nitrate and 30 mg/L phosphate.

5.3.2.1 Microorganisms

The microorganisms used in the experiments were developed in a laboratory scale biological denitrification unit. The culture was acclimated to the media for 2 weeks before used for denitrification. Enrichment cultures were prepared in 250 ml erlenmeyer flasks containing medium solution including 100 mg/L NO_3 (as $NaNO_3$) and 3 mg/L phosphate (as $Na_2HPO_4 \times 2H_2O$).

5.3.2.2 Analytical Determinations

Nitrate and nitrite-nitrogen were determined by using analytical kits for nitrate (14773) and nitrite (14776) and Merck photometer SQ 300. Dissolved organic carbon was determined by using a TOC analyser (Dohrmann DC-190).

5.3.3 Biological Removal of Selected Pesticides from Drinking Water Using Wheat Straw

5.3.3.1 Batch study

The bioreactor used for the batch experiments had a total volume of 250 mL and was filled with water including DOC from wheat straw. Wheat straw was soaked in pure water that was filtered prior to use to remove solid particles. Batch experiments were carried out for 45 mg NO_3-N/L and 67 mg NO_3-N/L. The microorganisms used in this study were taken from the biodenitrification batch unit wheat straw where was used as carbon source. The solution pH was adjusted to 7.5 and trifluralin and endosulfan ($\alpha+\beta$) were added into the batch unit. Experiments were carried out for 2 and 3 days for batch unit including 45 mg NO_3-N/L and 67 mg NO_3-N/L, respectively. Microorganisms were added to the flasks and cultures were placed on a labquake incubator at 27^0C and flasks were shaken manually two times a day.

5.3.3.2 Experimental Set-Up of Biological Denitrification Reactor

The experimental set-up consisted of cylindrical glass biodenitrification unit of 13 cm inner diameter and 14.5 cm height. The sand filter column had 8 cm diameter and 30 cm height. The slow sand filter column was filled with filter sand of an effective diameter of 0.5 mm and uniformity coefficient of 1.23. The sieves, which are consist of stainless steel, were placed at the inlet and the exit of the reactor to prevent washout of wheat straw fragments. Experimental set-up is presented in Figure 5.1.

The biodenitrification reactor packed with 160 g wheat straw was inoculated with microorganisms taken from the wheat straw batch unit. Experiment was operated up to the point where nitrate elimination efficiency drop to 60%. 16 g wheat straw was added to the column when the removal efficiency dropped down to 60%. Column was fed with distilled water containing 100 mg/L nitrates and 3 mg/L phosphates. Beginning pH was adjusted to 7.5 with NaOH solution. The solution was spiked with 10 μg/L trifluralin, 7.69 μg/L fenitrothion and 10.5 μg/L endosulfan (α+β). The flow rate was adjusted by using peristaltic pump and the column was operated in upflow mode. The inoculation lasted 3 days with daily replenishment of nitrate and phosphate. Column was allowed to stand for 3 days before the flow was initiated.

Samples were collected daily from the inlet and outlet of the biodenitrification reactor and slow sand filtration column and were routinely assayed for nitrate, nitrite, dissolved organic carbon (DOC), colour, pH and pesticides; trifluralin, fenitrothion and endosulfan (α+β). Experimental study was carried out at room temperature (31±1 ^{0}C in the summer).

5.3.3.3.1 Microorganisms

The microorganisms used in the experiments were taken from the batch unit of the wheat straw.

5.3.3.3. Adsorption Experiment with PAC

To remove colour and excess DOC, powdered activated carbon (PAC) adsorption study was performed. In this study, 15 g wheat straw was soaked in 2 litre pure water overnight at room temperature (31 ^{0}C). Constant volumes of liquids containing 190 mg DOC/L and 270 Pt-Co colour was then supplemented with a series of known weights of PAC in glass erlenmeyer flasks and the slurries were agitated at constant stirring velocity (125 rpm) on a shaker. Prior to use, The PAC was oven-dried at 105 ^{0}C for 2 hour and then cooled in desiccators.

5.3.3.4 Analytical Methods

Samples were taken from the effluent of the biological denitrification reactor and sand filter on daily basis and centrifuged at 6000 rpm for ½ hour. TOC, nitrate and nitrite analyses were carried out on clear supernatant. Nitrite-nitrogen was determined by using analytical kits (14776) and photometer Merck SQ 300 and nitrate-nitrogen was measured according to the brucine methods (APHA, 1985). Colour was measured by using an Apha platinum-cobalt standard 5543-colour filter (Heck Chemical Company). Dissolved organic carbon (DOC) was determined by using a TOC analyser (Dohrmann DC-190).

Silica gel (SiOH) disposable extraction column (J.T. Baker, Bakerbond SPE, 7086-07) and octadecylsilica (C_{18}) have been used for pesticide extraction and florisil from J.T. Baker was used to remove colour from the extract.

5.3.3.5 Pesticides Extraction Method for Water

In this study to measure pesticides concentration in water, Solid-Phase Extraction (the procedure is given in part 5.2.4) was performed.

5.3.3.6 Pesticides Extraction from Wheat Straw

In this study, mixture of 10 g wheat straw was taken from the biodenitrification reactor after finishing experimental study. Wheat straw was dried and mixed to obtain homogenous sample and extracted with acetone. At this step, 100 ml water was added which results in a ratio acetone/water during the extraction of 2+1 (v/v).

10 g wheat straw was mixed in a mechanical mixer in the 100 ml pure water and 20 ml acetone and homogenized for 3 min. 10 g celite was added followed by another homogenisation for 10 sec. The homogenate was filtrated. Filtrate was transferred into a separatory funnel. 10 g sodium chloride was added followed by vigorous shaking for 3 min. After addition of 100 ml dichloromethane the mixture was shaken for 2 min. and allowed to settle for 10 min. The lower aqueous phase was discarded. The upper aqueous phase was passed through the 25 g anhydrous sodium sulphate. The filtrate was collected in a round bottom flask and separatory funnel and filter were rinsed twice with 20 ml ethyl acetate each. After evaporation using rotary evaporator, the entire residue was dissolved by 5 ml hexane.

Silica gel (SiOH) disposable extraction column was used to collect pesticides. Prior to use silica gel column was washed with 10 ml hexane. Then pesticides and solvent mixture was passed through the silica gel column. Finally pesticides were collected with various tubes by using solvents hexane/toluene (v/v: 65/35), toluene/acetone (v/v: 95/5) and toluene/acetone (v/v: 65/35). Finally eluates were evaporated to dryness by nitrogen gas at 40 ^{0}C using rotary evaporator, the extract was then diluted with acetone and the internal standard was pentachloronitrobenzene was added for gas chromatographic analysis.

The efficiency of the method was determined using water sample, which has been contacted with 10 g wheat straw and spiked with the trifluralin, fenitrothion and endosulfan (α+β). Then extraction method given above was applied.

5.3.3.7 Gas Chromatographic Analyses

Chromatographic separation procedure of the pesticides was explained in part 5.2.5. The pesticide analysis was performed with a Varian Series gas chromatograph equipped with a Ni (63) electron capture detector and Varian Autosampler.

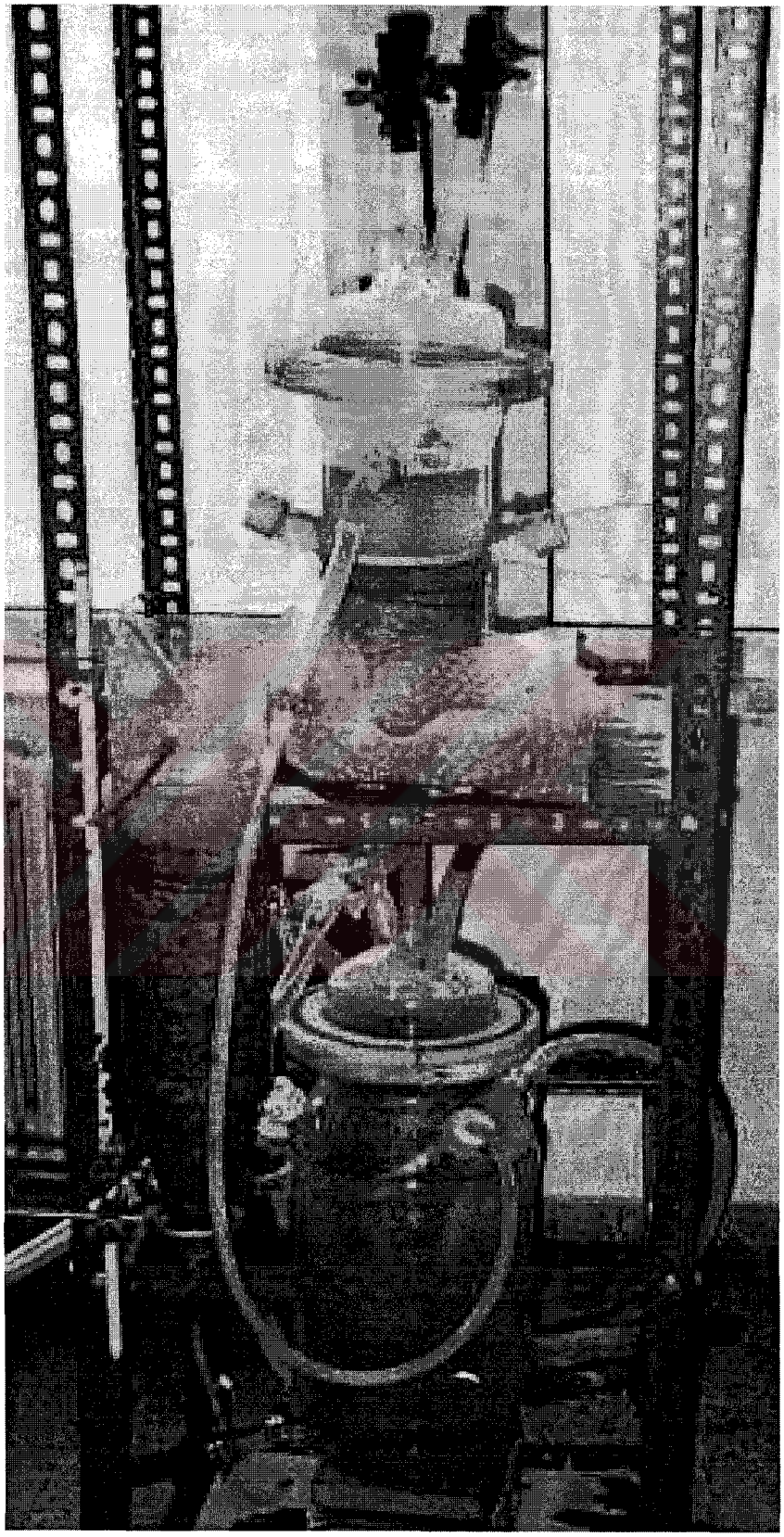


Figure 5.1 The picture of the experimental set-up packed with wheat straw.

5.4 Denitrification of Drinking Water Containing Pesticides by Using Ethanol as Carbon Source

5.4.1 Batch Experimental Studies

Batch experimental studies were performed for three days until about more than 90% of the nitrate elimination was observed, to determine the extend of pesticide mineralization, the ethanol and acetic acid requirements for nitrate removal and the percentage removal of nitrate and TOC. Batch experiments were performed to find suitable carbon source, optimum C/N ratio and pH and to determine temperature effects on the denitrification efficiency. Initial pH was adjusted at 7.5 with NaOH solution.

In the batch experiment, the external carbon source ethanol was added at a ratio of 1.5 of C/N, 22.6 mg and 45 mg /L of nitrate-nitrogen concentration was kept constant in the medium solution including trace elements, which was spiked with 0.394 μg/L trifluralin, 3.2 μg/L fenitrothion and 4.86 μg/L endosulfan (α+β) and starting MLSS concentration was 1.7 mg/L. Batch experiments were carried out two and three days for 22.6 mg NO_3-N/L and 45 mg NO_3-N/L, respectively.

5.4.2 Pesticide Adsorption on the Plastic Coils Materials and PAC

In order to investigate adsorption capacities of pesticides onto the plastic materials, batch experiments were performed and compared with the PAC. In this experiment, 500 mg PAC and plastic materials having about 8 cm^2 surface area placed in various 250 mL shake flask containing 125 ml distilled water spiked with 0.71 μg/L trifluralin, 4.33 μg/L fenitrothion and 5.87 μg/L endosulfan (α+β). Solutions were stirred with the shaker. Samples were taken at the beginning, 5^{th} min, 15^{th} min, 30^{th} min, 1^{st} h, 2^{nd}h, 4^{th}h, 24^{th} hours later, respectively.

5.4.3 Experimental Set-Up of Biological Denitrification Reactor

The experimental set-up consisted of cylindrical stainless steel biological reactor, 15 cm inner diameter and 60 cm height, completely submerged. The sand filter column, which was in 8 cm diameter and 30 cm height, was filled with filter sand of an effective diameter of 0.5 mm and uniformity coefficient of 1.23. The schematic

view of the experimental set-up is given in Figure 5.2. The biological reactor was operated with an up flow mode. The packed column was filled with 10 mm pieces of plastic coils materials given in Figure 5.3, which supported bacterial growth. Denitrification column has a liquid volume 5.3 L and support particle surface area was $1m^2$ resulting in 190 m^2/m^3 surface area.

5.4.3.1 Microorganisms

Denitrification microorganisms were taken from the denitrification reactor used in the laboratory.

5.4.3.2 Synthetic Medium Composition

The liquid medium used, consisted of a mineral base media supplemented with nitrate as sole electron donor, and acetic acid and ethanol as acceptor. Other constituents were KNO_3 (100 mg NO_3/L), KH_2PO_4, 150 mg/L, $NaHCO_3$, 325 mg/L. This basal medium was supplemented with 1% v/v of solution containing $FeSO_4.7H_2O$, titriplex, 0.565 mg/L, and 0.1% v/v of a trace nutrient solution $ZnSO_4.7H_2O$, 0.1 g/L, $MnCl_2.4H_2O$, 0.03 g/L, H_3BO_3, 0.3 g/L, $CoCl_2.6H_2O$, 0.2 g/L, $CuCl_2.2H_2O$, 0.01 g/L, $NiCl_2.6H_2O$, 0.02 g/L, $NaMoO_4.2H_2O$, 0.03 g/L. The final pH of the medium was adjusted at 7.0 and batch unit were placed incubator at 29 ^{0}C. The C/N ratio was varied from the 0.33 to 3.02 while the nitrate-nitrogen concentration was kept constant at 22.58 mg/L for batch study.

The synthetic medium solution for reactor study was including mineral base media; 100 mg NO^-_3/L and CH_3CH_2OH. Nitrate and ethanol were added so that the C/N ratio was 1.5. Medium solution was water spiked with 1.79 μg/L trifluralin, 7.59 μg/L fenitrothion and 10.92 μg/L endosulfan (α+β).

Biological denitrification study was carried on using tap water including 100 mg NO^-_3/L and CH_3CH_2OH added in such a way to adjust the C/N ratio to 1.5 and pesticides concentration varied. The final pH of the medium was adjusted to 7.5 for continuous study. The influent pH was adjusted with NaOH.

5.4.3.3 Analytical Methods

Effluent samples were collected on daily basis and tested for temperature, pH, turbidity, nitrates, nitrite, TOC, suspended solids, volatile suspended solids.

Samples were withdrawn daily from the reactor and sand filter influents and effluents and filtered by 0.45 μm, white 47 mm radius filter. Nitrate, nitrite and TOC analyses were performed with the clear samples. Biomass concentrations in the effluent samples were determined by filtering 100 ml samples from the filter and drying the filter paper in an oven at 103 ^{0}C temperature and then 550 ^{0}C until constant weight.

Nitrate was measured using the UV spectrophotometric screening method according to standard methods (1981). Nitrite and turbidity have been determined with a Merck photometer SQ 300. Merck Spectraquant analytical kit was used for nitrite (14776) analysis. Organic carbon was determined by means of a high-temperature TOC analyser (Dohrmann DC-190). Dissolved oxygen (DO) measurements were carried out by using WTW oxygen meter.

5.4.3.4 Solid Phase Extraction (SPE) Procedure for Pesticides Analysis

Samples were extracted by SPE method explained in part 5.2.4, except for florisil step.

5.4.3.5 Gas Chromatographic Analyses

Chromatographic separation procedure of the pesticides was explained in part 5.2.5. The pesticide analysis was performed with a Shimadzu GC-17A model gas chromatograph equipped with a Ni (63) electron capture detector and AOC-20i Autosampler.

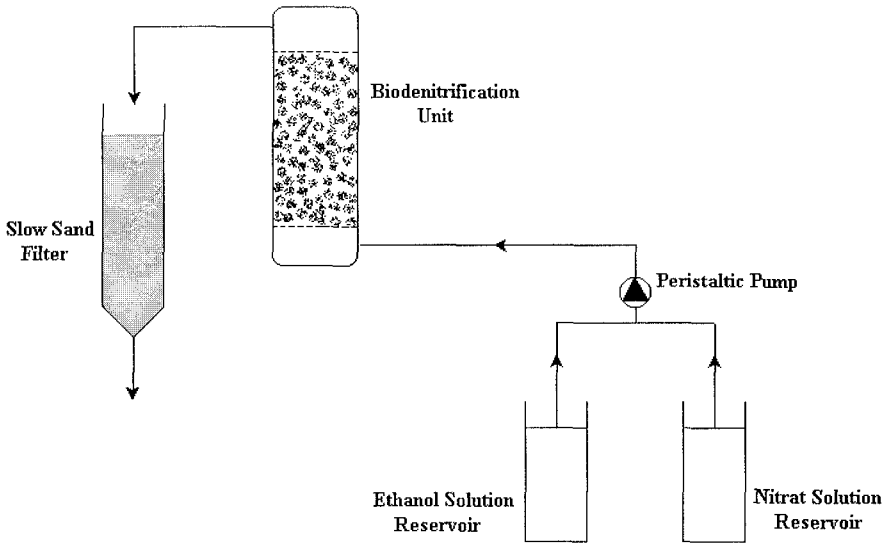


Figure 5.2 A Schematic view of the biological denitrification unit packed with plastic coils

Figure 5.3 Plastic coils materials used as filling material in biodenitrification unit

CHAPTER SIX
RESULTS and DISCUSSION

The study aimed removing of pesticides and nitrates simultaneously in biodenitrification unit. The pesticides are removed by cometobolism and sorption onto microbial flocs during biodenitrification. Experimental studies have been conducted to determine, optimum conditions for the pesticides and nitrate removal. In the following section the experimental data has been evaluated.

6.1 Recovery Efficiencies of the Solid Phase Extraction for the Selected Pesticides

During the experimental study, samples were extracted and preconcentrated by solid phase extraction prior to chromatographic analysis. Recovery was determined to evaluate the performance of the SPE method. Recovery data was used as a correction factor in the quantification of samples.

The solid phase extraction efficiency of the method for the pesticides is presented in Figure 6.1.1 and shows that the recoveries were higher than 90 % for trifluralin, fenitrothion and endosulfan-sulphate and was 70% for endosulfan (α+β).

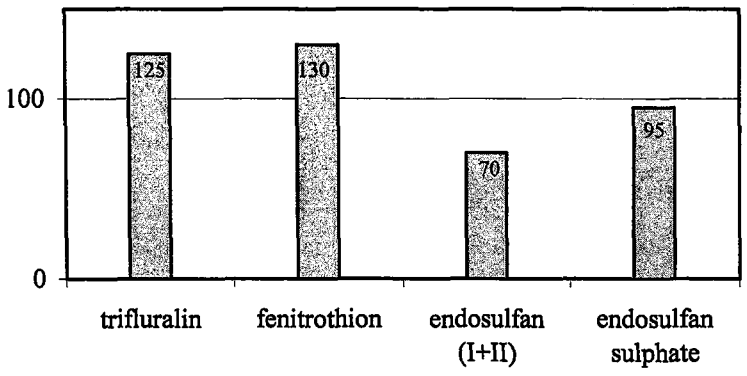


Figure 6.1.1 SPE recovery efficiencies of the selected pesticides

6.2 Adsorption Studies of the Pesticides on Various NOSS and Activated Carbon

When NOSS is used as carbon source in biodenitrification unit, adsorption of pesticides on NOSS takes place. To study the sorption capability of adsorbent, standard solution with individual pesticide concentrations of 10 μg/L were percolated through adsorbent column. This concentration was decided by considering literature indicating that pesticide concentrations in groundwater do not normally exceed 10 μg/L. Experimental results of sorption tests for poplar, pine shaving (the size of 500 and 2000 μm), wheat straw, and activated carbon are depicted in Figures 6.2.1, 6.2.2, 6.2.3, 6.2.4, and 6.2.5, (data at appx 9.1).

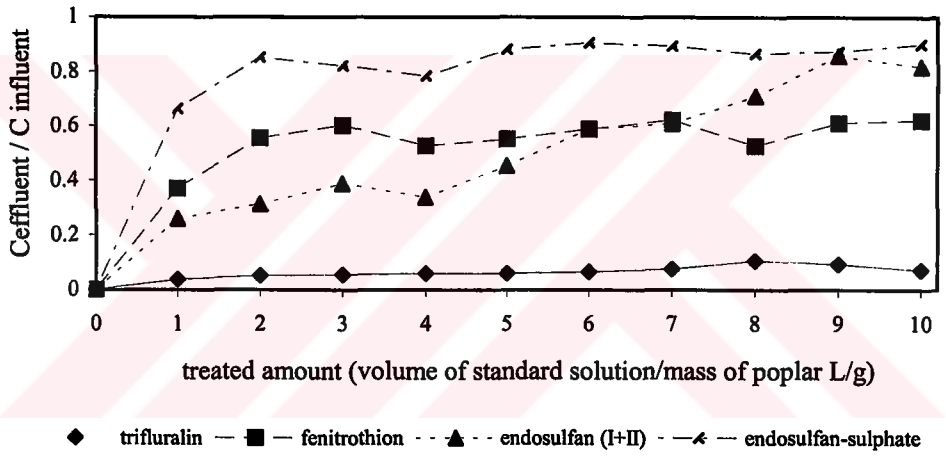


Figure 6.2.1 Adsorption of the selected pesticides on the poplar shaving

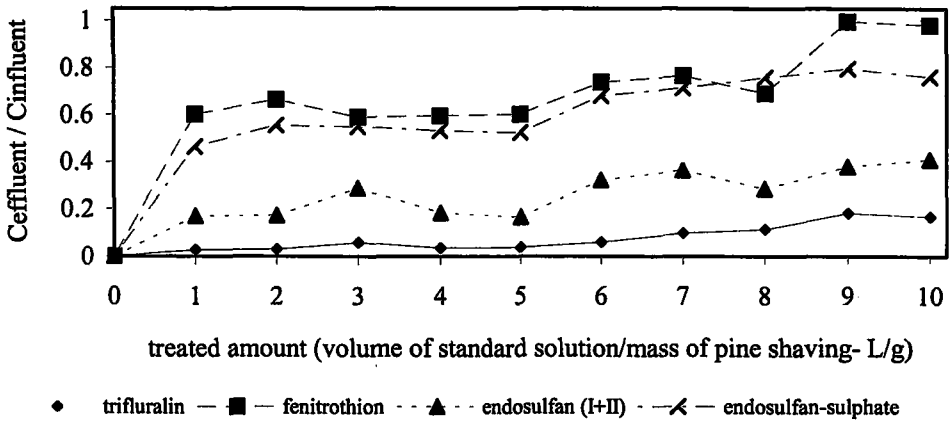


Figure 6.2.2 Adsorption of the selected pesticides on the pine shaving (500μm)

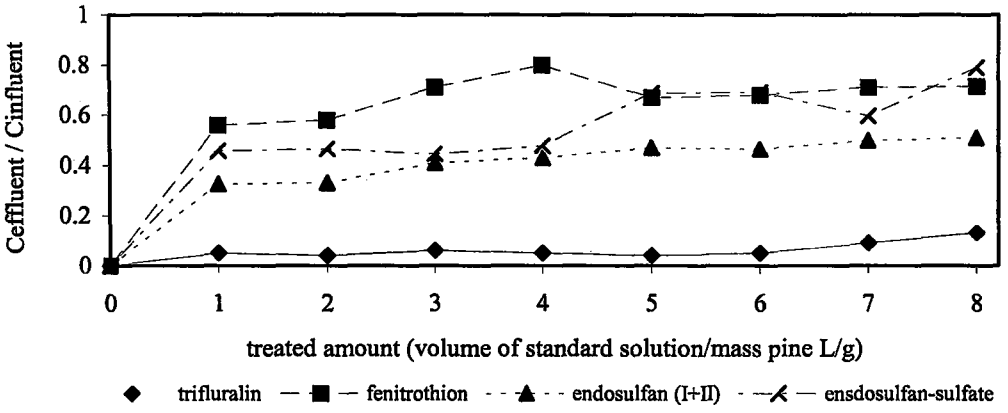


Figure 6.2.3 Adsorption of the selected pesticides on the pine shaving (2mm)

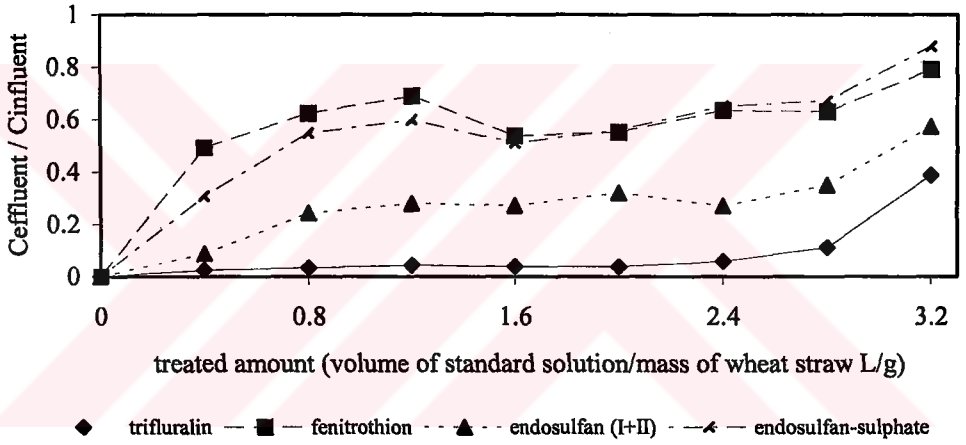


Figure 6.2.4 Adsorption of the selected pesticides on the wheat straw

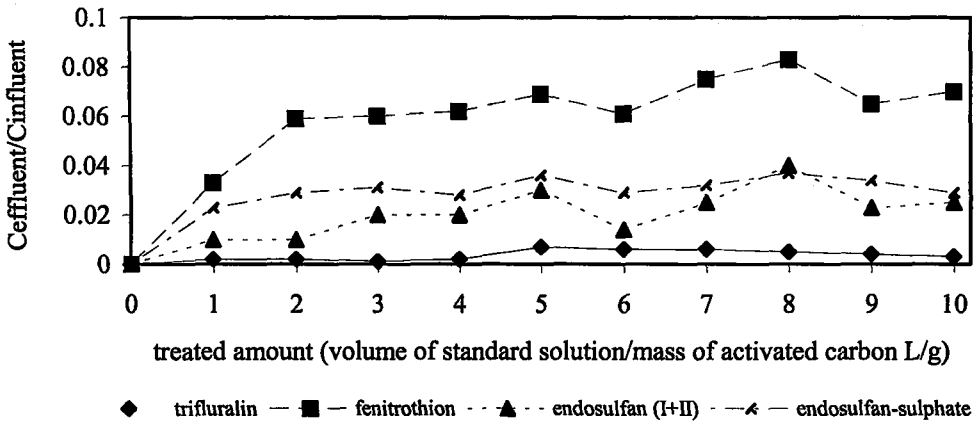


Figure 6.2.5 Adsorption of the selected pesticides on the activated carbon

During the experimental study with wheat straw and 2 mm pine shaving, bed compacting problem occurred therefore lower amount of water sample was passed through the NOSS column as compared to other experiments.

The breakthrough occurs when all the sites of the adsorbents are occupied and mass transfer zone is at the bottom of the column. Adsorption tests have been performed with the assumption that breakthrough curves obtained from labscale columns are similar to that of practical conditions. A standard solution of trifluralin, fenitrothion, endosulfan ($\alpha+\beta$), and endosulfan-sulphate were continuously passed through the column until a treated amount of 10 L of solution/g of adsorbent was reached. Only endosulfan-sulphate for pine shaving and wheat straw, and fenitrothion for pine shaving was nearly achieved to the breakthrough point if the breakthrough point was considered at 1.0.

Bras et al. (1999) studied organochlorine pesticides sorption to the pine bark and explained that the increase in the adsorbent weight did not significantly improve the efficiency of removal but particle size was an important parameter. When compared, particle size effect for pine shaving on the removal efficiency for the similar amount of treated volume (Figure 6.2.2 and 6.2.3), was not important for the selected pesticides except endosulfan ($\alpha+\beta$). Endosulfan ($\alpha+\beta$) was sorbed on 500 μm particles about 60% more as compared to 2000 μm particles. Although the activated carbon was far from the saturation point, wheat straw, pine and poplar shaving were nearly saturated under similar conditions. Fenitrothion, endosulfan ($\alpha+\beta$), and endosulfan-sulphate achieved the nearly breakthrough point. Only in the case of trifluralin the loads used in the experiments were probably far from the saturation of the adsorbents.

The lowest removal efficiency was observed with wheat straw at 3.2 standard solution/mass of wheat straw (L/g) ratio due to the particle size, which was the highest as compared to other NOSS's (Figure 6.2.4).

As expected, activated carbon has higher adsorption capacity than NOSS's except for trifluralin, which indicates approximately the same adsorption value for activated carbon and various NOSS's. Water solubilities of the selected pesticides are 21

mg/L, 0.32-0.33 mg/L and 0.221 mg/L and partition coefficients are (log Kow) 3.43, 4.74 – 4.79, and 5.27, for fenitrothion, endosulfan (α+β), and trifluralin, respectively. As a result of the study, the removal of pesticides on NOSS and activated carbon indicate the following order of decreasing removal efficiency: Trifluralin > Endosulfan > Fenitrothion

6.2.1 Activated Carbon and NOSS Adsorption

Activated carbon is the best known adsorbent for many organic micropollutants in waters, especially pesticides. In order to compare the adsorption capacities of NOSS's with activated carbon mini column experiments were performed under similar conditions. The sequence of the adsorption affinity for the pesticides were similar for activated carbon and other adsorbents (Trifluralin > Endosulfan > Endosulfan sulphate > Fenitrothion). Comparison of the activated carbon and NOSS adsorption capacities are depicted in Figure 6.2.6.

The pesticides adsorption experiments indicate the unreliable behaviour of NOSS's against pesticides. They selectively adsorb some of the pesticides while very small removal is observed for some others.

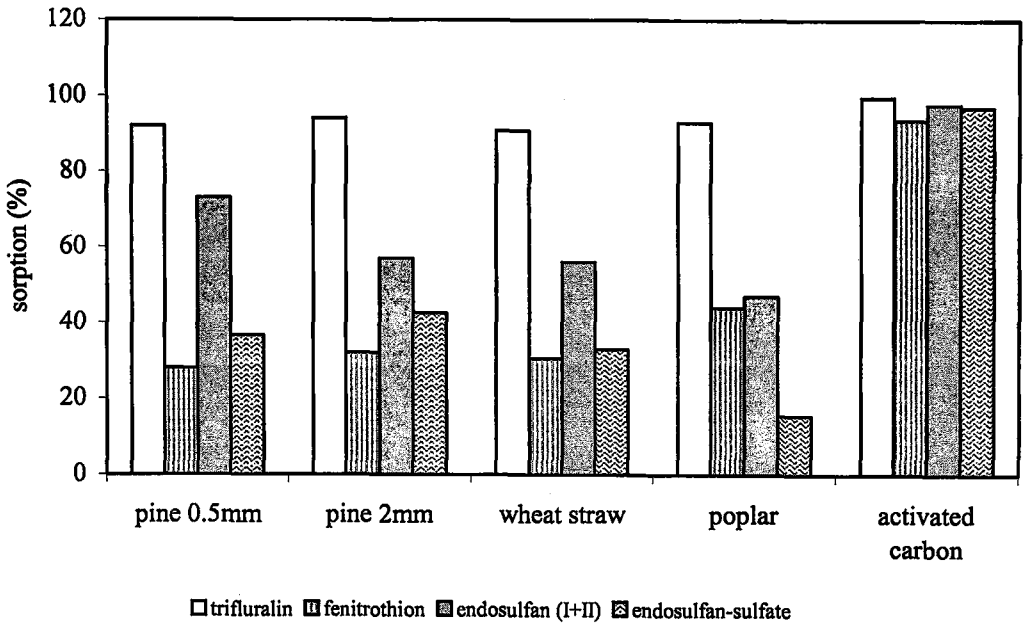


Figure 6.2.6 Pesticides removal efficiencies for various NOSS and activated carbon

6.3. Experimental Study to Define Dissolved Organic Carbon (DOC) of the Various NOSS

Dissolved organic carbon contents of the water samples containing hornbeam, poplar, wheat straw, and pine are given in Figure 6.3.1, 6.3.2, 6.3.3, and 6.3.4, respectively (data appx: 9.2.1). Wheat straw released higher amount of DOC (about 130 mg/L) than the others (about 40 mg/L). After autoclaving DOC content is enhanced about 3, 2, and 1.5 times for pine, hornbeam and poplar shaving, respectively. However high temperature did not increase DOC of wheat straw as much as others because it released organics easily to the water at room temperature.

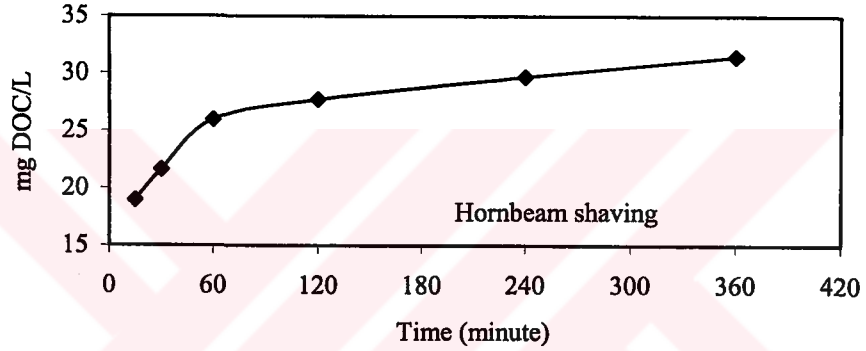


Figure 6.3.1 DOC release of the hornbeam shaving

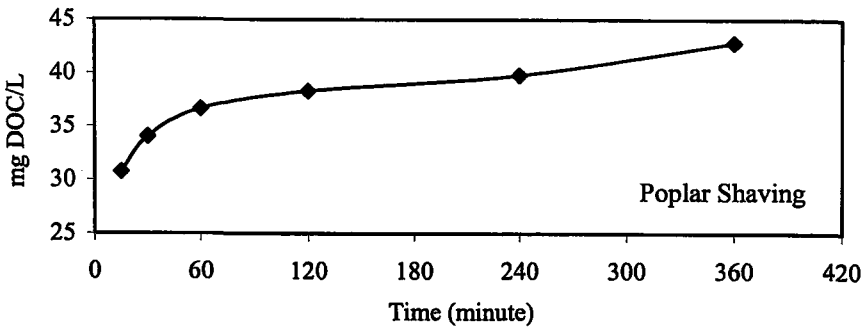


Figure 6.3.2 DOC release of the poplar shaving

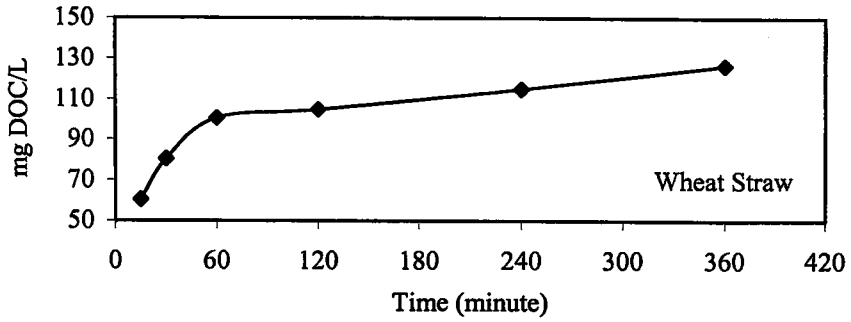


Figure 6.3.3 DOC release of the wheat straw

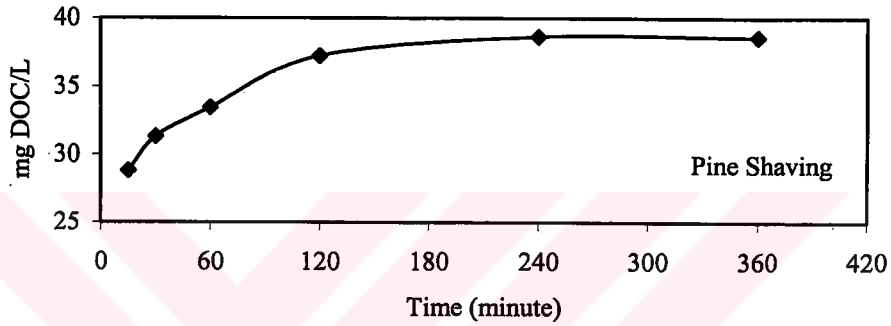


Figure 6.3.4 DOC release of the pine shaving

6.4 Biodenitrification Batch Study by Using Various NOSS

In this series of experiments, batch biodenitrification tests have been conducted. The overall amount of nitrate removed during the batch study amounted to about 30 mg, 40 mg, 60 mg and 185 mg in 250 mL for poplar, hornbeam, pine shaving and wheat straw, respectively. Figure 6.4.1, 6.4.2, 6.4.3, and 6.4.4 depict the nitrogen elimination for the poplar, wheat straw, hornbeam, and pine shaving, respectively, (data appx: 9.3). Nitrogen elimination was higher for wheat straw and pine shaving as compared to the others. (Arrows indicate the addition of fresh wheat straw in the batch reactor).

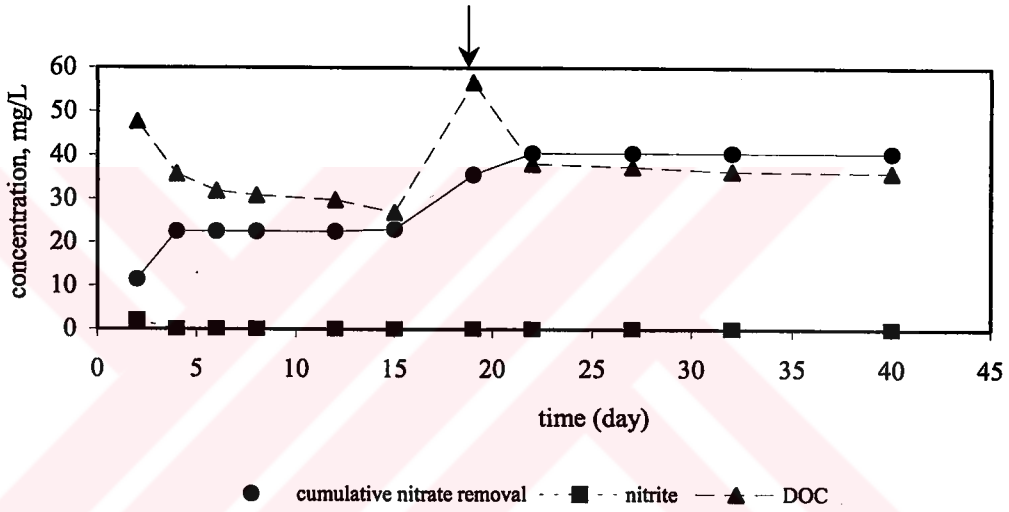


Figure 6.4.1 Nitrate removal, nitrite and DOC contents in batch unit containing hornbeam shaving

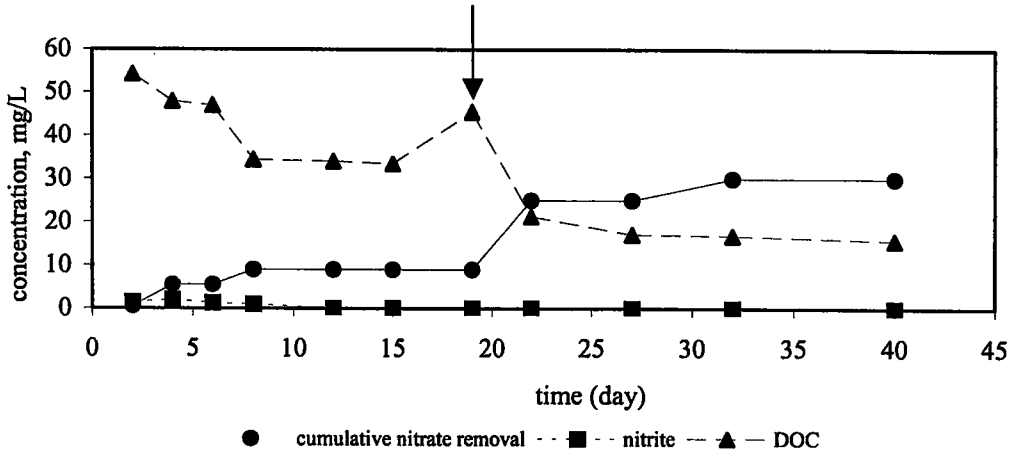


Figure 6.4.2 Nitrate removal, nitrite and DOC contents in batch unit containing poplar shaving

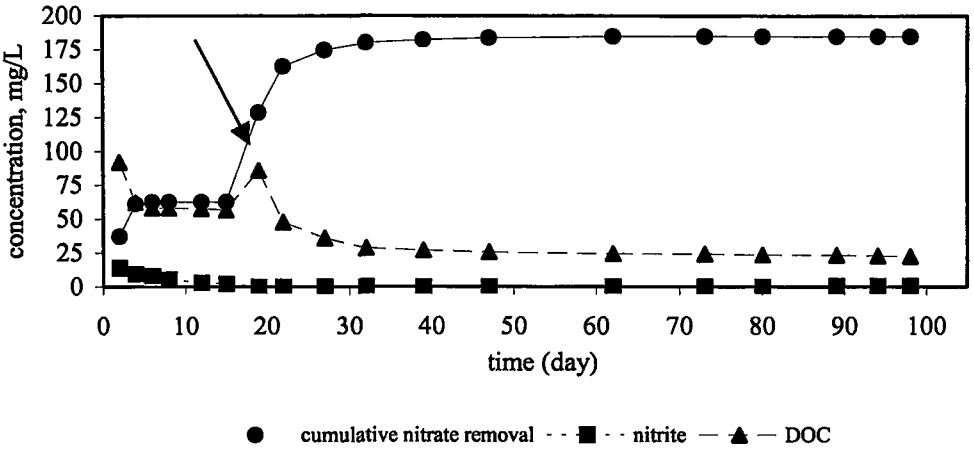


Figure 6.4.3 Nitrate removal, nitrite and DOC contents in batch unit containing wheat straw

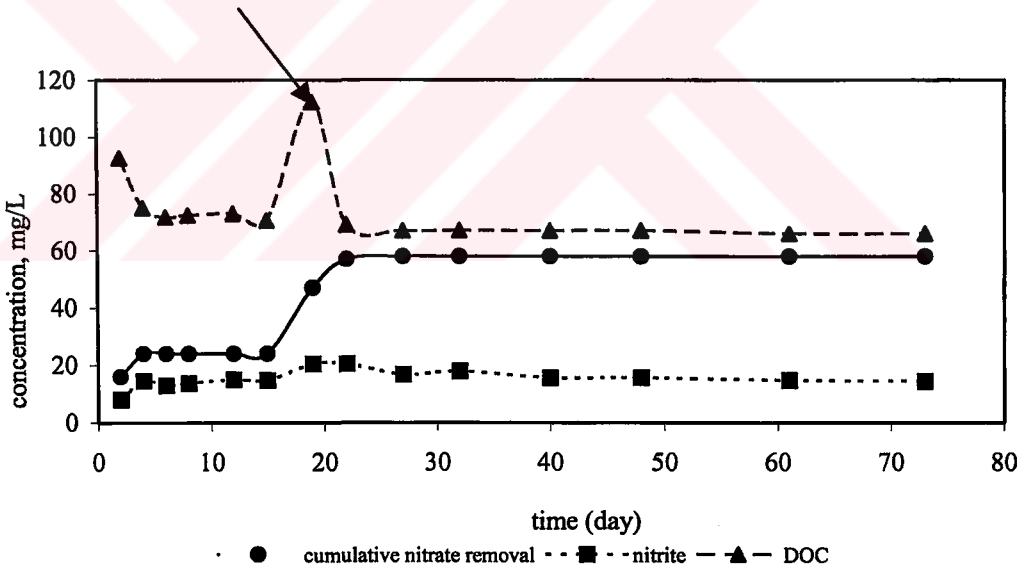


Figure 6.4.4 Nitrate removal, nitrite and DOC contents in batch unit containing pine shaving

Because of the low carbon content of the poplar and hornbeam shaving (about 60 mg/L), significant nitrate elimination was not observed. Using hornbeam 23 mg NO^-_3 elimination was obtained when DOC concentration was about 27 mg/L during 15 days. After adding 500 mg hornbeam, cumulative nitrate elimination increased to 40.5 mg in 22 days and DOC concentration dropped to 36 mg/L, which could not be used by microorganisms, and nitrite was not observed except for first sample (Figure 6.4.1).

On the 8^{th} day, the cumulative nitrate removal was 9 mg in the poplar batch unit (Figure 6.4.2). After adding extra poplar, DOC content was enhanced from 33.5 mg/L to 45.5 mg/L on day 20. Nitrate elimination was increased to 30 mg and DOC content dropped to 15.7 mg/L at the end of the study. At the beginning of operation, nitrite-nitrogen concentration was not exceeded 1.5 mg/L and after 8 days, nitrite was not observed at all.

The DOC level of wheat straw and pine shaving were about the same at the beginning of the batch experiment (Figure 6.4.3 and 6.4.4). However low rate of nitrate removal and high nitrite accumulation was observed with pine shaving. Nitrite concentration did not drop below 13 mg NO^-_2-N/L and about 65.9 mg DOC/L remained in the batch unit. It might be due to the hard breakdown of the carbon chain by microorganisms.

The highest nitrate removal was observed with the wheat straw. The soluble fraction of carbon present in the wheat straw allowed rapid microbial growth therefore high nitrate removal efficiency was observed in the batch unit. During the six days period, microorganisms consumed about 57% soluble fraction of DOC and 62.6 mg nitrate was eliminated. Nitrite accumulation was observed in the first day of operation, but nitrite decreased gradually from 14 mg/L to near zero level.

After adding extra wheat straw, nitrate elimination was enhanced to 129 mg in the forth day. Nitrite was not observed except after 73 days for operation. Due to the low DOC content, nitrate elimination was not determined after 40 days. When DOC concentration drops below 25 mg/L, nitrate elimination slows down considerably.

By autoclaving, wheat straw releases carbon fractions, some of which are biodegradable and some not. In the first step of the study when DOC concentration dropped to 56.5 mg/L, nitrate elimination was not observed anymore. However after adding DOC in the second step, nitrate elimination has started and continued down to the level of 22.5 mg DOC/L. It can be assumed that consumable fraction of the DOC enhanced the microbial activity. Soares and Abeliovich (1998) used wheat straw as a carbon source for biological denitrification and explained that all water soluble component and a good proportion of the cellulose and hemicellulose had been lost by the end of the experiment while lignin and mineral components remained unchanged.

As a result of the batch study, wheat straw was selected as carbon source and support particles for biological denitrification reactor for further studies.

6.5 Biological Elimination of Nitrate and Selected Pesticides in Drinking Water Using Wheat Straw

6.5.1 Batch Experiments

In the batch study, no other carbon source was added except for DOC that was released by the wheat straw. At the end of the batch experiments, about complete NO_3-N, about 30 % trifluralin and 65% endosulfan ($\alpha+\beta$) elimination were obtained for 45 mg NO_3-N/L and about %80 trifluralin and endosulfan ($\alpha+\beta$) removal was observed for 67 mg NO_3-N /L. Because of the longer retention time, higher pesticides removal efficiency for 67 mg NO_3-N/L was observed in the batch unit. Results of this experiment are given in Figure 6.5.1.

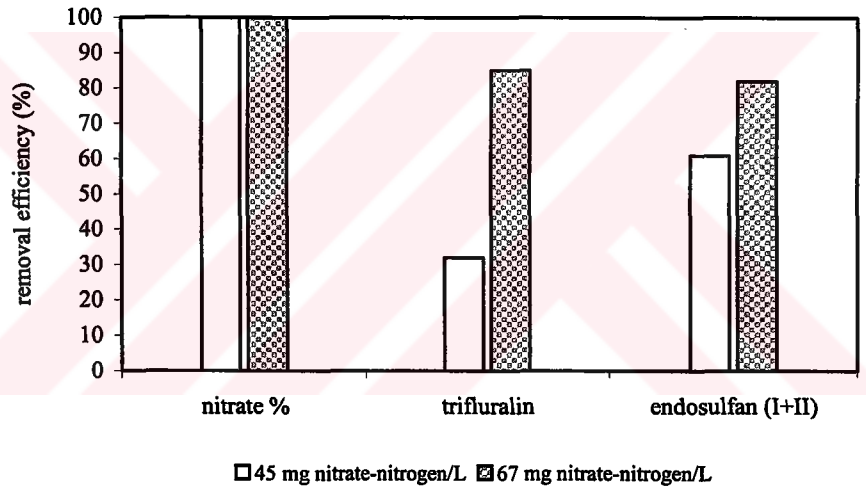


Figure 6.5.1 Trifluralin and endosulfan ($\alpha+\beta$) removal performance for various nitrate concentration in the batch unit

6.5.2 Continuous Experiments

A column packed with 160 g of wheat straw was operated since NO_3-N concentration was about 9 mg/L in the effluent water at the first step of operation. Extra wheat straw was put in the packed column for supplying carbon source for denitrification microorganisms in the second step. After adding 16 g wheat straws, which was the 10% of the beginning amount of the substances, experiment was performed up to the point where effluent water contains 10.2 mg NO_3-N/L and low

DOC content. Experimental results for the nitrate and nitrite-nitrogen and pH and water velocities of the effluent water are depicted in Figure 6.5.2. (data at appx. 9.4).

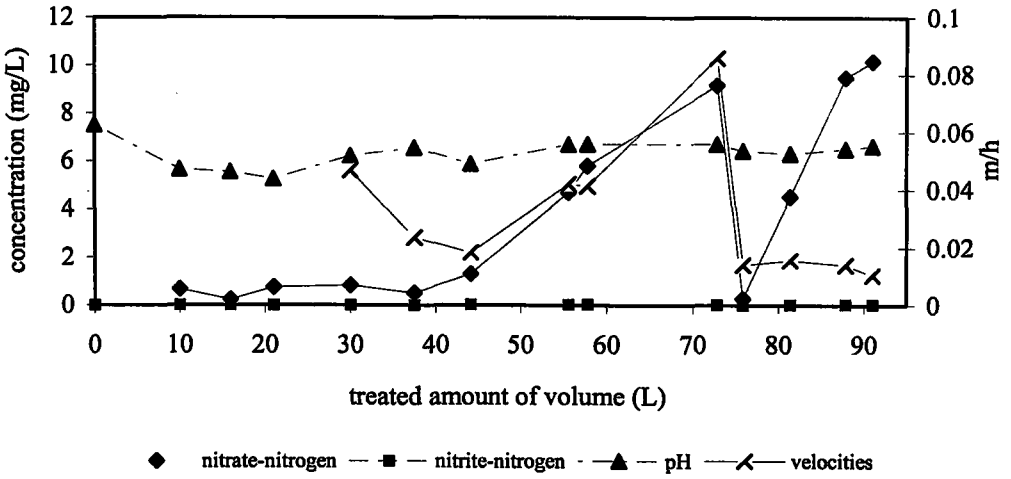


Figure 6.5.2 Concentration of NO_3-N, NO_2-N, and pH in the effluent of the reactor that operated at various water velocities

During the inoculation period, approximately complete removal of 22.6 mg NO_3-N/L was achieved at average daily temperature of 31 ^{0}C and nitrite was not detected. Although the high nitrogen elimination was observed during the first days of operation, high DOC and colourful water was washed out from the packed column reactor (Figure 6.5.3). The easily soluble fraction of carbon causes rapid microbial growth therefore high nitrate removal efficiencies were obtained. A colour of about 560 Pt-Co unit, dissolved organic carbon content of about 500 mg/L and odour were observed in the effluent water during the inoculation period because of the high temperature, about 31 ^{0}C, in summer.

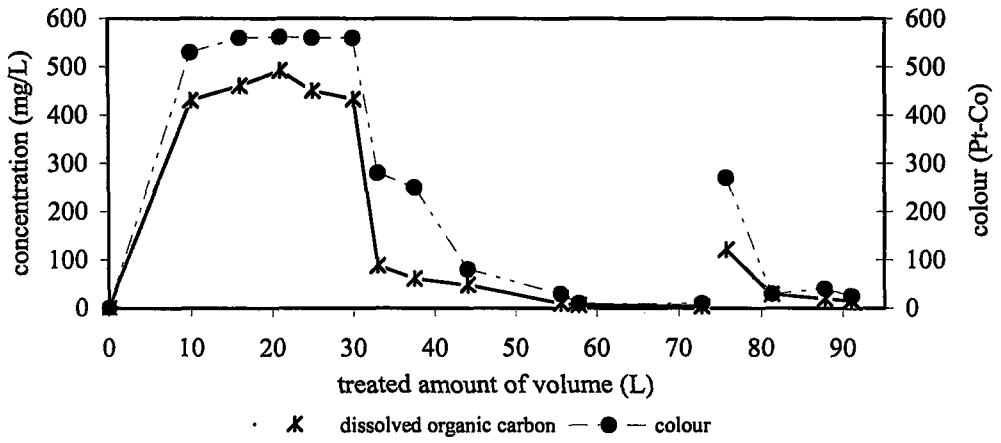


Figure 6.5.3 Concentration of dissolved organic carbon and colour in the effluent

As more water passes through the reactor, decrease in colour and DOC content of the effluent was observed. In fact, the concentration of DOC was 500 mg/L and colour was 560 Pt-Co during the inoculation period and decreased gradually to about 4 mg DOC/L and 10 Pt-Co values. At this time nitrite-nitrogen concentration was 0.03 mg/L and nitrate elimination efficiency was lower than 60%, therefore extra wheat straw was added. After about 73 litre of water passed through the reactor, due to the consumption soluble fraction of wheat straw, nitrate elimination slowed down and drinking water standard was exceeded (Figure 6.5.4).

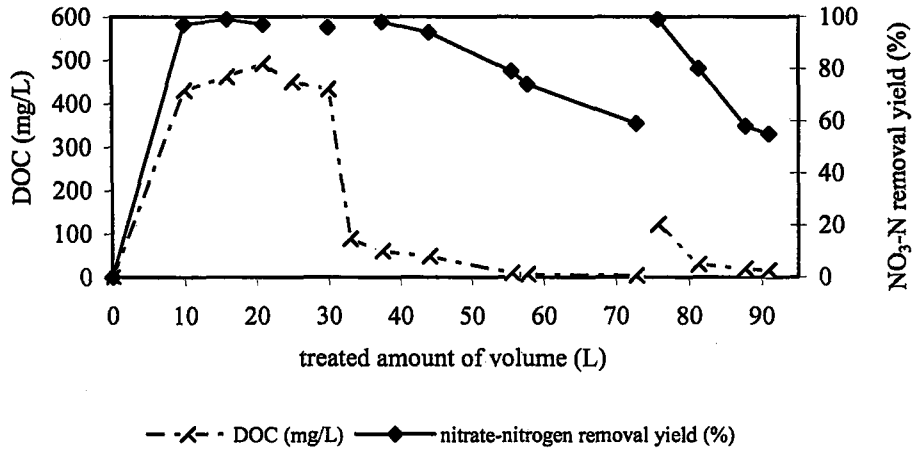


Figure 6.5.4 NO_3-N removal efficiency and DOC concentration in the effluent water in the continuous reactor study

Using wheat straw, significant nitrate elimination was determined up to the point where effluent water contains about 4 mg DOC/L. At this point nitrate nitrogen concentration was about 9 mg/L, which is acceptable level for drinking water. During this experimental study, nitrite-nitrogen was not exceeded 0.04 mg/L in the effluent water.

After adding extra wheat straw, DOC and colour content were increased to about 122 mg/L and 300 Pt-Co in the reactor from about 3.5 mg DOC/L and 10 Pt-Co. High nitrate elimination was observed when DOC concentration was increased to 122 mg/L and DOC was consumed rapidly. Because sufficient DOC was present in the reactor, nitrite was not observed. After passing 5.5 L treated water, DOC content was decreased to the about 30 mg/L in the effluent water. The replenished conditions increased the nitrogen removal efficiencies for a short time, on the other hand, the fresh soluble carbon was washed out from the packed reactor.

At the end of the biological denitrification study, the packing wheat straw was removed from the column, dried and weighed. During the operation period, 23.4 % of the initial weight of wheat straw was lost and 24 g of it was exhausted per g of nitrogen removed. Cumulative nitrate removal and DOC concentrations in the effluent water are depicted in Figure 6.5.5. The wheat straw consumption reported in this study was higher than the values given in the literature (11 g of wheat straw were consumed per g N eliminated, Soares and Abeliovich, 1998). Washed out wheat straw fragment from the reactor was not detected.

During the experimental study, the water velocities varied between 0.014-0.086 m/h. Although the Soares and Abeliovich (1998) mentioned that the water velocity was an important parameter on the denitrification performance, significant differences was not observed in this study due to the low water velocities. The high velocity may cause wash out of microorganisms and soluble fraction of dissolved organic carbon from the reactor.

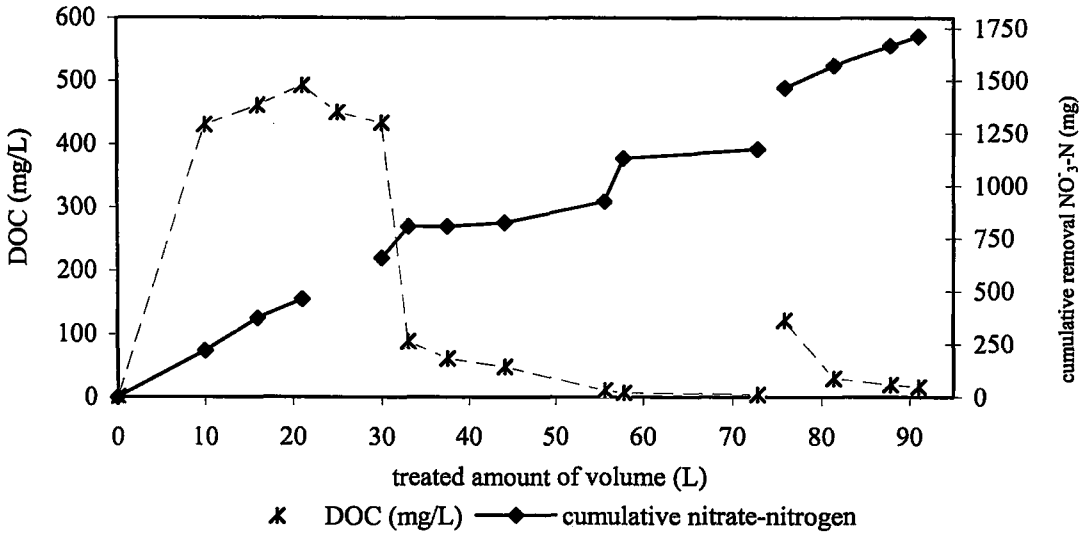


Figure 6.5.5 Concentration of the dissolved organic carbon of the effluent water and cumulative NO_3-N at the study

DOC content in the column plays an important role on the denitrification performance of the system. When the DOC concentration in the effluent water was below 45 mg/L, NO_3-N removal efficiency drop below 90%. After adding extra wheat straw in the column, denitrification performance increased and than fall off gradually because of the decreasing DOC content in the reactor. Dissolved oxygen concentration was not exceeded 0.3 mg/L in the biological denitrification reactor.

The effluent from the biological denitrification reactor entered the sand filtration where suspended solids in the water were removed. Using the sand filter system, between 16-19 % nitrate-nitrogen removal efficiency were obtained when DOC contents and nitrate-nitrogen were sufficient in the effluent water from the reactor. Under these conditions slow sand filter unit behaves like biodenitrification reactor. Experimental results for the nitrate and nitrite-nitrogen concentrations and pH in the effluent water from the sand filter unit are depicted in Figure 6.5.6.

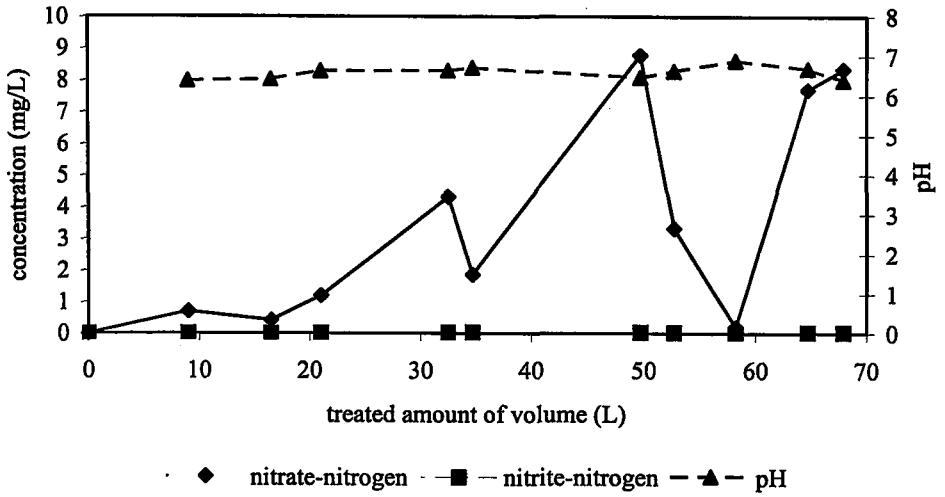


Figure 6.5.6 Concentration of NO_3-N, NO_2-N, and pH in the effluent of the sand filter unit operated at various water velocities

The mineralization of selected pesticides as a co-carbon source was studied in the continuous biological reactor using wheat straw. The influent pesticides concentrations were 10 μg/L, 7.7 μg/L, and 10.5 μg/L for trifluralin, fenitrothion and endosulfan (α+β), respectively. During the continuous experimental study; between 95.4-99.8, 84.4-99.4, and 83.7-97.4 % the removal efficiencies were obtained for trifluralin, fenitrothion and endosulfan (α+β), respectively. Experimental results are given in Figure 6.5.7.

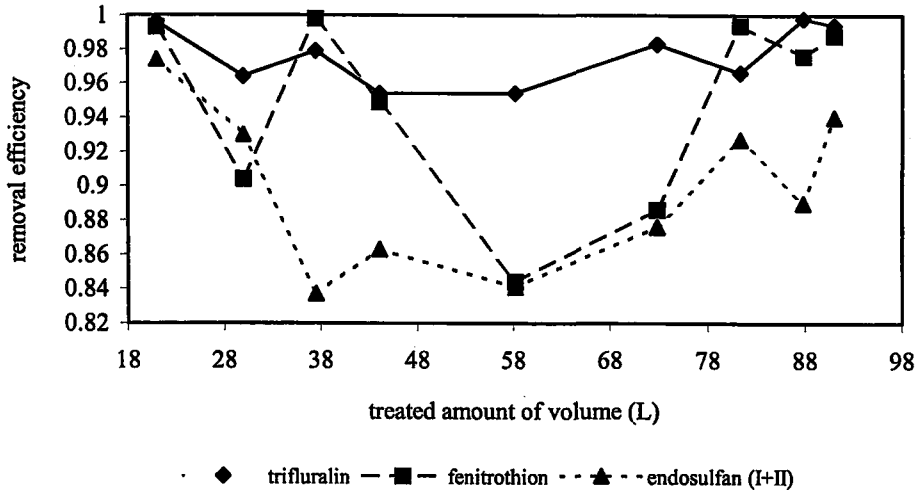


Figure 6.5.7 Removal efficiency of the selected pesticides in the effluent water of the continuous reactor

In this series of experiments all the pesticides concentrations exceeded drinking water standards. The effluent trifluralin concentration, which has high sorption capacity onto the wheat straw, exceeded five times drinking water standards (0.1 μg/L for single compounds and 0.5 μg/L for sum of the pesticides). The effluent concentrations from the continuous reactor are given in Figure 6.5.8.

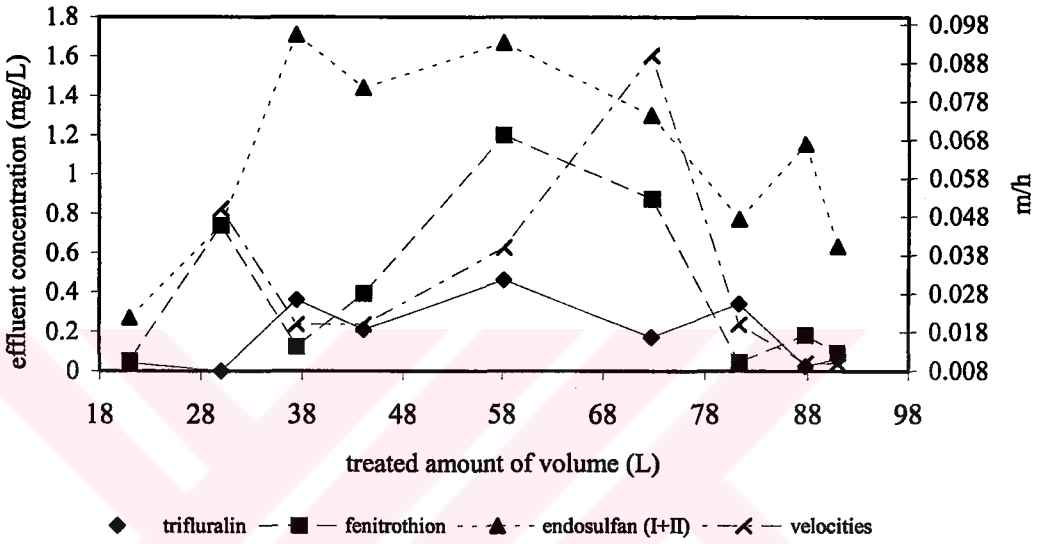
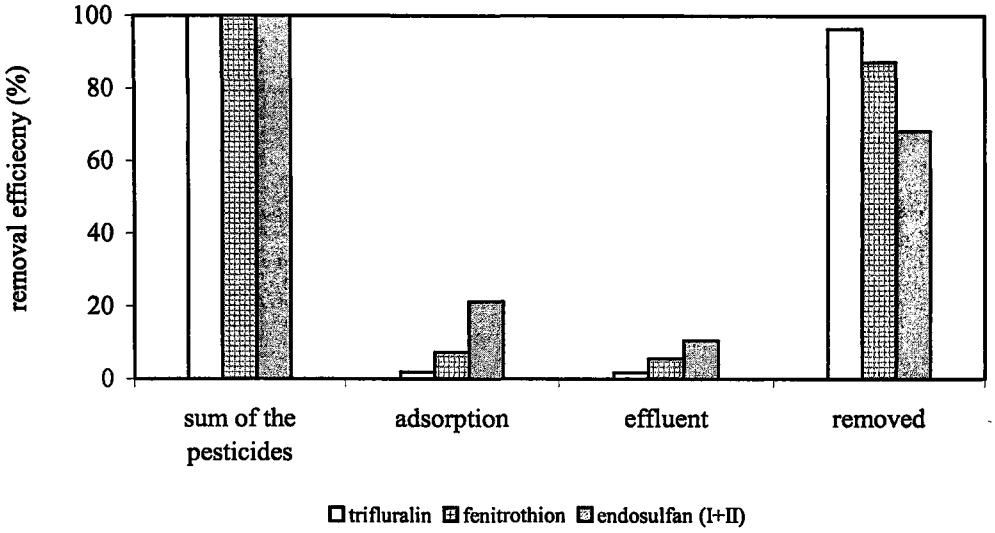


Figure 6.5.8 Concentration of the selected pesticides in the effluent water and water velocities in the continuous reactor study.

The high nitrate-nitrogen elimination was observed using wheat straw; as DOC concentration was sufficient for biological denitrification. Although the high removal efficiency was observed for the selected pesticides in the biological denitrification packed with wheat straw and sand filter units, the effluent water could not be used for drinking purposes because of the unacceptable level of pesticides (higher than 0.5 μg/L), colour problem and dissolved organic content, especially during the first days of operation.

At the end of the operation, the wheat straw was removed from the column and dried at room temperature and mixed. 10 g of the mixed wheat straw was taken for determination of pesticide amount which was adsorbed onto the solid particles. Summary of the experimental results are given in Figure 6.5.9.



Adsorption; removal efficiency of the selected pesticides adsorbed to the wheat straw, *effluent*; sum of the pesticides in the effluent water, *removed*; sum of the pesticides removed in biological reactor

Figure 6.5.9 Summary of the pesticides removal in the biological denitrification reactor

As can be seen from the Figure 6.5.9, about 96 %, of trifluralin, 87 % fenitrothion, and 68% endosulfan (α+β) were removed from the water in the biological denitrification reactor using wheat straw as solid particles.

Significant pesticides removal was not observed in the sand filter unit. Slow sand filtration is used especially for removing solid particles, escaping from bioreactor due to the high water velocities. The pesticides concentrations in the effluent water from the sand filter unit are given in Figure 6.5.10

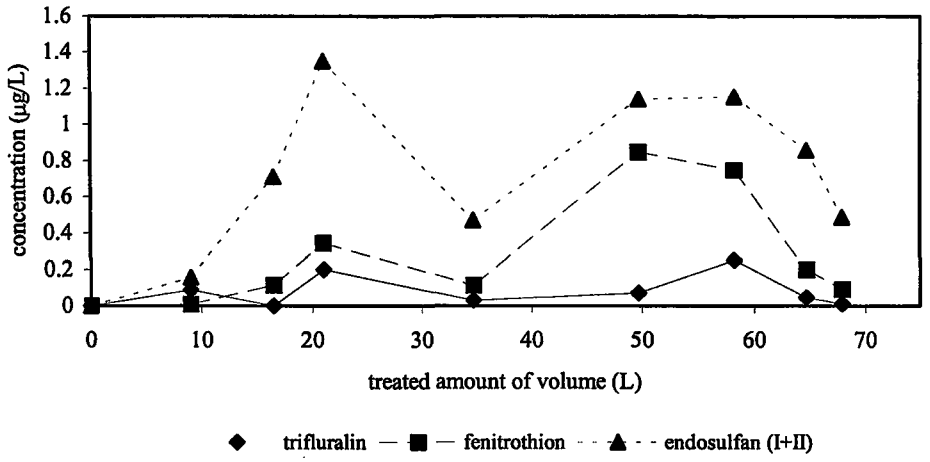


Figure 6.5.10 Pesticides concentrations of the effluent water and water velocities in the continuous reactor study

As a conclusion, although high nitrate and average 98, 95, and 90 % removal efficiencies were obtained in using wheat straw for trifluralin, fenitrothion, and endosulfan (α+β), respectively, the post treatment such as activated carbon adsorption should be applied to the effluent water from the biological denitrification and sand filter system.

Because of the unacceptable concentrations of pesticides in effluent water, post treatment like activated carbon adsorption is needed. As can be seen in Figure 6.2.5, high pesticides removal could be obtained by applying activated carbon adsorption.

6.5.3 Adsorption Experiment to Determine Optimum PAC Amount

Post treatment can be used to remove colour in the effluent water because it includes DOC and high colour, especially in the first days operation.

In this series, 100 mg NO^-_3/L was supplemented to the water containing 190 mg DOC/L. In order to reduce DOC content in the effluent water, PAC adsorption unit is required. Even though high concentration of DOC is washed from the biological denitrification and sand filter system; considerable amount of DOC might be removed by using PAC.

To remove excess DOC and colour from the effluent, adsorption study was performed using powdered activated carbon (PAC). As a result of the study, 52% DOC removal (from 190 mg/L DOC to 91 mg/L) was obtained with 1.5 g PAC as depicted in Figure 6.5.11. Complete colour removal was achieved with 1 g PAC for 100 ml of water containing 270 Pt-Co colour (Figure 6.5.12). 1.5 g PAC was used for further studies, which was applied at different agitation times.

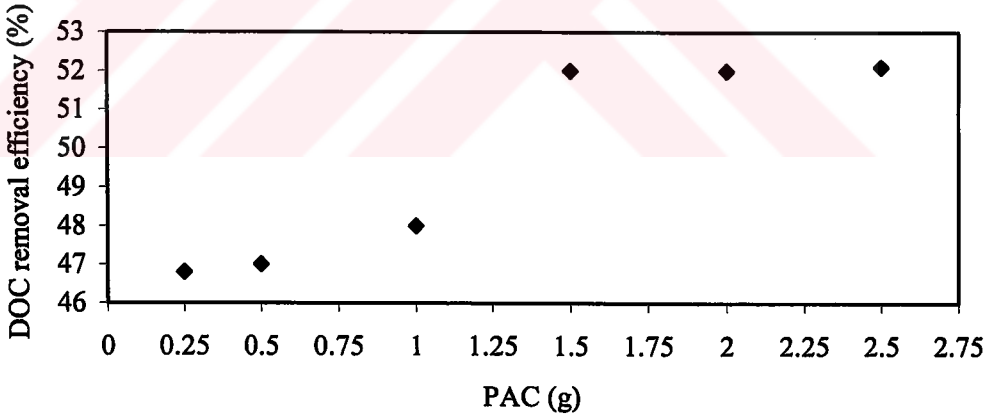


Figure 6.5.11 Dissolved organic carbon removal by using various PAC amounts

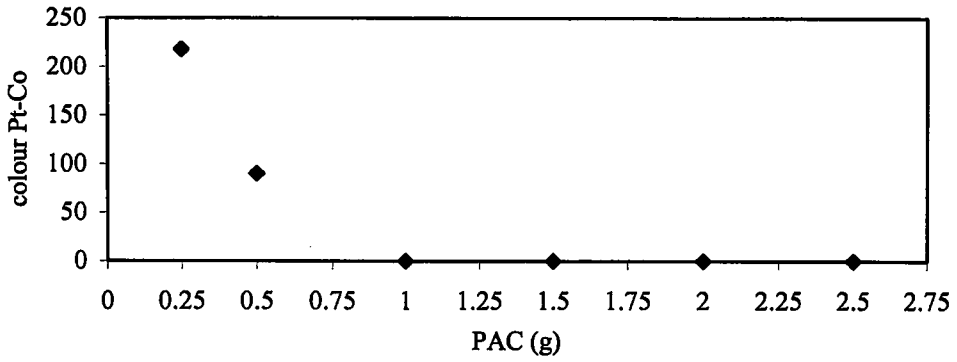


Figure 6.5.12 Colour removal by using various PAC amounts

As can be seen from Figure 6.5.13, about 63% nitrate and 98% DOC removal efficiencies were observed in 24 hours time.

Experimental results indicate that high quality of water can be obtained by using PAC adsorption after biological denitrification packed with wheat straw and sand filter unit.

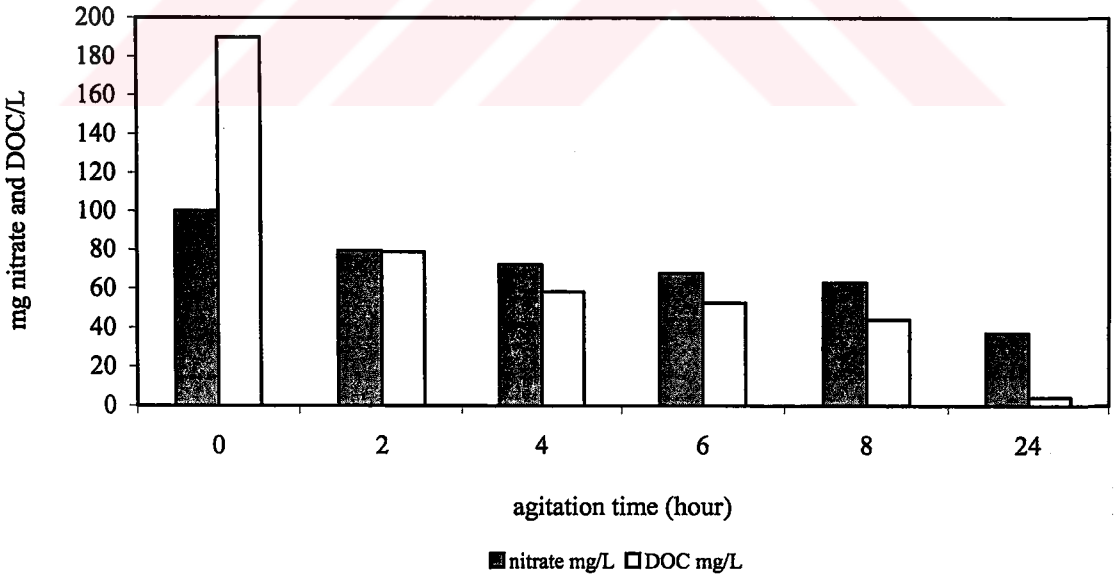


Figure 6.5.13 DOC and nitrate removal by PAC

6.6 Biological Elimination of Nitrate and Pesticides in Drinking Water Using Chemicals as Carbon Source

6.6.1 Pesticides Adsorption Capacities of the Plastic Materials and PAC

Plastic material has a certain adsorption capacity for organic chemicals. Thus, some part of pesticides spiked into the water will be removed by adsorption on plastic filling material of the reactor.

In order to determine adsorption capacities of the plastic materials and powdered activated carbon (PAC) of the pesticides, adsorption batch experiments were performed. Plastic materials, which were used in the continuous reactors as a support particles and PAC were placed in separate shake flaks at pH= 6.0, 125 rpm rotation speed at room temperature (19 ^{0}C). Initial pesticides concentration of the water was measured after adding in the batch unit. The batch experiments were performed for 24 hours. Experimental results and removal efficiencies are given in Figure 6.6.1, 6.6.2, and 6.6.3. (data at appx. 9.5.1).

About 90%, 12%, and 50 % of removal yield were observed within 1 hour for trifluralin, fenitrothion and endosulfan (α+β), respectively. At the end of the study, above 90 % of trifluralin, 90 % endosulfan (α+β) and 40% of fenitrothion were adsorbed onto the plastic materials. Pesticide removal performance was 100% within 1 hour when PAC was used as a adsorbent, as expected.

In water treatment plant applications, plastic filling material will adsorb pesticides at the beginning of the operation. Later on, because adsorption capacity of the plastic is exhausted and microorganism is covered, no more adsorption will take place.

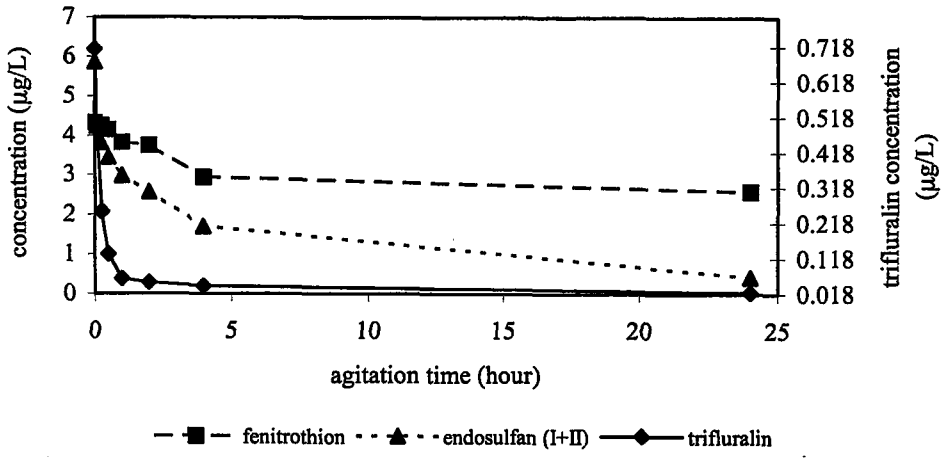


Figure 6.6.1 Pesticides adsorption capacity of the plastic materials

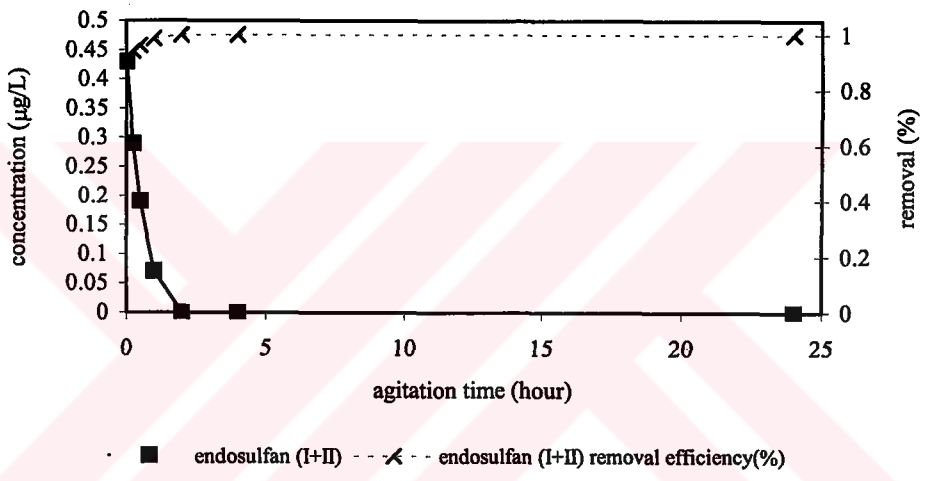


Figure 6.6.2 Endosulfan (α+β or I+II) adsorption capacity of the PAC

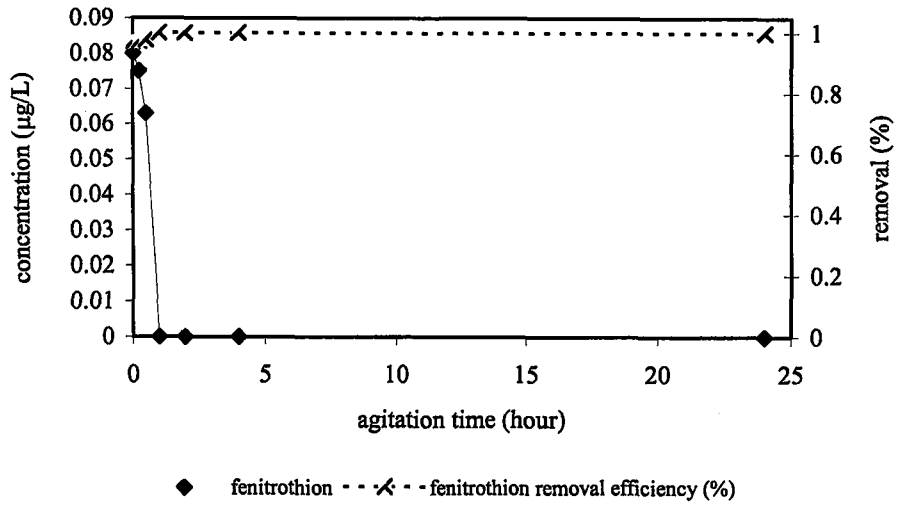


Figure 6.6.3 Fenitrothion adsorption capacity of the PAC

6.6.2 Biological Denitrification of Drinking Water Using Acetic Acid and Ethanol as Carbon Sources

An external organic carbon source must be added to the water for denitrification to occur. To evaluate organic carbon requirements, ethanol and acetic acid, widely used denitrification, were studied in the batch unit. In the denitrification of drinking water, the excess amount of carbon, which is not consumed by the microorganisms, should be kept as low as possible for sanitary reasons.

Batch experimental study was undertaken to optimize acetic acid and ethanol to nitrate-nitrogen ratio, to determine nitrate removal efficiency and suitable carbon source for further continuous biological denitrification reactor study.

6.6.2.1 Ethanol and Acetic Acid Requirements

Batch experiments were performed to find the ethanol and acetic acid requirements for nitrate removal. The influent pH was adjusted at 7.5 with NaOH solution in the batch unit.

The optimum acetic acid and ethanol to nitrate-nitrogen ratio achieves maximum removal of nitrate with minimum excess carbon in the effluent, were determined in this part of the experimental study. The C/N ratios varied from 0.3 to 3.2 for ethanol and 0.5 to 4.2 for acetic acid, while the nitrate-nitrogen concentration was kept constant at 22.58 mg/L (100 mg NO^{-}_{3}/L). The effect of the C/N ratio on the nitrate, ethanol and acetic acid removal are shown in Figure 6.6.4 and 6.6.5 (data at appx. 9.5.2),

The optimum acetic acid and ethanol to nitrate ratios were found to be 1.61 and 1.35, respectively. At the optimum C/N ratio, the nitrate and carbon removal yields were above 90% for both carbon sources. At C/N ratios below the optimum point, the nitrate removal was found to be dependent upon the carbon concentrations, causing a significant fall on nitrate elimination due to lack of sufficient organic substance in the batch unit. When C/N ratio for acetic acid was 1.4 and below, nitrite was observed. It is clear that under limited carbon conditions the nitrate elimination decreases and nitrite concentration increases in the effluent water.

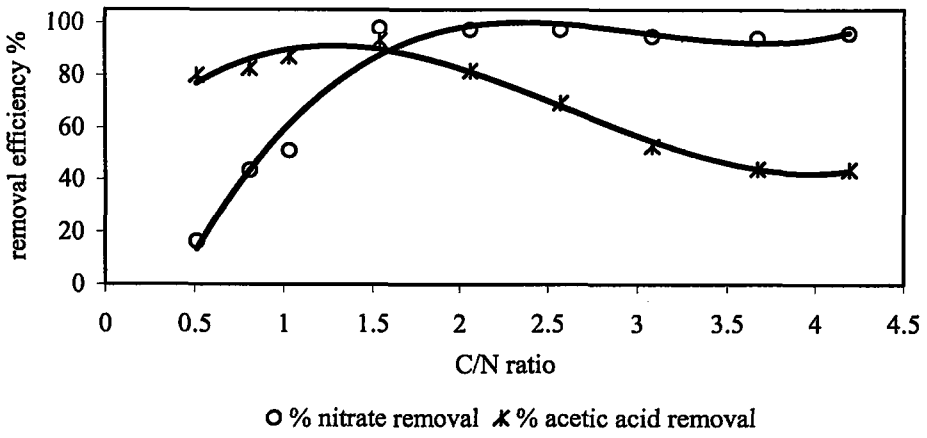


Figure 6.6.4 Effect of various C/N ratios on the nitrate and acetic acid removal efficiencies

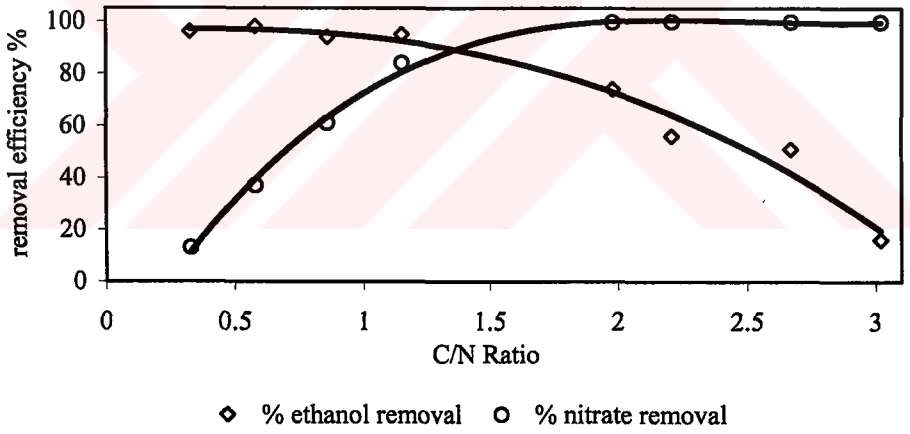


Figure 6.6.5 Effect of various C/N ratios on the nitrate and ethanol removal efficiencies

When the C/N ratio for ethanol was 1 (optimum ratio: 1.35), the nitrate removal efficiency dropped to 70%. Although no significant improvement in nitrate elimination was observed with a C/N ratio in excess of the optimum value, excess amount of carbon remained in the water.

The low nitrite concentration indicated that most of the nitrate was ultimately reduced to harmless nitrogen gas. Nitrite has been shown to be a key factor in the denitrification process, because of its human toxic effects (Mohsani-Bandpi et al., 1999). Balszczyk et al, (1980) pointed out that using acetic acid as an electron donor could have a significant effect on the production of nitrite in the reactor.

The type of carbon source affects nitrite production during the biological denitrification process. High accumulation of nitrite was observed when glucose was used as a carbon source; however, when the acetate was used, the effluent water contained very low nitrite concentration (Balszczyk et al, 1980). The main disadvantage of acetic acid, as compared to other carbon sources is its high consumption ratio and high cost (Mohsani-Bandpi et al., 1999).

As a result of this study, ethanol was selected for further experiments as carbon source. The critical ratio was 1.5 for C/N as shown in Figure 6.6.5. Below this value nitrate removal efficiency was decreased and nitrite was observed in the effluent water from the continuous reactor. Above that value, denitrification was almost complete but excess amount of carbon remained in the effluent. Thus the optimum ethanol to nitrate-nitrogen (C/N) ratio was selected as 1.5. The carbon consumption reported here is in the range of the values obtained by Richard (1989) and is about the same by Delanghe et al. (1994), but is 50% higher than the values given by the Dahab and Sirigina (1994).

6.6.2.2 Effect of the pH on the Nitrate and Ethanol Elimination

Batch experiments were operated at various pH values. The relationship between the nitrates, carbon removal efficiencies and pH are depicted in Figure 6.6.6. The optimal pH values lie between 5-9 in the batch unit and within this range, nitrate and ethanol removal efficiencies were about 90% and 70%, respectively. Biological performance decreased sharply below and above this range in the batch unit. MLSS concentration and pH in the water at the end of the batch experiment are given in Figure 6.6.7, (data at appx. 9.5.3).

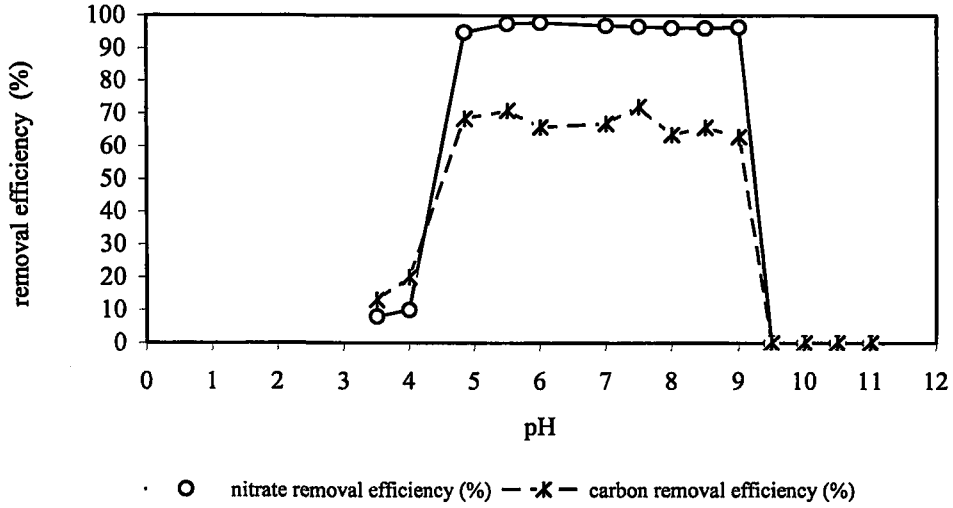


Figure 6.6.6 Effect of the pH on the nitrate and carbon removal efficiency

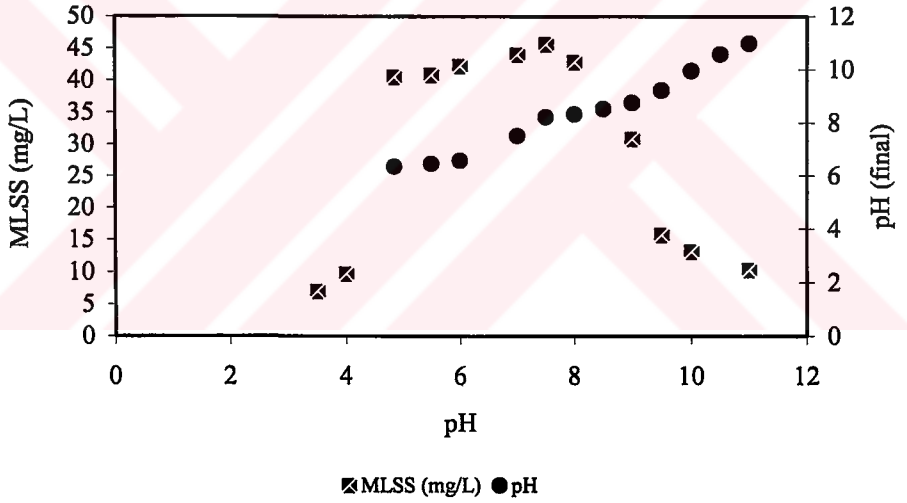


Figure 6.6.7 MLSS concentration and pH at the end of the batch study

Alkalinity is produced during the conversion of nitrate to nitrogen gas resulting in an increase in pH. At the end of the batch experiment, final pH was higher than initial pH. The microbial activity drop down sharply above pH: 9 (Figure 6.6.7).

Delanghe et al. (1994) explained that optimum pH was about 8 for biological denitrification. This value is slightly lower than those reviewed by Hiscook et al. (1991). However, these results are unlike the conclusions of Wattanachira and Fujita

(1990) who did not find any pH effect. Till et al. (1998) studied various pH and explained that pH did not have statistically distinguishable effect on nitrate removal in the range of 6.0-9.0. The inhibitory effect was likely due to an increase in pH beyond the tolerance range (> 10) of the bacteria.

Van der Hoek and Klapwizk (1987), and Van der Hoek et al., (1988) studied biological denitrification of brine solution in ion exchanger and observed that high pH values ranged from 7.7 to 8.6 and 8.9 did not caused pH inhibition on the nitrate elimination process.

As a result of this study significant pH effect is not observed on biological denitrification systems except for pH lower than 5.0 and higher than 9.0.

Considering the results of the batch experiments; ethanol was selected as a carbon source and optimum ethanol to nitrate-nitrogen (C/N) ratio as 1.5 and pH of the feeding solution as 7.5 for continuous experiment.

6.6.2.3 Effect of the Temperature on Denitrification Activity

The temperature dependence of the biological reaction is very important in assessing the overall efficiency of a biological treatment process. The temperature affects the removal rate of nitrate and the microbial growth rate. The organisms are sensitive to changes in temperature.

Since the temperature is an important parameter on the microbial activity, in order to investigate temperature effects on the denitrification performance, batch experiments were carried out at various temperatures.

The denitrification activity was found to be a function of temperature (Figure 6.6.8). Although Delanghe (1994) was observed nitrate elimination at 5 ^{0}C, no significant elimination of nitrate was observed at 5 ^{0}C in the batch unit in this study.

In order to evaluate temperature effects on biological denitrification, batch experiments were carried out at the room temperature between 9-15 ^{0}C and in incubators at 5 ^{0}C, 15 ^{0}C, 22 ^{0}C, 27 ^{0}C, and 37 ^{0}C.

Figure 6.6.8 depicts the nitrate and ethanol removal and MLSS concentrations at different temperatures. About 100 % nitrate elimination was observed at temperature between 22 to 37 ^{0}C. When the temperature was below 22 ^{0}C, the removal efficiency decreased from about 100 % to 14 %. No significant nitrate elimination was observed (about 1.1 %) at 5 ^{0}C. Although the temperature was above at 5 ^{0}C at the room temperature, nitrate elimination was not observed due to the temperature oscillation, which causes microorganisms inhibition.

These results indicated that denitrification microorganisms couldn't perform efficiently at temperatures lower than 22 ^{0}C and they are negatively affected by temperature oscillation.

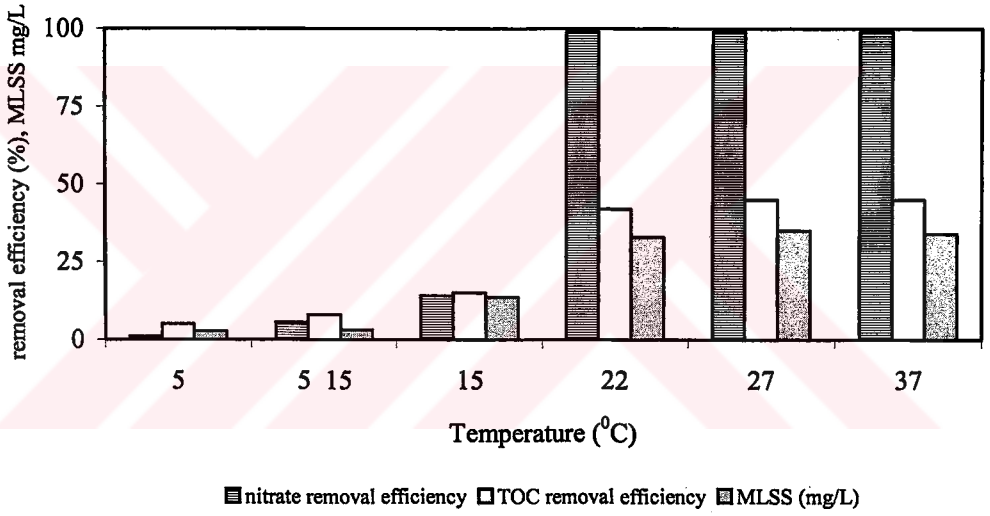


Figure 6.6.8 Temperature effects on the denitrification performance

6.6.3. Biological Pesticides Removal in the Denitrification Reactor Using Ethanol as Carbon Source

The biodenitrification reactor packed with plastic materials was inoculated with microorganisms acclimatized to ethanol taken from the batch unit. The inoculation lasted 3 days for microbial growth and attachment onto the plastic coils with daily replenishment of nitrate, ethanol in medium solution. The inoculation period was carried out in the batch mode of the reactor. The nitrate was almost completely removed for C/N ratio of 1.5 in 24 hours after start-up. Nitrite-nitrogen concentration was below 0.1 mg/L and most of the samples did not contain any NO_2-N. After this period, reactor was operated at continuous flow.

The biodenitrification reactor was operated for one month for microbial growth before studying on hydraulic residence time. During this period, nitrate, nitrite, TOC, MLSS, turbidity, pH, and temperature of the effluent water were measured daily in order to monitor system performance.

6.6.3.1 Effect of Hydraulic Residence Time (θ_h) on Nitrate Removal Efficiency

The major aim of this experimental study was to investigate nitrate removal efficiency at various hydraulic residence times. Influent flow rates were changed in this experiment in order to evaluate the effects of hydraulic residence time on the system performance. Nitrate concentration was selected as 100 mg/L (as 22.6 mg NO_3-N/L) and C/N ratio was kept constant at 1.5 in the influent water. Temperature was 22±1 ^{0}C in the laboratory during the study. Experimental results are depicted in Figures 6.6.9-6.6.12 (data at appx. 9.5.4).

The hydraulic residence time dependence of the biological reaction is very important in assessing the overall efficiency of the nitrate removal efficiency. When the hydraulic residence time decreased below 2 hours, nitrate concentration was increased and nitrite was observed in the effluent water. At the lowest hydraulic residence time, breakthrough of nitrate and nitrite occurred, reaching concentrations

of about 30 and 6 mg/L for 1.0 hour and about 51 and 8.4 mg/L for below 1 hour hydraulic residence time values, respectively.

Increasing hydraulic residence time higher than 2.4 hours, had little effect on the effluent concentration of nitrate and organic carbon, but above this point no nitrite was observed. Ammonia was never detected. Dissolved oxygen concentration did not exceed 0.3 mg/L in the biological denitrification reactor.

The nitrate removal efficiency dropped to 46 % when θ_h lower than about 2.5 hours and nitrite was observed because of the low contact time for microbial activity (Figure 6.6.11).

When the hydraulic residence time was decreased below the 2.5 hours, because of the microorganisms washout from the reactor, MLSS concentration and turbidity increased to about 25 mg/L and 30 FAU, respectively (Figure 6.6.12).

As a result of this experimental study, hydraulic residence time was decided to be greater than 2 hours for further studies

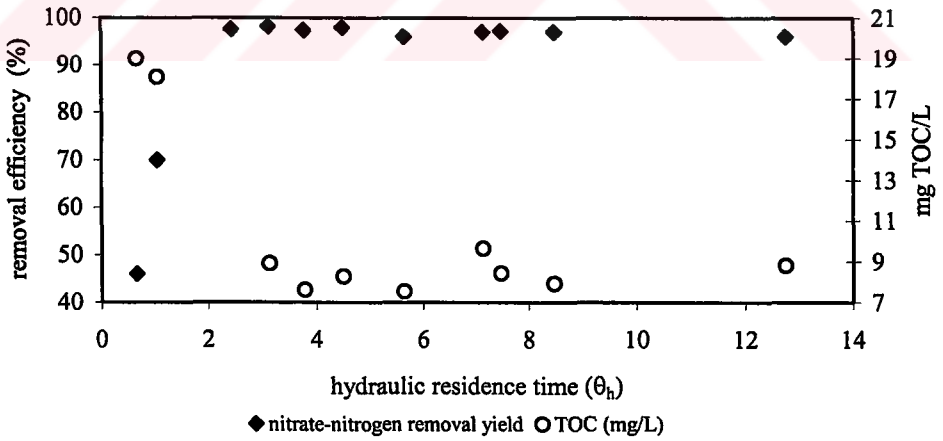


Figure 6.6.9 Effect of the hydraulic residence time on the TOC washout and nitrate removal efficiency

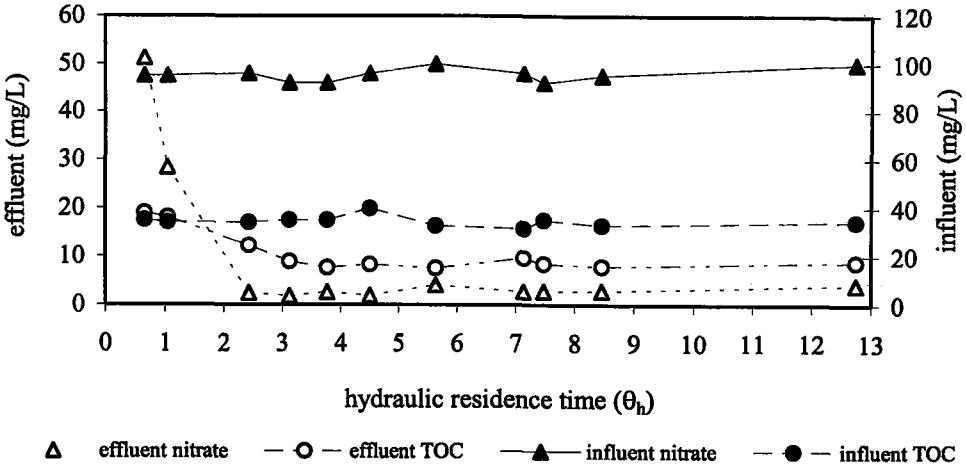


Figure 6.6.10 Effluent and influent nitrate and TOC concentrations for various θ_h

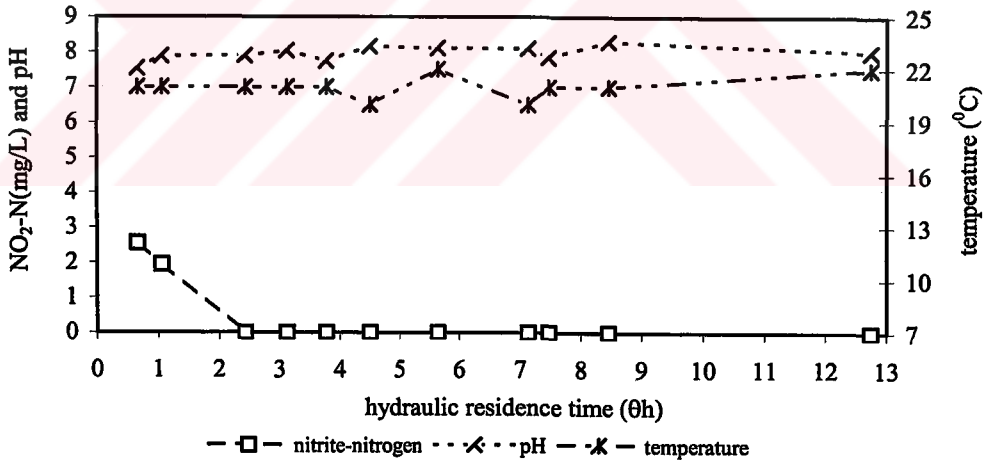


Figure 6.6.11 Nitrate, nitrite-nitrogen and TOC concentrations and pH and temperature of the effluent water

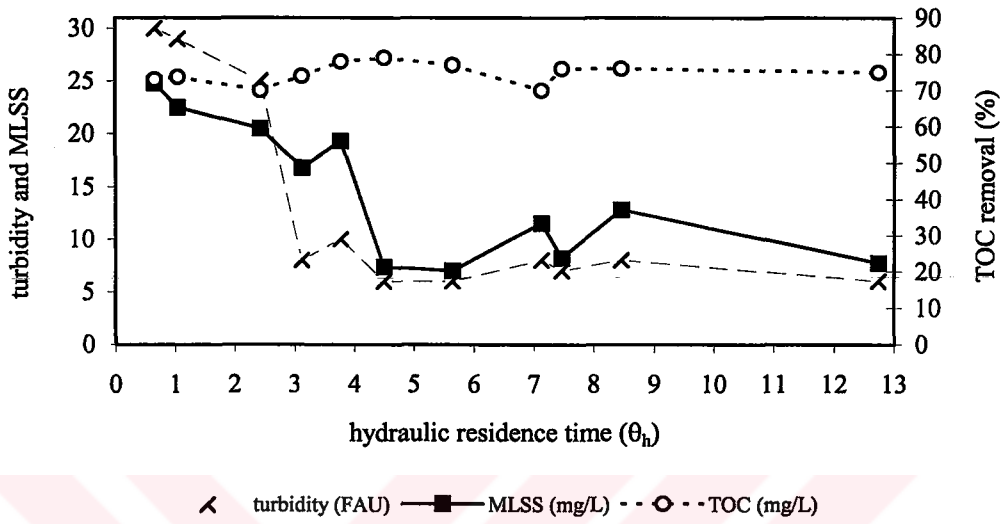


Figure 6.6.12 Effect of the hydraulic residence time on the MLSS concentration and turbidity in of the effluent

6.6.3.2 Nitrates and Pesticides Removal from Drinking Water Using Biodenitrification and Slow Sand Filter Systems

Biological denitrification was studied using two different types of water including medium solution; pure and tap water. Ethanol was used as a feed stock carbon source with C/N ratio of 1.5 for both of the studies when the NO_3-N was 22.6 mg/L (100 mg as NO^-_3/L). The biodenitrification reactor was operated for about two months before studying pesticides elimination. Microorganisms covered the plastic filling materials.

In this experimental study, the biodegradability of pesticides, which are trifluralin, fenitrothion, and endosulfan (α+β or I+II) were evaluated in the biodenitrification reactor packed with plastic coils.

The column packed with plastic materials was fed with medium solution prepared in the pure and tap water and pH was adjusted using NaOH solution. Medium solution spiked with selected pesticides; trifluralin, fenitrothion, and endosulfan (α+β) were prepared daily.

6.6.3.2.1 Pesticides Mineralization in the Batch Unit

In order to evaluate biodegradability of the selected pesticides, biological denitrification batch experiments were operated for two and three days.

At the end of the second day, while about 95 % of NO_3-N elimination was obtained, 40, 13, and 52 % elimination was observed for trifluralin, fenitrothion, and endosulfan (α+β), respectively and microbial growth was 8.5 mg MLSS/L. Although similar nitrate removal efficiency was observed, 76, 50, and 72 % of mineralization of trifluralin, fenitrothion, and endosulfan (α+β) were obtained for the second study, which lasted for three days, and approximately 13 mg MLSS/L of microbial growth was obtained. Experimental results are given in Figure 6.6.13.

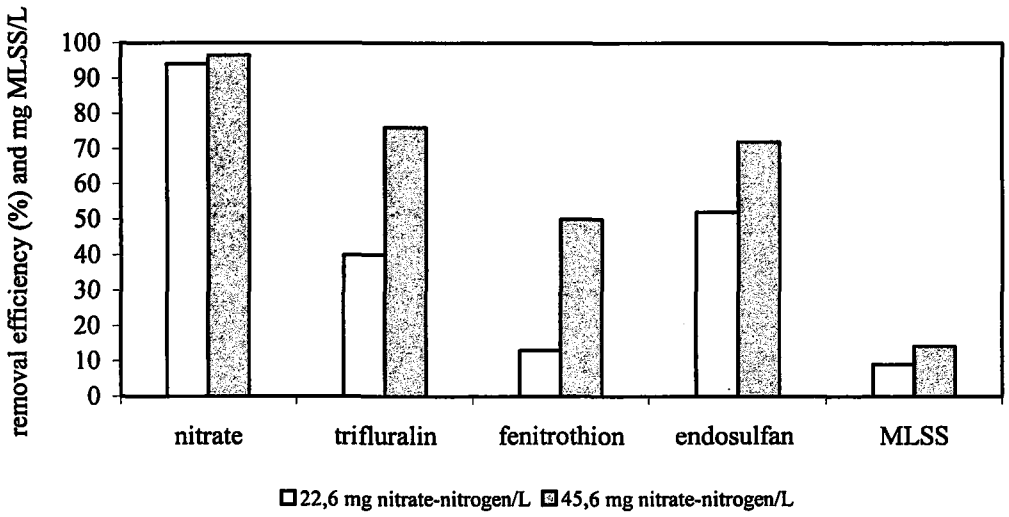


Figure 6.6.13 Nitrate and selected pesticides elimination and microbial growth in the biological denitrification batch unit

6.6.3.2.2 Biological Pesticides Mineralization in Biological Denitrification Reactor Using Medium Solution in Pure Water

The reactor was operated by feeding nitrate and pesticides containing solution at various hydraulic residence times, which was above 2 hours to avoid possible washout of denitrifiers from the reactor and low nitrate elimination. During the study, between 93 to 98 % of nitrate removal efficiency was observed and nitrite concentrations were quite low (below 0.16 mg/L) for θ_h values higher than 2 hours. Effluent nitrate and nitrite concentrations increased with decreasing θ_h. The reactor reduced nitrates from 100 mg/L concentration to the range of 1.5 to 9 mg NO_3/L for various θ_h. Because of the low contact time, microorganisms were washed out and excess amount of ethanol, which was not consumed by denitrifiers, was released from the reactor when hydraulic residence time was 2 hours (Figure 6.6.14) (experiments raw data at appendixes 9.5.5, 9.5.6, 9.5.7). During the study, effluent water temperature was 19±1 ^{0}C and pH between 7.7-8.4. Dissolved oxygen concentration was below 0.3 mg/L in the biological denitrification reactor.

Effluent TOC increased from the 5 mg/L at 6.8 hours to about 15 mg/L at 2 hours residence time. As can be seen from the Figure 6.6.15, no significant nitrate removal efficiency improvements were observed with the θ_h was higher than 2.5 hours. On the other hand TOC removal was better. Variation of effluent MLSS concentrations and turbidity with hydraulic residence time are depicted in Figure 6.6.16

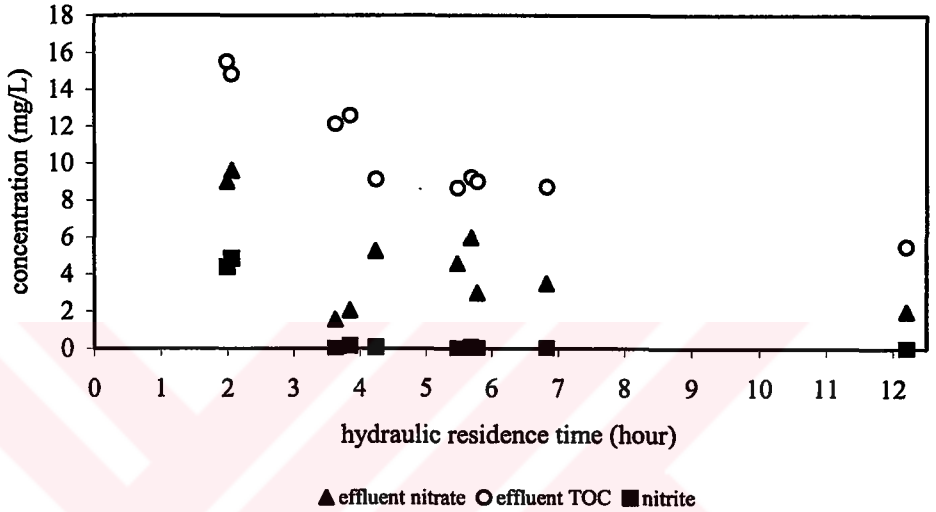


Figure 6.6.14 Effluent nitrate and TOC concentrations for various θh

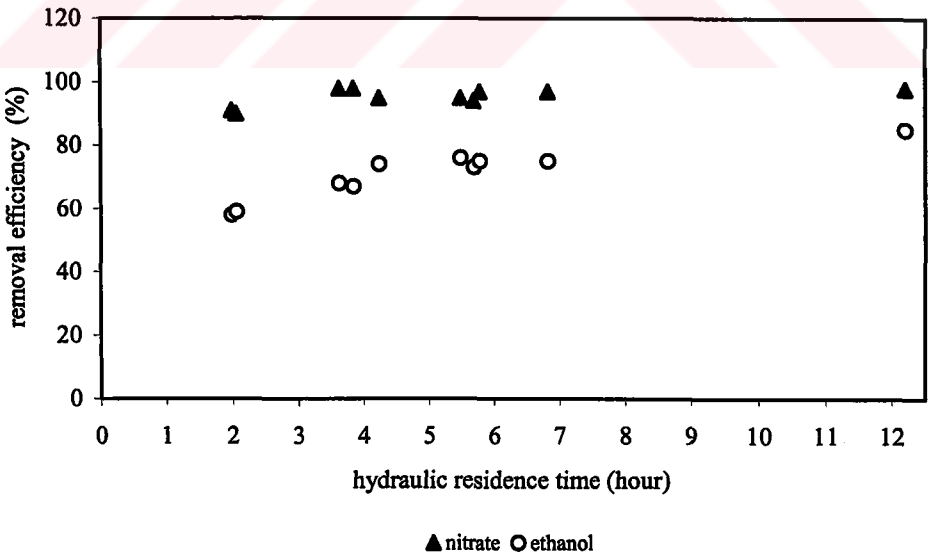


Figure 6.6.15 Nitrate and ethanol removal values for various θh

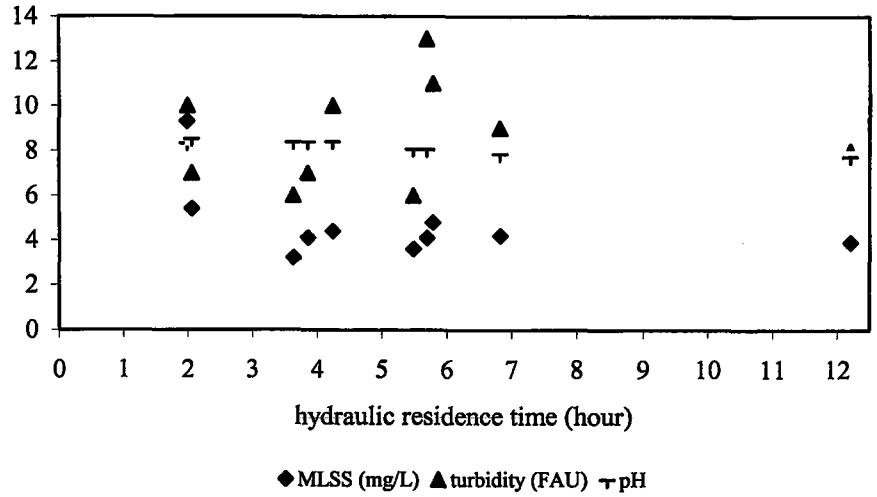


Figure 6.6.16 MLSS concentrations, turbidity of the effluent water for various θ_h values

The highest trifluralin, fenitrothion, and endosulfan ($\alpha+\beta$) removal efficiencies were observed at θ_h =12h. Although no significant improvement in nitrate and organic carbon eliminations were observed at θ_h=12 hours, 100% of pesticides elimination was obtained. This may mean that pesticides are used as carbon source for microorganisms at high residence time.

In this part of the study, higher than 95, 91, and 95 % removal efficiencies were observed for trifluralin, fenitrothion, and endosulfan ($\alpha+\beta$), respectively when θ_h was lower than 12 hours. Although the high pesticides removal efficiencies were obtained using packed column biological denitrification reactor, effluent water could not be used for drinking purpose, because of the total pesticides concentrations when the θ_h was lower than 12 hours (Figure 6.6.17-18). Effluent pesticides concentrations increased with decreasing hydraulic residence times.

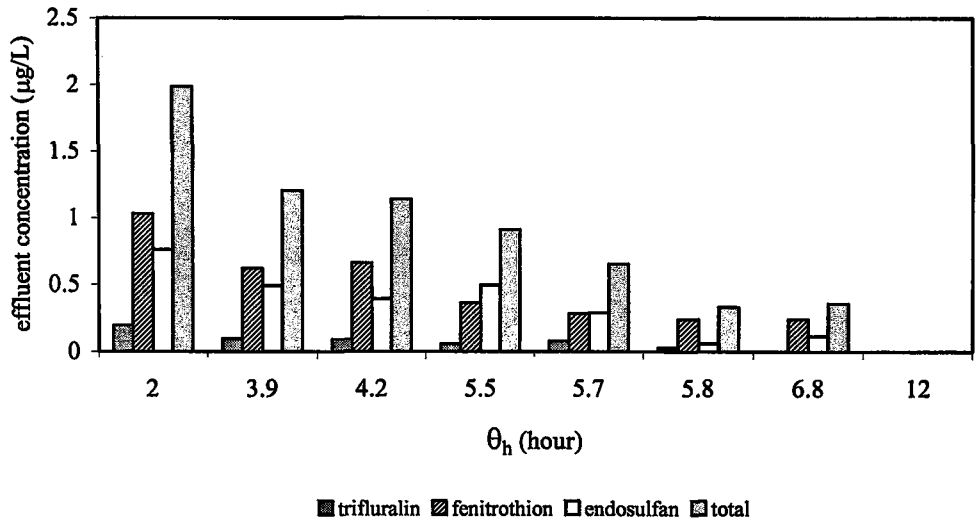


Figure 6.6.17 Pesticides concentrations in the effluent water for various θ_h

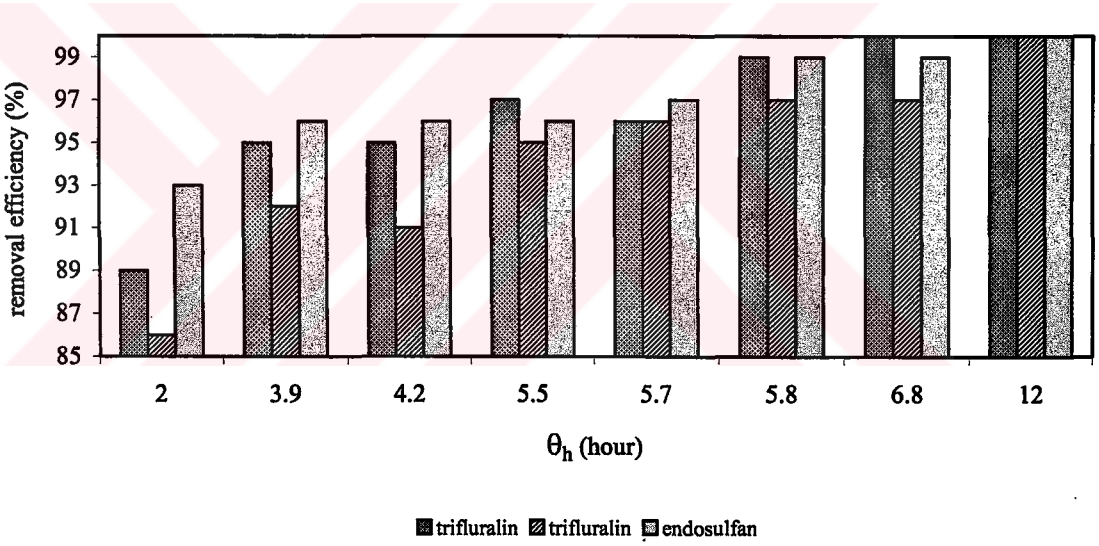


Figure 6.6.18 Pesticides removal efficiency in the biodenitrification reactor for various θ_h

The highest pesticides exit from the reactor occurs when the nitrate removal efficiency is too low at θ_h =2h.

Although high removal efficiency (higher than 95 %) was obtained at 5.5 hours residence time, effluent water still contains unacceptable total pesticides concentrations (>0.5 µg/L). Increasing hydraulic residence time above 5.7 hours resulted lower pesticides concentration than the limit value in effluent.

Considering the nitrate and pesticides elimination in the biological denitrification reactor, hydraulic residence time was the most important parameter. No significant improvement in nitrate elimination was observed when θ_h>2.5 hours, but effluent pesticides concentrations were not acceptable level. Pesticides elimination was the critical restrictive parameter in this system. Breakdown products of the endosulfan were not detected in the effluent water during the study. It was assumed that they were below the detection limits.

6.6.3.2.3 Effect of Slow Sand Filter on Nitrate and Pesticides Elimination

The effluent from the biological reactor was given to slow sand filter unit. In slow sand filter significant nitrate elimination was obtained when the effluent from the biological unit include sufficient TOC. Nitrite was not observed. The pH of the effluent from slow sand filter was slightly lower than the effluent of the biological unit. The slow sand filter system improved the quality of the denitrified water considerably. Significant MLSS (about ≈ 60- 86 %) removal was observed as expected. Experimental results of the slow sand filter effluent are depicted in Figure 6.6.19.

Because selected pesticides have a moderate capacity to adhere to soils, some of them were removed in the slow sand filter unit. Pesticides in the effluent water were measured for 5.7, 5.5, and 6.8 hours θ_h values, and pesticides concentrations in the effluent of the reactor was very close to the limit value. Pesticides concentrations were reduced between 20-55% by using slow sand filter for various θ_h values.

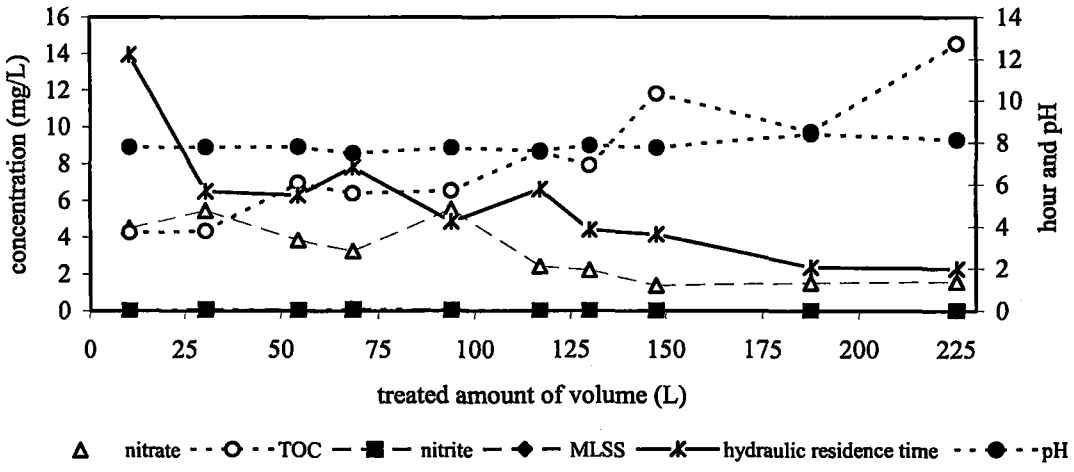


Figure 6.6.19 Characteristics of the effluent water of slow sand filter unit

6.6.3.2.3 Biological Pesticides Mineralization in the Biological Denitrification Reactor Using Tap Water

The performance of the biological denitrification reactor was also evaluated using tap water. In this part of the study, medium solution was prepared by using tap water whose composition is given in Table 6.1.

Table 6.1 Composition of the tap water

Components	Concentrations
Total hardness	240 mg $CaCO_3$/L
Ca^{++}	44 mg/L
Mg^{++}	32 mg/L
Total alkalinity	116 mg $CaCO_3$/L
Cl^-	40 mg/L
Electrical conductivity	335 μmhos
pH	7
AOX	150-190 μg/L
TOC	3-5 mg/L

The reactor was operated by feeding nitrate and pesticides solution. In the study, about 99% of nitrate removal was observed, but most of the samples included nitrite (Figure 6.6.20 and 21) (data at appx. 9.5.8-9.5.10). Using biodenitrification unit, nitrate concentration in the effluent water was in the range of 0-5.5 mg/L. During the study, because of the temperature oscillation, nitrate concentration decreased to the 37 mg/L (removal efficiency was 63%), but high nitrite washout occurs from the reactor. Temperature was an important parameter on the nitrate removal and nitrite formation.

Different mechanisms have been found to be responsible for nitrite accumulation, like repression of the nitrite reductase synthesis in the presence of oxygen (Gomez et al., 2000 and 2002) or inhibition of the enzymatic activity by pH.

When the temperature dropped sharply from 18 ^{0}C to 14 ^{0}C, the lowest removal efficiency of nitrate was 63 %. 73, 77, and 80 % removal for trifluralin, fenitrothion and endosulfan (α+β), respectively, was observed and the highest nitrite concentration (16 mg/L) was determined in effluent of the reactor (Figure 6.6.20 and

6.6.23). In the study up to 95 % removal of pesticides were observed. However effluent water still could not meet the requirements of drinking water. Pesticides removal yields of the biological denitrification reactor are given in Figure 6.6.24. Breakdown products of the endosulfan were not detected in the effluent water. It was assumed that they were below the detection limits.

In this series of experiments although the reactor was worked at 14 ^{0}C, nitrate and pesticides elimination were quite high. When the temperature was stable at 14 ^{0}C, denitrification organisms were not negatively affected except for lower than 10 ^{0}C. Temperature oscillation affects the denitrifiers activities (Figure 6.6.8).

Volokita et al. (1996) also mentioned about the temporary breakthrough effects on the nitrate removal performance. In the newsprint packed columns, nitrate removal rate at 14 ^{0}C was approximately one-third of the rate of observed at 32 ^{0}C. Because of the temperature oscillation, nitrate elimination decreased from 99.9% to 63% and high nitrite washout occurs from the reactor.

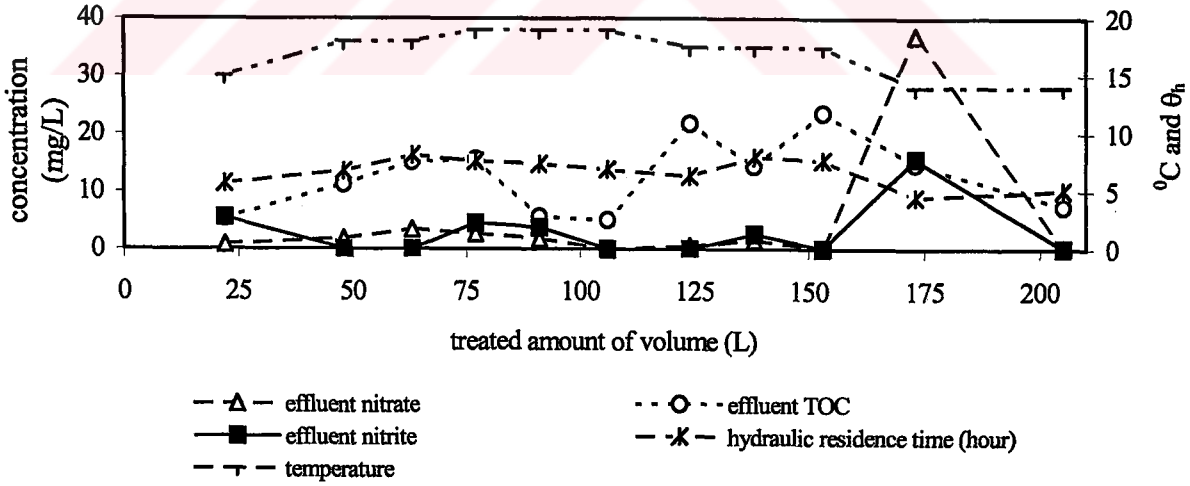


Figure 6.6.20 Effluent nitrate, nitrite and TOC concentrations for various θh and water temperature values

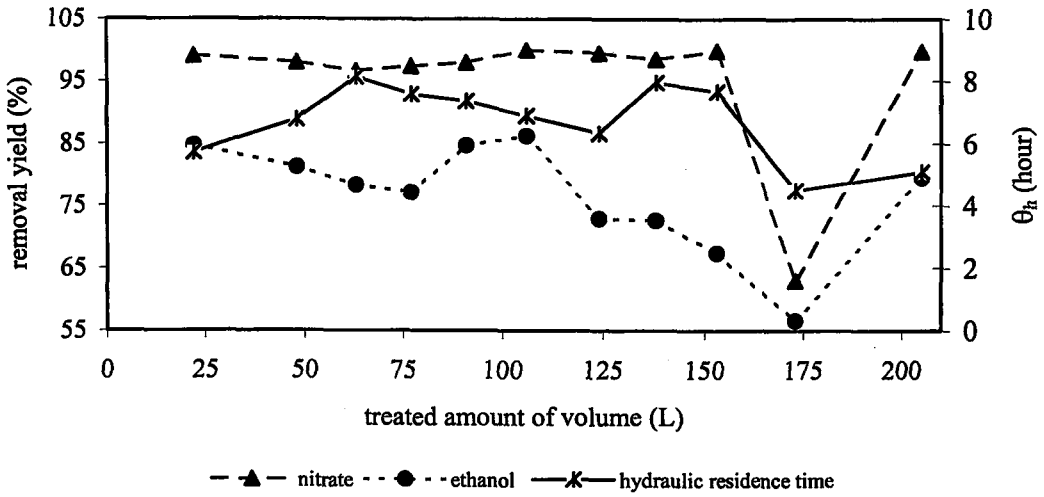


Figure 6.6.21 Nitrate and ethanol removal efficiency for various θh

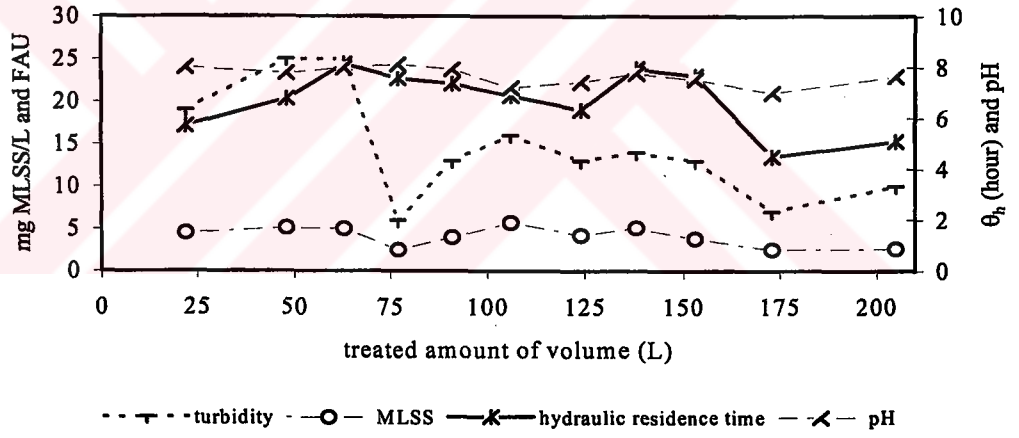


Figure 6.6.22 MLSS concentrations, turbidity and temperature of the effluent water

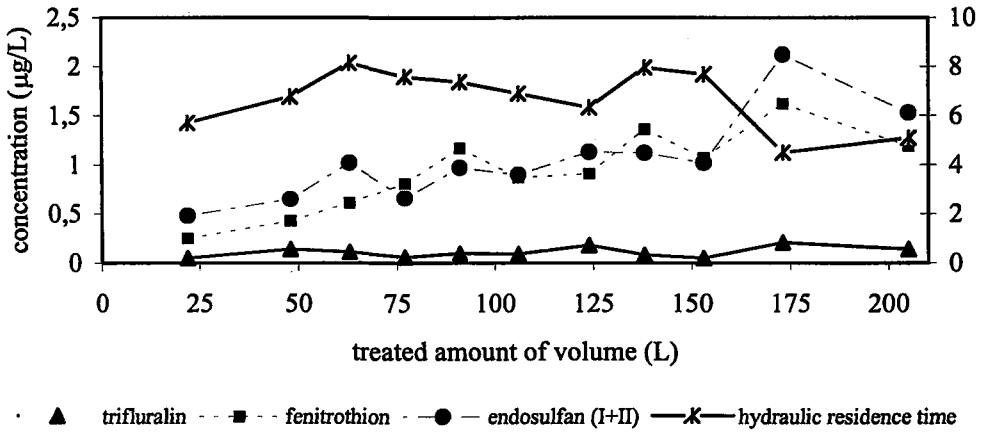


Figure 6.6.23 Pesticides concentrations in the effluent water from the biological denitrification unit

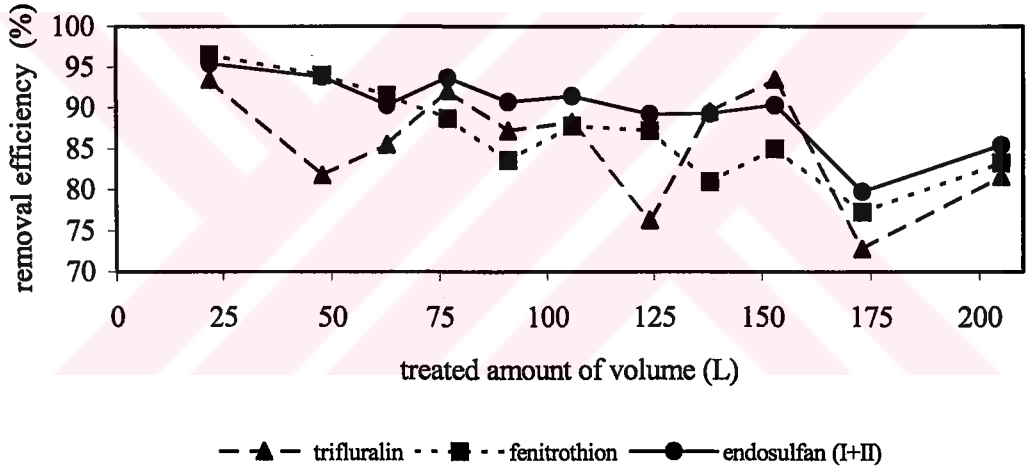


Figure 6.6.24 Pesticides removal efficiency in the biodenitrification reactor

In this part of the study, high nitrate elimination so as to meet drinking water standards was observed, despite the negative effects of the temperature. But pesticides concentrations were not at acceptable level and nitrite was the problem in the effluent water. About 20 % of the remaining NO_3 was removed, no nitrite was observed and significant turbidity was eliminated in the slow sand filter unit (6.6.25). A significant variation was observed in NO_3 concentration and turbidity at the slow sand filter outlet. Pesticides removal rated between 24 and 42 % of in the slow sand filter unit at θh value between 4.5-7.5.

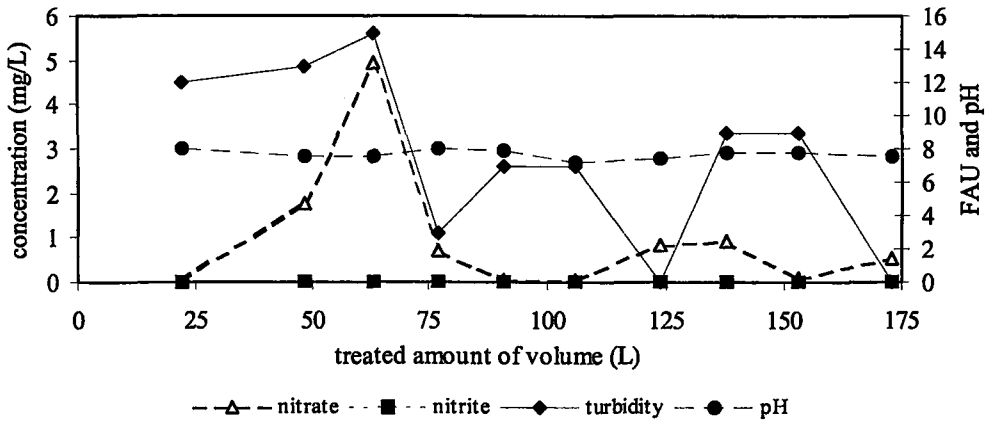


Figure 6.6.25 Characteristics of effluent water from the slow sand filter unit

CHAPTER SEVEN
CONCLUSIONS and RECOMMENDATIONS

7.1 Conclusions

In order to determine pesticides adsorption capacities of the various natural organic solid substrates and to compare with activated carbon, batch adsorption experiments were carried out.

As expected, activated carbon has higher adsorption capacities than has NOSS except for trifluralin, which indicates that approximately same adsorption capacities for activated carbon and various NOSS's. As a result of the study the removal of pesticides on NOSS and activated carbon are indicating following order of decreasing efficiency; trifluralin > endosulfan > fenitrothion

Batch experiments were performed with various substances like poplar, hornbeam, pine shaving, and wheat straw to select suitable carbon source for biodenitrification reactor. As a result of the batch study, wheat straw was selected as carbon source and support particles for biological denitrification reactor for further studies because the highest nitrate removal.

The high nitrate-nitrogen elimination was observed using wheat straw; since released DOC concentration was sufficient for biological denitrification. Although the high removal efficiency was observed for the selected pesticides using the biological denitrification packed with wheat straw and sand filter unit, the effluent water could not be used for drinking purposes because of the unacceptable level of pesticides, colour problem and dissolved organic content, especially during the first days of operations.

As a result of the experiments, high nitrate and average 98, 95, and 90 % removal efficiencies are obtained using wheat straw for trifluralin, fenitrothion, and endosulfan ($\alpha+\beta$), respectively, but, the post treatment such as activated carbon adsorption should be applied to the effluent water from the biological denitrification and sand filter system when the effluent water is to be used for drinking purpose.

A series of experiment was designed to investigate optimum carbon to nitrate ratio for acetic acid and ethanol and to define the most suitable carbon source for biological denitrification experiment. The optimum acetic acid and ethanol to nitrate ratio was found to be 1.61 and 1.35, respectively. At the optimum C/N ratio, the nitrate and carbon removal efficiencies were above 90% for both of the carbon sources. At C/N ratios below the optimum value, the nitrate removal yield was found to be dependent upon the carbon concentrations, causing a significant falls in the nitrate elimination due to lack of sufficient organic substance in the batch unit. When C/N ratio for acetic acid was 1.4 and below, nitrite was observed. The main disadvantage of acetic acid, as compared to other carbon source is its high consumption. As a result of the batch experiments ethanol was selected as a carbon source for the continuation of the study.

Considering the results of the batch and continuous experiments, carbon/nitrogen ratio, pH, temperature, and the hydraulic residence time are very important in assessing the overall efficiency of the nitrate and pesticides removal yield.

The optimal pH values lie between 5-9 in the batch unit and nitrate and ethanol removal efficiencies were about 90% and 70%, respectively. Biological performance decreased sharply below and above this range in the batch unit. The denitrification activity was found to be a function of temperature. The hydraulic residence time dependence of the biological reaction is very important in assessing the overall efficiency of the nitrate and pesticides removal.

By applying slow sand filter significant MLSS and nitrate eliminations were obtained and nitrite was not observed. Because selected pesticides have a moderate capacity to adhere or adsorb to soils, some part of them were removed in the sand

filter unit. Removal efficiency of pesticides was between 20-55% in slow sand filter unit.

7.2 Recommendations

Since pesticides and nitrate pollution of drinking water takes place mainly in rural areas of Turkey, this study has been performed considering small communities i.e. water treatment plants of villages.

As a result of the study it can be concluded that an additional treatment will be necessary to meet the drinking water standards. Thus in addition to biodenitrification and slow sand filter units like activated carbon adsorption will be necessary. It has should be pointed out that the operating conditions of the water treatment plant will be different than lab-scale units. It is expected that better operating conditions will be achieved in drinking water treatment plant since in the laboratory conditions, adjustment of water flow rate was a problem.

The slow sand filter unit is suitable for small water treatment system in order to improve effluent water quality. It is worked as a post treatment unit for microorganisms, which were released from the biodenitrification unit. In addition, organic materials like pesticides, which have a capacity to adhere onto the sand, can be removed from the effluent from the biological unit using slow sand filter.

Following recommendations may be given for further studies;

1. Various natural organic solid substrates as carbon source may be evaluated for biological denitrification studies.

2. The system may be operated with real groundwater including pesticides and nitrate contamination.

3. Various bacterial or fungal species may be used for effective pesticides removal.

4. Pesticides adsorption studies may be carried out using low-cost adsorbents like natural materials.

CHAPTER EIGHT

REFERENCES

8. References

Abacı, S., (1997). Groundwater Quality Problems for Domestic Use, Proceedings of the International Conference on Water Problems in the Mediterranean Countries, II, 799-804.

APHA, AWWA, WPCF (1985). Standard Methods for the Examination of Water and Wastewater, 16th Edition. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Aslan, S., Türkman, A., Övez, B., Yüksel, M., Sağlam, M., Alyanak, İ., (2001). Ege Bölgesi, Urla ve Menemen Yöresinde Yeraltısuyu Kirliliğinin Belirlenmesi, 1.Çevre ve Jeoloji Sempozyumu, Izmir, 125-131.

Aspelin, A.L., (1997). Pesticides Industry Sales and Usage: 1994-95 Market Estimates, U.S. Environmental Protection Agency, Washington, DC.

Avcı, M., (1988). Bornova Ovasında Mevcut Çöp ve Katı Atıkların Bertarafi, DEU Çevre Mühendisligi Bölümü Bitirme Projesi.

Awasthi, N., Ahuja, R. and Kumar, A., (2000). Factors influencing the degradation of soil-applied endosulfan isomers, Soil Biology δ Biochemistry, 32, 1697-1705.

Badriyha, B. N., (1996).Advanced Oxidation Processes, Carbon Adsorption, and Biofilm Degradation of Synthetic Organic Chemicals in Drinking Water, PhD, Thesis, Faculty of the Graduate School, University of Southern California).

Balinova, A. M., Mondesky, M., (1999). Pesticide Contamination of Ground and Surface Water In Bulgarian Danube Plain, Journal of Environmental Science Health, B34 (1), 33-46.

Balinova, A., (1996). Strategies for Chromotographic Analysis of Pesticide Residues in Water, Journal of Chromotoraphy A, 754 ,125-135.

Balszczyk, M., Przytocka, M., and Mycielski, R., (1981). Denitrification of High Concentrations of Nitrites and Nitrates in Synthetic Medium with Different Sources of Organic Carbon, Acta Microbiologica, Polonica, 30, 49-58.

Barreiros, A.M., Rodrigues,C.M., Crespo, J.P.S.G., and Reis, M.A.M., (1998). Membrane Bioreactor for Drinking Water Denirification, Bioprocess Engineering, 18, 297-302.

Bending, G. D., Friloux, M., and Walker, A., (2002). Degradation of Contrasting Pesticides by White Rot Fungi and its relationship with Ligninolytic Potential, FEMS Microbiology Letters, 10507, 1-5.

Boley, A., Müller, W-R. and Haider, G., (2000). Biodegradable Polymers as Solid Substrate and Biofilm Carrier for Denitrification in Recirculated Aquaculture Systems, Aquacultural Engineering, 22, 75-85.

Bras, I., P., L., Santas, and Alves, A., (1999). Organochlorine Pesticides Removal by Pinus Bark Sorption, Environmental Science and Technology, 33, 631-634.

Brereton, C., House, W. A., Armitage, P. D. and Wotton, R. S., (1999). Sorption of Pesticides to Novel Materials; Snail Pedal Mucus and Black fly Silk, Environmental Pollution, 105, 55-65.

Briggs, S. A. (1992) Basic Guide to Pesticides: Their Characteristics and Hazards. Hemisphere Publishing Corp. Washington, Philadelphia, London.

Celik, M. and Arıgun, Z., (2001). Yerköy (Yozgat) Ovası Yüzey ve Yeraltısularının Kalitesi ve Kirliliği, 1. Çevre ve Jeoloji Sempozyumu, Izmir, 159-172.

Columé, A., Cárdenas, S., Gallego, M. and Valcárcel, M.,(2001). Evalutaion of an Automated Solid-Phase Extraction System for the Enrichment of Organochlorine Pesticides from Waters, Talanta, 54, 943-951.

Colina C., Rasero, S. F., Cancela, G. D., Taboada, R. E., and Pena, A., (1995). Use of Solid Phase Extraction Method for the Anlysis of Pesticides in Groundwater by Gas Chromatography with Electron Capture and Flame Photometric Detectors, Analyst, 120, 1723-1728.

Colina C., Rasero, S. F., Dios, G., Romero, E., and Pena, A., (1997). Effect of Storage on the Recovery of Different Types of Pesticides Using a Solid-Phase Extraction Method, Analyst, 122, 7-11.

Csandy, M. and Straub, I., (1995). Health Damage due to Water Pollution in Hungary, IAHS Wallingford 233, 147-152.

Dahab, M.F. and Sirigina, S., (1994). Nitrate Removal From Water Supplies Using Biodenitrification and GAC-Sand Filter System, Water Science and Technology, 30, 9, pp. 133-139.

Dahab, M. F. and Kalagari, J., (1996). Nitrate Removal from Drinking Water Using Cyclically Operated Fixed-Film Bio-Denitrification Reactors, Water Science and Technology, 34, 1-2, 331-338.

Delange, B., Nakamura, F., Myoga, H., Magarat, Y., and Guibal, E., (1994). Drinking Water Denitrification in a Membrane Bioreactor, Water Science and Technology, 30, 6, 157-160.

Delen, N., Tosun, N. and Yıldız, Z., (1998). Türkiye'de Tarım İlacı Kullanımı ve Bu Kullanımın Büyük Menderes Havzası Açısından Değerlendirilmesi, Büyük Menderes Havzası 3. Tarım ve Çevre Sempozyumu, 2-4 Eylül, Söke-Aydın

DSİ (2000). Devlet Su İsleri'nin Tanıtımı, Ankara.

Eisentraeger, A., Klag, P., Vansbotter, B., Heymann, E., and Dott, W., (2001). Denitrification of Groundwater with Methane as Sole Hydrogen Donor, Water Research, 35, 9, 2261-2267.

EPA (1990). Natioanl Survey of Pesticides in Drinking Water Wells, Phase 1 report, November.

Fan, A.M. and Steinberg, V. E., (1996). Health Implications on Nitrate and Nitrite in Drinking Water : an update on methaemoglobinemia occurrence and reproductive and development Toxicity, Regul. Toxicol., Pharmacol, 23 (1 part 1) 35-43.

Feleke, Z. and Sakakibara, Y., (2001). Nitrate and Pesticide Removal by a Combined Bioelectrochemical/Adsorbtion Process, Water Science and Tchnology, 43, 11, 25-33.

Fonseca, A.D., Crespo, J.G., Almedia, J.S., and Reis, M.A., (2000). Drinking Water Denitrification Using A Novel Ion-exchange Membrane Bioreactor, Environmental Science Technology, 34, 1557-1562.

Foster, D.B., Mice, M.A., Raschal, A.J., and White, S.L., (1991). New Treatment Process for Pesticides and Chlorinated Organics Control in Drinking Water, J.IWEM, 5, August, 466-477.

Geyikçi, F. and Büyükgüngör, H., (2002). The Research of Pollution Spring and Surface Waters Caused by Benzene Hegzachloride Isomers and Benzene Hegzachloride which are Organic Chlorinated Pesticides, Çevre Bilimleri, Sayı 5, 39-45.

Goebel, H., Gorbach, S., Knauf, W., Rimpau, R. H., Huttenbach, H., (1982). Properties, Effects, Residues and Analytics of the Insecticide Endosulfan, Residue Reviews 83, 1-122.

Gomez, M. A., Gonzales-Lopez, J., Hontorie-Garcia, E., (2000). Influnce of Carbon Source on Nitrate Removal of Contaminated Groundwater in a Denitrifying Submerged Filter, Journal of Hazardous Materials, B80, 69-80.

Gomez, M. A., Hontorie-Garcia, E., Gonzales-Lopez, J., (2002). Effect of Oxygen Concentration on Nitrate Removal from Groundwater using a Denitrifying Submerged Filter, Journal of Hazardous Materials, B90, 267-278.

Green, M., Schnizer, M., Tarre, S., Bogdan, B., Shelef, G. and Sorden,C. J., (1994a). Groundwater Denitrification Using an Upflow Sludge Blanket Reactor, Water Research, 28, 3, 631-637.

Green, M., Schnizer, M., Tarre, S., Bogdan, B., Shelef, G. and Sorden,C. J., (1994b). Fluidized Bed Reactor Operation for Groundwater Denitrification, Water Science Technology, 29, 10-11, 509-515.

Guerrero, V.N.R., Taylor, M.G., Davies, N.A, Lawrence, M.A.M., Edwards, P.A., Simkiss, K., and Wider, E.A., (2002). Evidence of Differences in the Biotransformation of Organic Contaminants in three Species of Freshwater Invertebrates, Environmental Pollution, 117, 523-530.

Gullon, M. I. And Font R., (2002). Dynamic Pesticide Removal with Activated Carbon Fibers, Water Research, 35, 2, 516-520.

Gökçe, O., Kaya, F. and Atış, İ. (2001). Tarımda Yeraltısuyu Kullanımı ve Cevre İliskileri: Izmir ve Manisa İlleri Örnegi, 1. Cevre ve Jeoloji Sempozyumu, Izmir, 77-82.

Hallberg, R., (1987). Agricultural Chemicals in Groundwater: Extent and Implications, American Journal of Alternative Agriculture, 2(1), 3-15.

Hiscock, K., M., Lloyd, J., W., and Lerner, D., N., (1991). Rewiev of Natural and Artificial Denitrification of Groundwater, Water Research, 25, 1099-1111.

Howard, P. H., (1991) Ed. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Vol 3, Pesticides. Lewis Publishers, Boca Raton, FL.

Hudson, R. H., Tucker, R. K. and Haegele, M. A., (1984). Handbook of Toxicity of Pesticides to Wildlife. Resource Publication 153. U.S. Department of the Interior, Fish and Wildlife Service, Washington, DC, 10-64.

INCO-DC Project, (1997). Development of a Simple Technology in Drinking Water Treatment for Nitrate and Pesticide Removal, Contract No EU Project: ERBIC18CT970167.

Johnson, W.W. and Finley, M.T., (1980). Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates, Resource Publications, 137, U.S. Department of the Interior, Fish and Wildlife Service, Washington, D.C.

Kaçaroğlu, F. and Günay, G., (1997). Groundwater Nitrate pollution in an Alluvium Aquifer, Eskisehir Urban Area and its Vicinity, Turkey, Environmental Geology, 31 (314), June.

Karaguzel, R. and Irlayıcı, A., (1998). Groundwater Pollution in Isparta Plain, Turkey, Environmental Geology, 34 (4), June 1998.

Karaguzel, R and Scholz B. E. (1999). Hydrogeological Investigation of Antalya Basin Concerning the Future Domestic Water Needs of Antalya City (Turkey), Environmental Geology 38 (2) July 1999.

Karamfilow, V. K., Fileman, T. W., Evans, K. M. and Mantaura, R. F. C., (1996). Determination of Dimethoate and Fenitrothion in Estuarine Samples by C-18 Solid Phase Extraction and High resolution Gas- Chromatography with Nitrogen-Phsophhorus Detection, Analytica Chimica Acta, 335, 51-61.

Kamrin, A. M.,(Eds.) (1997). Pesticide Profiles, Toxicity, Environmental Impact, and Fate, Baco Raton, ISBN 1566701902.

Kidd, H. and James, D. R., (Eds.) (1991) The Agrochemicals Handbook, Third Edition. Royal Society of Chemistry Information Services, Cambridge, UK, (as updated), 5-14.

Kikuchi, R., Yasutaniya, T., Takimoto, Y., Yamada, H., and Miyamoto, J. (1984) Accumulation and Metabolism of Fenitrothion in Three Species of Algae, J. Pestic. Sci., 9: 331-337.

Koenig, A. and Liu, L.H., (2001). Kinetic Model of Autotrophic Denitrification in Sulphur Packed-Bed Reactors, Water Research, 35, 8, 1969-1978.

Kraemer, M. Baumgaertner, M., Bender, M., and Conrad, R. (1990). Consumption of NO by Methanotrophic Bacteria in Pure Culture an in Soil. FEMS Microbial Ecol. 73 (4), 345-350.

Lacorte, S., Ehresmann, N., and Barcelo, D., (1995). Stability of Organophosphorus Pesticides on Disposable Solid-Phase Extraction Precolumns, Environmental Science and Technology, 29, 2834-2841.

Lal, S., Lal, R. and Saxena, D., M., (1987) Bioconcentration and Metabolism of DDT, Fenitrothion and Chlorpyrifos by the Blue-green Algae *Anabaena* sp. and *Aulosira fertilissima.* Environ. Pollut., 46: 187-196.

Lee, D, Lee, I., Choi, Y., and Bae, J., (2001). Effect of external Carbon Source and Empty Bed Contact Time on Simultaneous Heterotrophic and Sulfur-Utilizing Autotrophic Denitrification, Process Biochemistry, 36, 1215-1224.

Lin, H.S. and Wu, C.L., (1996). Removal of Nitrogenous Compounds from Aqueous Solution by Ozonation and Ion Exchange, Water Research, 30, 8, 1851-1857.

Liska, I. and Bilikova K., (1998). Stability of Polar Pesticides on Disposable Solid-Phase Extraction Precolumns, Journal of Choromatography A, 795, 61-69.

Liu, L.H. and Koenig, A., (2002). Use of Limestone for pH Control in Autotrophic Denitrification: Batch Experiments, Process Biochemistry, 37, 885-893.

Lopez F. J., Beltran, J., Forcana, M. and Hernandez, F., (1998). Comparison of Simplified Methods for Pesticide Residue Analysis use of Large-Volume Injection in Capillary gas Chromatography, Journal of Choromatography A, 823, 25-33.

Lu, F. C., (1995). A Review of The Acceptable Daily Intakes of Pesticides Assessed By The World Health Organization. Regul. Toxicol.Pharmacol. 21, 351-364.

Mac Rae,I.,C., (1985). Removal Of Pesticides in Water by Microbial Cells Adsorbed To Magnetite, Water Research, 19, 7, 825-830, 1985.

Maguire, R. J. and Hale, E. J., (1980) Fenitrothion Sprayed on a Pond: Kinetics of Its Distribution and Transformation in Water and Sediment. J. Agric. Food Chem., 28: 372-378.

Maguire,R.J., (1992). The Importance of Pesticide Volatilization from the Surface Microlayer of Natural Waters After Aerial Spraying, Water Science Technology, 25, 11, 111-116.

Mallet, V. N., (1980) A Chemical Residue Survey in Relation to the 1980 Spruce Budworm Spray Program in New Brunswick, Moncton, Canada, University of Moncton, Chemistry Department, 54 pp (Report No. 80-CP-18).

Mansell, B.O. and Schroeder, E.D., (1999). Biological Denitrification in a Continuous Flow Membrane Reactor, Water Research, 33, 8, 1845-1850.

Mansour, M., (1993). Fate Prediction of Environmental Chemicals in Soils, Plants and Aquatic Systems, Lewis Publishers, Boca Raton, ann Arbor (USA), London, Tokyo.

Mansour, M., Scheunert, I., and Korte, F., (1993). Fate of Persistent Organic Compounds in Soil and Water, NATO ASI Series G, Springer Verlag, Berlin, Heidelberg, 111.

Marshall, W. K. and Robert, J. R., (1977) Simulation Modelling of the Distribution of Pesticides in Ponds. In: Proceedings of a Symposium on Fenitrothion, Ottawa, National Research Council of Canada, 253-278 (Publication NRCC No. 16073).

Matatov-Meytal, Y., Barelko, V., Yuranov, I., Kiwi-Misker, L., Renken, A., and Sheintuck, M., (2001). Cloth Catalysts for Water Denitrification II. Removal of Nitrates Using Pd-Cu Supported on Glass Fibers, Applied Catalysis 3: Environmental, 31, 233-240.

Mirvish, S. S., (1991). Formation Properties and Significance for Human Health of Nitrate, Nitrite and N-nitroso compounds, in Nitrate Contamination; Exposure, Consequences, and Control, NATO ASI Series, vol G30, eds. I Bogardi and R.D. Kuzelska. Springer verlag, Berlin.

Miyamoto, J., (1977). Degradation of Fenitrothion in Terrestrial and Aquatic Environments Including Photolytic and Microbial Reactions. In: Proceedings of a Symposium on Fenitrothion, Ottawa, National Research Council of Canada, pp. 105-109 (Publication NRCC No. 16073).

Mohsani-Bandpi, M. A., Elliott, D. J., and Memeny-Mazdek, A., (1999). Denitrification of Groundwater Using Acetic Acid as a Carbon Source, Water Science and Technology, 40, 2, 53-59.

Moraes Suarez Varela, M. M. Llopis Gonales, A., and Tejerizo Perez, M. L., (1995). Impact of Nitrates in Drinking Water on Cancer Mortality in Valencia, Spain, Eur. J. Epidemiol., 11 (1). 15-21.

Morin, R., Gabcury, G. and Manarbachi, G. (1986). Fenitrothion and Aminocarb Residues in Water and Balsam fir Foliage Following Spruce Budworm Spraying Programs in Quebec, 1979-1982. Bull. environ. Contam. Toxicol., 36: 622-628.

Mutlu, I., Mutlu, T., Demirpence, G., and Boybay, M., (1999). The Investigation of Quality Level of Drinking Water in Elazıg and Environment, Kent Yönetimi İnsan ve Çevre Sorunları Sempozyumu, İstanbul, 179-185.

Nuhoğlu, A., Pekdemir, T., Yıldız, E., Keskinler, B. and Akay, G., (2002). Drinking Water Denitrification by a Membrane Bio-Reactor, Water Research, 36, 1155-1166.

Ormad, P., Cortes, S., Puig, A., and Ovelleiro, J.L., (1997). Degradation of Organochloride Compounds by O_3 and O_3/H_2O_2, Water Research, 31, 9, 2387-2391.

Ozcelik,S. and Sarıiz, K., (2001). Eskisehir Ovası Yeraltısuyu Kirliliginde 1995 Sonrası Olumlu Gelismeler, 1. Cevre ve Jeoloji Sempozyumu, 21-23 Mart 2001, Izmir, 231-246.

Pimentel, D., Acquay, H., Biltonen, M., Rice, P., Silva, M., Nelson, J., Lipner, V., Giordano, S., Horowitz, A., D'Amore, M., (1992). Environmental and Human Costs of Pesticide Use, Bioscience, 42, 750-760.

Pimentel, D., (1996). Green Revolution Agriculture and Chemical Hazards, Sci. Tot. Environ, 188, S86-S98).

Pimentel, D. and Greiner, A., (1997). Environmental and Socio-economic Costs of Pesticide Use, In. Pimentel, D., (Ed.), Techniques for Reducing Pesticide Use: Economic and Environmental Benefits. John Wiley and sons, Chichester, pp.51-78.

Pirbazari, M., Badriyha, B.N., Kim, S.H., and Miltner, R.J., (1992). Evaluating GAC adsorber for the removal of PCBs and toxaphane, J. Amer. Water Works Assoc., 84,(2): 83-90.

Quest, J. A., Phang, W., Hamernic, K. L., et al., (1989). Evaluation of the Carcinogenic Potantial of Pesticides, 1.Acifluorfen. Regul. Toxicol. Pharmacol., 10, 149-159.

Quintana, J., Marti, I. and Ventura, F, (2001). Monitoring of Pesticides in Drinking and Related Waters in NE Spain with a Multiresidue SPE-GC-MS Method Including an Estimation of the Uncertainty of the Analytical Results, Journal of Chromatography A, 938, 3-13.

Rajapakse, J., P., and Scutt, J., E., (1999). Denitrification with Natural Gas and Various New Growth Media, Water Research, 33, 18, 3723-3734.

Richard, Y., R., (1989). Operating Experience of Full-scale Biological and Ion-exchange Denitrification Plants in France, J. Inst. Water Environmental Management, 3, 154-165.

Rioboo, C., Franqeira, D., Canle, M.L., Herrero, C., and Cid, A., (2001). Microalgal Bioassays as a Test of Pesticide Photodegradation Efficiency in Water, Environmental Contamination and Toxicology, 67, 233-238.

Rovedatti, M. G., Castane, P., M. Topalian, M. L., and Salibian, A., (2001). Monitoring of Organochlorine and Organophophorous Pesticides in the Water of the Reconquista River (Buenos Aires, Argentina), Water Research, 14, 3457-3461.

Shrimali, M. and Singh, K. P., (2001). New Methods of Nitrate Removal from Water, Environmental Pollution, 112, 351-359.

Soares, M. I. M., Abeliovich, A., (1998). Wheat Straw as Substrate for Water Denitrification, Water Research, 32, 12, 3790-3794.

Soares, M. I., (2002). Denitrification of Groundwater with Elemental Sulfur, Water Research, 36, 1392-1395.

Sorokin, D.Y., Kenen, J.G., Jetten, M.S.M., (2001). Denitrification at Extremely High pH Values by the Alkaliphilic, Obligately Chemolithoautotrophic, Sulfur-Oxidizing Bacterium Thialkalivibrio Denitrificans Strain ALJD, Arch Microbiol, 175, 94-101.

Spence, M.J., Bottrell, S.H., Higgo, J.J.W., Harrison, I., and Fallick, A.E., (2001). Denitrification and Phenol degradation in a Contaminated Aquifer, Journal of Contaminant Hydrology, 53, 305-318.

Spencer, E. Y. (1981). Guide to the Chemicals Used in Crop Protection. 7th edition. Publication 1093. Research Branch. Agriculture Canada.

Steen, R.J.C.A., Freriks, I.L. Cofino, W.P., Brinkman, U.A.Th., (1997) Chim. Acta 353, 153.

Sundaram, K.M.S., (1973) Degradation Dynamics of Fenitrothion in Aqueous Systems, Ottawa, Environment Canada, Forestry Service, Chemical Control Research Institute, 19 (Information Report CC-X-44).

Suzuki, T., Kondo, H., Yaguchi, K., Maki, T. and Suga, T., (1998). Estimation of Leachability and Persistence of Pesticides at Golf Courses from Point-Source Monitoring and Model to Predict Pesticide Leaching to Groundwater, Environmental Science Technology, 32, 920-929.

Tanabe, A., Mitobe, H., Kawata, K., Sakai, M., (1996). Monitoring Of Herbicides In River Water By Gas Chromatography-Mass Spectrometry and Solid-Phase Extraction, Journal of Chromatography A, 754, 159-168.

Tarre, S., Armon, R., Shelef, G., Shelef, G., and Green, M., (1994). Effects of Water Characteristics on Granular Sludge Formation in a USB Reactor for Denitrification of Drinking Water, Water Science Technology, 30, 9, 141-147.

TDWS, (1997) 4 Eylul 1988 Tarih ve 199/19 sayili Resmi Gazete

Teixeira, P. and Oliveira, R., (2001). Denitrification in a Closed Rotating Biological Contactor: Effect of Disk Submergence, Process Biochemistry, 37, 345-349.

Thomson, W. T. (1982). Insecticides, Acaricides, and Ovicides. Agricultural Chemicals. Book I. Thomson Publications, Fresno, CA., 5-23.

Thomson, T. S., (2001). Nitrate Concentration in Private Rural Drinking Water Supplies in Saskatchewan, Canada, Bull. Environmental Contamination and Toxicology, 66:64-70.

Till, A.B., Weathers, L.J., and Alvarez, P.J (1998). Fe^0 supported Autotrophic Denitrification, Environmental Science Technology, 32, 634-639.

Toller, G. and Flaim, G.M. (1988). A Filtering Unit for the Removal of Pesticide Residues from Aqueous Solutions, Water Research, 22, 5, 657-661.

Treavisan, M., Montepiani, C., Ragozza, L., Bartoletti, C., Ioannilli, E., Del Re, A., A., M., (1993). Pesticides in Rainfall and Air in Italy, Environmental Pollution, 80, 31-39.

Türkman, A. (1986). Groundwater Pollution by Sewerage Intrusion, Conference on Groundwater in Arid and Semiarid Regions, 5-8 May, Water Research and Study Center, Amman, Jordan

Türkman, A., (1998). Overview on Pesticide Situation in İzmir-Development of a Simple Technology in Drinking Water Treatment for Nitrate and Pesticide Removal, Short Activity Report.

Türkman A., Aslan, S, Yılmaz, Z., (2001). Groundwater Quality and Pollution Problems in Izmir Region, NATO/ARW Workshop on "Current Problems of Hdrogeology in Urban Areas, Urban Agglomerates and Industrial Centers" May 29- June 3, Baku, Azerbaijan.

U.S. Public Health Service (1995) Hazardous Substance Data Bank. Washington, DC, 5-9

Van der Hoek, J.P and Klapwijk, A., (1987). Nitrate Removal from Groundwater, Water Research, 21, 8, 989-997.

Van der Hoek, J.P, Van der Ven, P.J.M. and Klapwijk, A., (1988). Combined Ion Exchange/Biological Denitrification for Nitrate Nitrate Removal from Groundwater Under Different Process Conditions, Water Research, 22, 6, 679-684.

Vidal, J. M. L., Espada, M. C. P., Frenich, A. G. and Arrebola, F. J., (2000). Pesticides Trace Analysis Using Solid-Phase Extraction and Gas Chromatography with Electron-Capture and Tandem Mass Spectrometric Detection in Water Samples, Journal of Chromatography A, 867, 235-245.

Van der Hoek J.P., Hofman, J.A.M.H., and Graveland (1999). The Use of Biological Activated Carbon Filtration for the Removal of Natural Organic Matter and Organic Micropollutants from Water, Water Science Technology, 40, 9, 257-264.

Van der Bruggen, B., Everaert, K., Wilms, D., and Vandecasteele, C., (2002). Application of Nanofiltration for Removal of Pesticides, Nitrate and Hardness from Groundwater: Rejection Properties and Economic Evaluation, Journal of Membrane Science, 193, 239-248.

Volokita, M., Belkın, S., Abeliovich, A., and Soares, M. I. M., (1996a). Biological Denitrification of Drinking Water Using Newspaper, Water Research, 30, 4, 965-971.

Volokita, M., Abeliovich, A., and Soares, M. I. M., (1996b) Denitrification of Groundwater Using Cotton as Energy Source, Water Science and Technology, 34, 1-2, 379-385.

Wan, M. T., Szeto, S., and Price, P., (1995). Distribution of Endosulfan Residues in the Drainage Waterways of the Lower Fraser Valley of British Columbia, Journal of Environmental Science, Health, B30 (3), 401-433.

Wasik, E., Bahdziewicz, J., and Blasszczyk, M., (2001a). Removal of Nitrate Ions from Natural Water Using a Membrane Bioreactor, Seperation Purification Technology, 22-23, 383-392.

Wasik, E., Bahdziewicz, J., and Blasszczyk, M., (2001b). Removal of Nitrates from Groundwater by a Hybrid Process of Biological Denitrification and Microfiltration Membrane, Process Biochemistry 37, 57-64.

Wattanachira, S. and Fujita, K., (1990). The Effects of Filtrate Rate, Temperature, pH, Alkalinity on Biological Denitrification in Granular Filters, Journal of Japan, Water Works Ass., 59, 2-8.

Wauchope, R. D., Buttler, T. M., Hornsby A. G., Augustijn Beckers, P. W. M. and Burt, J. P. SCS/ARS/CES, (1992). Pesticide Properties Database for Environmental Decision Making. Rev. Environ. Contam. Toxicol. 123: 1-157, 10-12

WHO (1984). Guidelines for Drinking Water Quality, 1, Geneva

WHO (1986). Environmental Health Criteria, No 63, Geneva

Wilson, C., (1998). Cost and Policy Iplications of Agriculture Pollution with Special reference to Pesticides, PhD. Thesis Department of Economics, University of St. Andrews, Scotland, UK.

Wilson, C. and Tisdell, C., (2001). Why Farmers Continue to Use Pesticides Despite Environmental, Health and Sustainability Costs, Ecological Economics, 39, 449-462.

Worthing, C. R. (ed.) (1987). The Pesticide Manual: A World Compendium. Eigth edition. Published by The British Crop Protection Council.

Wotzka, P.J., Lee, J., Capel, P., Ma, L., (1994). Pesticide concentrations and fluxes in an urban watershed, in Proceedings of the American Water Resources Association's National Symposium on Water Quality: American Water Resources Association Technical Publication TPS-94-4, Herndon, VA, 135-145.

Yang, P.Y. Nitisaravut, S., and See, T.S., (1993). Entrapment of Mixed Microbial Cells for Water and Wastewater Treatment, Water Science Technology, 28, 7, 165-170.

Yatong, X., (1996). Volatile Fatty Acids Carbon Source for Biological Denitrification, Journal of Environmental Sciences, September, 8, 3, 257-269.

Yu, Z. and Smith G.B., (2000). Dechlorination of Polychlorinated Methanes by a Sequential Methanogenic-Denitrifying Bioreactor System, Appl. Microbial Biotechnol., 53, 484-489.

Zouari, H., Labat, M., and Sayadi, S., (2002). Degradation of 4-chlorophenol by the White Rot Fungus Phanerochaete chrysosporium in free and Immobillized Cultures, Biosource Technology, 84, 145-150.

CHAPTER NINE
APPENDIXES

9.1 Raw Data for Adsorption Studies of the Pesticides on Various NOSS's and Activated Carbon*

Table 9.1.1 Raw data for adsorption of the pesticides on the poplar shaving (the size of 500 μm)

sample volume/mass of poplar L /g	trifluralin C_{eff}/C_{inf}	fenitrothion C_{eff}/C_{inf}	endosulfan (α+β) C_{eff}/C_{inf}	endosulfan-sulfate C_{eff}/C_{inf}
0	0	0	0	0
1	0,037	0,371	0,26	0,664
2	0,051	0,556	0,313	0,852
3	0,055	0,602	0,388	0,822
4	0,06	0,527	0,339	0,784
5	0,06	0,552	0,454	0,882
6	0,066	0,589	0,588	0,906
7	0,076	0,621	0,608	0,894
8	0,1066	0,527	0,711	0,866
9	0,094	0,611	0,858	0,875
10	0,073	0,621	0,818	0,902

Table 9.1.2 Raw data for adsorption of the pesticides on the pine shaving (the size of 500 μm)

sample volume/ mass of pine (L /g)	trifluralin C_{eff}/C_{inf}	fenitrothion C_{eff}/C_{inf}	endosulfan (α+β) C_{eff}/C_{inf}	endosulfan-sulfate C_{eff}/C_{inf}
0	0	0	0	0
1	0,027	0,602	0,17	0,465
2	0,03	0,665	0,173	0,556
3	0,059	0,591	0,289	0,55
4	0,036	0,597	0,184	0,533
5	0,038	0,603	0,166	0,525
6	0,06	0,738	0,323	0,681
7	0,0982	0,765	0,365	0,714
8	0,1146	0,692	0,286	0,759
9	0,183	0,995	0,38	0,796
10	0,168	0,98	0,41	0,761

Table 9.1.3 Raw data for adsorption of the pesticides on the pine shaving shaving (the size of 2000 μm)

sample volume/ mass of pine L /g	trifluralin C_{eff}/C_{inf}	fenitrothion C_{eff}/C_{inf}	endosulfan (α+β) C_{eff}/C_{inf}	endosulfan-sulfate C_{eff}/C_{inf}
0	0	0	0	0
1	0,05	0,56	0,325	0,46
2	0,04	0,58	0,33	0,47
3	0,06	0,71	0,41	0,44
4	0,05	0,8	0,43	0,48
5	0,04	0,67	0,47	0,69
6	0,05	0,68	0,465	0,69
7	0,09	0,71	0,5	0,597
8	0,13	0,715	0,51	0,79

Table 9.1.4 Raw data for adsorption of the pesticides on the wheat straw

sample volume/ mass of wheat straw (L /g)	trifluralin C_{eff}/C_{inf}	fenitrothion C_{eff}/C_{inf}	endosulfan (α+β) C_{eff}/C_{inf}	endosulfan-sulfate C_{eff}/C_{inf}
0	0	0	0	0
0,4	0,025	0,4915	0,087	0,307
0,8	0,033	0,623	0,243	0,549
1,2	0,043	0,69	0,28	0,597
1,6	0,038	0,537	0,271	0,51
2	0,038	0,552	0,32	0,56
2,4	0,058	0,634	0,27	0,65
2,8	0,112	0,63	0,35	0,671
3,2	0,387	0,79	0,572	0,878

Table 9.1.5 Raw data for adsorption of the pesticides on the AC (30-50 mesh)

sample volume/ mass of activated carbon (L /g)	trifluralin C_{eff}/C_{inf}	fenitrothion C_{eff}/C_{inf}	endosulfan (α+β) C_{eff}/C_{inf}	endosulfan-sulfate C_{eff}/C_{inf}
0	0	0	0	0
1	0,002	0,033	0,01	0,023
2	0,002	0,059	0,01	0,029
3	0,001	0,06	0,02	0,031
4	0,002	0,062	0,02	0,028
5	0,007	0,069	0,03	0,036
6	0,006	0,061	0,014	0,029
7	0,006	0,075	0,025	0,032
8	0,005	0,083	0,04	0,037
9	0,004	0,065	0,023	0,034
10	0,003	0,07	0,025	0,029

* These experiments were performed within the scope of INCO-DC (ERBIC 18 CT 970167) project

9.2 Raw Data for DOC Contents of Various NOSS's

9.2.1 Raw data for DOC contents of the NOSS's

time minute	pine shaving	poplar shaving	hornbeam shaving	wheat straw
15	28,81	30,73	18,95	60,35
30	31,32	34,03	21,62	80,3
60	33,45	36,64	25,95	100,5
120	37,25	38,31	27,7	104,8
240	38,64	39,78	29,68	114,9
360	38,59	42,84	31,45	126,4

9.3 Raw Data for Biodenitrification Batch Experiments using Various NOSS's

Table 9.3.1 Raw data for nitrate elimination, nitrite and DOC contents in the poplar and hornbeam shaving batch unit

time	poplar shaving (mg/L)			hornbeam shaving (mg/L)		
days	NO^-_3	NO^-_2	DOC	NO^-_3	NO^-_2	DOC
2	0,5	1,5	54,19	11,5	2	47,66
4	5,5	2	47,92	22,5	0	35,66
6	5,5	1,25	47	22,5	0	31,77
8	9	0,96	34,39	22,5	0	30,75
12	9	0	34	22,5	0	29,76
15	9	0	33,5	23	0,01	26,92
19	9	0	45,51	35,5	0	56,64
22	25	0	21,28	40,5	0	38
27	25	0	17,11	40,5	0	37,25
32	30	0	16,83	40,5	0	36,25
39	30	0	15,7	40,5	0	36

Table 9.3.2 Raw data for nitrate elimination, nitrite and DOC contents in the pine shaving and wheat straw batch unit

time	pine shaving (mg/L)			wheat straw (mg/L)		
days	NO^-_3	NO^-_2	DOC	NO^-_3	NO^-_2	DOC
2	16	8	92,61	37	14	92,04
4	24	14,5	75	61	9,5	62,02
6	24	13	71,77	62,55	8	58,03
8	24	13,75	72,36	62,55	5,6	58
12	24	15	73	62,55	3	57,43
15	24	14,8	70,47	62,55	2,4	56,5
19	47	20,4	112,3	128,55	0	85,92
22	57	20,4	69,03	162,55	0	47,7
27	58	16,8	66,95	174,55	0	35,9
32	58	17,84	67	180,05	0	28,59
39	58	15,6	66,95	182,05	0	27
47	58	15,6	67	183,55	0	25,5
62	58	14,8	65,9	184,75	0	24,27
73	58	14,4	65,9	184,75	0,01	24
80				184,75	0	23,5
89				184,75	0,8	23,45
94				184,75	0,8	22,89
98				184,75	0,8	22,5

9.4 Raw Data for Biodenitrification Continuous Experiments Using Wheat Straw

Table 9.4.1 Raw data for nitrate- nitrogen elimination, nitrite-nitrogen, DOC and colour content and pH and velocities of the effluent water and cumulative nitrate-nitrogen removal for continuous reactor

Volume (L)	NO^{-}_{3}-N (mg/L)	NO_2-N (mg/L)	pH	Velocities (mh^{-1})	DOC (mg/L)	Colour (Pt-Co)	Cumulative NO^{-}_{3}-N (mg)	NO^{-}_{3}-N Removal yield %
0		0	7,5	0	0	0	0	0
10	0,67	0	5,65	0	430	530	219	97
16	0,23	0	5,55	0	460,5	560	373,6	99
21	0,75	0	5,26	0	492	562	462,5	97
25					450	560		
30	0,83	0	6,21	0,0467	433	560	658,2	96
33					87,98	280	806,2	
37,5	0,51	0	6,54	0,0235	60,6	250	806,9	98
44,1	1,3	0,03	5,88	0,0183	47,5	80	823,9	94
55,6	4,7	0,03	6,69	0,042	9,86	30	924,7	79
57,8	5,8	0,04	6,7	0,0414	6,4	10	1130,4	74
72,8	9,16	0,03	6,71	0,0858	3,74	10	1174,1	59
					121,7	300		
75,8	0,27	0	6,42	0,014	121,2	270	1466,2	99
81,3	4,52	0,03	6,3	0,0156	29,26	30	1573,2	80
87,8	9,48	0,04	6,5	0,014	19,23	40	1667	58
91	10,16	0,04	6,62	0,0104	15,5	25	1711,7	55

Table 9.4.2 Raw data for trifluralin, fenitrothion, and endosulfan(α+β) concentrations and water velocities of the for continuous reactor

Volume (L)	Trifluralin C_{eff}/C_{inf}	Fenitrothion C_{eff}/C_{inf}	Endosulfan C_{eff}/C_{inf}	Velocities mh^{-1}
30	0,004	0,006502	0,025714	
37,5	0	0,096099	0,070381	0,05
44,1	0,036	0,015995	0,162857	0,02
55,6	0,021	0,051105	0,137143	0,02
57,8	0,0462	0,156047	0,158857	0,04
72,8	0,017	0,113654	0,12381	0,09
81,3	0,034	0,005852	0,073333	0,02
87,8	0,0025	0,023667	0,11	0,01
91	0,0062	0,011964	0,060276	0,01

Table 9.4.3 Raw data for nitrate- nitrogen elimination, nitrite-nitrogen, trifluralin, fenitrothion, and endosulfan(α+β) concentrations and pH of the effluent water for the sand filter unit

Volume (L)	Trifluralin (µg/L)	Fenitrothion (µg/L)	Endosulfan (α+β) (µg/L)	NO^-_3-N (mg/L)	NO_2-N (mg/L)	pH
9	0,088	0,008	0,157	0,7	0	6,38
16,5	0	0,115	0,71	0,42	0	6,42
21	0,2	0,346	1,35	1,2	0,01	6,63
32,5				4,32	0,03	6,64
34,7	0,03	0,113	0,47	1,87	0,04	6,71
49,7	0,07	0,846	1,14	8,78	0,04	6,47
52,7				3,33	0,03	6,63
58,2	0,25	0,746	1,152	0,2	0	6,89
64,7	0,045	0,2	0,857	7,7	0,04	6,69
67,9	0,0112	0,092	0,486	8,35	0,04	6,4

9.5 Raw Data for Biological Elimination of Nitrate and Pesticides in Drinking Water Using Chemicals as Carbon Source

9.5.1 Raw data for adsorbtion capacities of the plastic materials and PAC

	Plastic materials µg/L			PAC µg/L %	
Time	Trifluralin	Fenitrothion	Endosulfan (α+β)	Fenitrothion	Endosulfan (α+β)
0	0,71	4,33	5,87	2,83	4,86
0,08	0,479	4,24	4,29	0,08	0,43
0,25	0,25	4,257	3,82	0,075	0,29
0,5	0,13	4,15	3,45	0,063	0,191
1	0,06	3,825	2,98	0	0,071
2	0,05	3,75	2,57	0	0
4	0,04	2,936	1,705	0	0
24	0,0227	2,59	0,425	0	0

9.5.2 Raw Data for Nitrate and carbon removal efficiency for ethanol and acetic acid

Ethanol			Acetic acid		
C/N ratios	TOC removal yield(%)	NO^-_3 removal yield (%)	C/N ratios	NO^-_3 removal (%)	TOC removal (%)
0,33	96	13	0,514	16,5	80
0,58	98	37	0,808	43,6	82,7
0,86	94	61	1,03	51,2	87
1,15	95	84	1,54	97,9	93,2
1,98	74	99,6	2,06	97,3	81,5
2,21	56	99,8	2,57	97,3	69,3
2,67	51	99,7	3,08	94,7	52,87
3,02	16	99,7	3,671	93,96	43,9
			4,19	95,8	43,7

9.5.3 Raw data for pH effect on the nitrate and ethanol removal in the batch unit

pH	NO^-_3 removal yield (%)	TOC removal yield (%)	MLSS (mg/L)	Final pH
3,5	8	13	7	
4	10	20	9,7	
4,85	94,8	68,5	40,5	6,35
5,5	97,5	70,9	40,8	6,45
6	97,8	65,8	42,2	6,58
7	96,9	66,9	44	7,51
7,5	96,6	72,1	45,6	8,21
8	96,2	63,51	42,8	8,32
8,5	96,1	65,72		8,53
9	96,4	62,95	30,8	8,76
9,5	0	0	15,7	9,22
10	0	0	13,1	9,95
10,5	0	0		10,57
11	0	0	10,3	10,98

Table 9.5.4 Raw data for various hydraulic residence time study

Q_h	NO_3 influent (mg/L)	NO_3 effleunt (mg/L)	NO_2-N (mg/L)	TOC effluent (mg/L)	%TOC	MLSS (mg/L)	Turbidity FAU	pH
0,66	95	51,25	2,56	18,98	73	20,5	30	7,53
1,05	95	28,38	1,94	18,07	73,7	24,8	29	7,88
2,43	96	2,41	0	12,2	70	22,5	25	7,9
3,12	92	1,8	0	8,91	74	16,8	8	8,03
3,77	92	2,59	0	7,61	78	19,3	10	7,74
4,5	96	1,95	0	8,28	79	7,35	6	8,15
5,64	100	4,05	0	7,54	77	7	6	8,11
7,13	96	2,73	0	9,65	70	11,53	8	8,1
7,47	92	2,79	0	8,43	76	8,2	7	7,84
8,46	95	2,84	0	7,93	76	12,8	8	8,3
12,74	100	4,13	0	8,81	75	7,73	6	8

9.5.5 Raw Data for continuous study using ethanol as a carbon source in pure water

θ_h hour	NO^-_3 mg/L	TOC mg/L	pH	NO^-_3 mg/L	NO^-_3 %	NO_2 mg/L	TOC mg/L	TOC %	^0C	Turbidity FAU	MLSS mg/L
1,99	100	36,7	8,32	9	91	4,4	15,5	58	18,5	10	9,3
2,06	100	36,4	8,51	9,61	90	4,86	14,83	59	19	7	5,4
3,63	100	37,75	8,36	1,55	98	0	12,12	68	19,5	6	3,2
3,85	100	37,75	8,38	2,06	98	0,16	12,58	67	19	7	4,1
4,24	100	34,54	8,39	5,26	95	0,07	9,12	74	19	10	4,4
5,48	96	35,5	8,06	4,57	95	0	8,65	76	18,5	6	3,6
5,69	95,3	34,24	8,05	5,97	94	0,07	9,22	73	18,5	13	4,1
5,78	100	35,715		2,99	97	0	9	75	19	11	4,8
6,82	100	35	7,85	3,49	97	0	8,7	75	19	9	4,2
12,2	100	37	7,7	2	93	0	5,5	85	19	8	3,9

9.5.6 Raw Data for continuous study using ethanol as a carbon source in pure water

θ_h hour	Trifluralin µg/L	Trifluralin %	Fenitrothion µg/L	Fenitrothion %	Endosulfan µg/L	Endosulfan %	Sum of the pesticides µg/L
2,06	0,195	89	1,03	86	0,76	93	1,985
3,85	0,095	95	0,62	92	0,49	96	1,205
4,24	0,09	95	0,66	91	0,391	96	1,141
5,48	0,054	97	0,36	95	0,494	96	0,908
5,69	0,08	96	0,282	96	0,29	97	0,652
5,78	0,029	99	0,24	97	0,06	99	0,329
6,82	0	100	0,241	97	0,115	99	0,356
12,2	0	100	0	100	0	100	0

9.5.7 Raw Data for sand filter unit of continuous study using ethanol as a carbon source in pure water

Treated volume L	θh hour	PH	NO^-_3 mg/L	NO_2 mg/L	TOC mg/L	MLSS mg/L	Trifluralin µg/L	Fenitrothion µg/L	Endosulfan µg/L
10,4	12,2	7,78	4,5	0	4,25	0,9			
30,4	5,69	7,79	5,46	0,09	4,35	1,4	0,0296	0,08	0,07
54,4	5,48	7,79	3,83	0	6,93	1,2	0,035	0,118	0,207
68,4	6,82	7,5	3,24	0,09	6,4	4,2	0,0296	0	0,105
93,9	4,24	7,76	5,53	0,04	6,54	0,6			
116,9	5,78	7,6	2,42	0	8,64	1,2			
129,9	3,85	7,86	2,2	0	7,91	3,3			
147,4	3,63	7,75	1,38	0	11,82	4,5			
187,4	2,06	8,41	1,52	0	9,72	3,5			
225	1,99	8,13	1,58	0	14,55	3,2			

9.5.8 Raw Data for continuous study using ethanol as a carbon source in tab water

influent				effluent						
Treated volume L	θh hour	NO^-_3 mg/L	TOC mg/L	pH	NO^-_3 mg/L	NO_2 mg/L	TOC mg/L	Turbidity FAU	^0C	MLSS mg/L
22	5,67	100	34,5	8	0,84	5,5	5,29	19	15	4,5
48	6,77	100	34,5	7,77	1,83	0	11,26	25	18	5,1
63	8,13	100	34,5	7,97	3,39	0	15,13	25	18	5
77	7,57	100	36,7	8,11	2,65	4,5	15,54	6	19	2,5
91	7,36	100	36,7	7,93	1,77	3,7	5,6	13	19	4
106	6,89	100	36	7,2	0,013	0	4,98	16	19	5,7
124	6,33	100	34	7,42	0,53	0	21,71	13	17,5	4,2
138	7,95	100	34	7,76	1,49	2,6	14,41	14	17,5	5,1
153	7,67	100	35	7,53	0,087	0,1	23,59	13	17,5	3,8
173	4,49	100	34	7	37	15,6	14,74	7	14	2,5
205	5,09	100	36	7,63	0,19	0,1	7,39	10	14	2,6

9.5.9 Raw Data for continuous study using ethanol as a carbon source in tab water

Treated volume L	θh hour	trifluralin µg/L	trifluralin %	fenitrothion µg/L	fenitrothion	endosulfan µg/L	endosulfan %
22	5,67	0,05	93,4	0,25	96,5	0,48	95,4
48	6,77	0,138	81,8	0,43	94	0,65	93,8
63	8,13	0,11	85,5	0,61	91,5	1,02	90,3
77	7,57	0,06	92,1	0,81	88,7	0,66	93,7
91	7,36	0,097	87,2	1,17	83,6	0,97	90,7
106	6,89	0,09	88,2	0,87	87,8	0,9	91,4
124	6,33	0,18	76,3	0,91	87,2	1,13	89,2
138	7,95	0,08	89,5	1,36	81	1,12	89,3
153	7,67	0,05	93,4	1,07	85	1,02	90,3
173	4,49	0,207	72,8	1,62	77,3	2,12	79,8
205	5,09	0,14	81,6	1,19	83,3	1,53	85,4

9.5.10 Raw Data for sand filter unit using tab water

Treated volume L	NO^-_3 mg/L	Turbidity FAU	NO^-_2 mg/L	pH	°C	trifluralin µg/L	fenitrothion µg/L	endosulfan µg/L
22	0	12	0	8				
48	1,778	13	0	7,58	15	0,08	0,08	0,36
63	4,92	15	0	7,56	18			
77	0,7	3	0	7,95	18	0,07	0,68	0,79
91	0,024	7	0	7,9	19	0,05	0,29	0,242
106	0,025	7	0	7,2	19			
124	0,84	0	0	7,46	19			
138	0,93	9	0	7,74	17,5			
153	0,087	9	0	7,75	17,5			
173	0,53	0	0	7,48	17,5	0	0,298	0,67