T.C.
KONYA TECHNICAL UNIVERSITY
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SYNTHESIS OF FLOCCULANTS FROM WASTE PLASTICS BY SULFONATION AND INVESTIGATION OF THEIR EFFECTIVENESS IN PLASTIC WASHING WASTEWATER TREATMENT

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MASTER OF SCIENCE

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THESIS ACCEPTANCE AND APPROVAL

Thesis namely “Synthesis of flocculants from waste plastics by sulfonation and investigation of their effectiveness in plastic washing wastewater treatment” prepared by Sofia SAFI was accepted as MASTER OF SCIENCE THESIS by below jury members with unanimity on the date of 01/08/2019 at Environmental Engineering Department of Konya Technical University the Institute of Graduate Studies.

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Chair **Assoc.Prof.Dr. Serdar AYDIN**	....
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Member **Prof.Dr. Bilgehan NAS**	....

I approve the result above.

Prof. Dr. Hakan KARABÖRK
Head of Institute

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DECLARATION PAGE

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

TEZ BİLDİRİMİ

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Sofia SAFI
10/07/2019

ABSTRACT

MASTER OF SCIENCE THESIS

SYNTHESIS OF FLOCCULANTS FROM WASTE PLASTICS BY SULFONATION AND INVESTIGATION OF THEIR EFFECTIVENESS IN PLASTIC WASHING WASEWATER TREATMENT

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The continuous rising of plastic demand led to the growth in waste accumulation in the environment every year. Only 2% of all plastics are closed-loop recycled although with technological advancements in industry all types of polymers can be recycled. Sulfonation is one of the most common methods to modify the surface properties of polymers in order to achieve certain characteristics of desired water absorption, biocompatibility, ion exchange capacity, swelling, etc. In plastics recycling industry the collected waste plastic has been cut into smaller pieces, and then the stock usually needs to be washed in order to remove lingering dirt or attachments. The washing effluent that is produced in washing process is collected as wastewater. The main pollutant parameters in such wastewaters are chemical oxygen demand (COD), suspended solids and high pH. Thus, the washing water needs to be purified prior to discharge. In this study first several polymeric flocculants were synthesized with waste polystyrene (PS) and waste PET by modifying the conventional PS sulfonation process. The synthesized materials were characterized and sulfonation was confirmed. Then the effectiveness of those synthesized materials in coagulation/flocculation treatment of plastic washing wastewaters in terms of turbidity, COD, and TSS removals were investigated. Synthesized flocculants have higher performance under the same conditions as their conventional counterparts, PEL. The highest turbidity removal (86%) was obtained at original pH with a dose of 50 mg.L^{-1} FSPET2 flocculant in HDPE WPWW and the highest COD (79%) and TSS (52%) removals were achieved in PS and PET WPWWs. PS and HDPE WPWWs treatment performances were high at the original pH, whereas LDPE and PP wastewaters had the best treatment at pH 7, PET and mixed plastic wastewater had high treatment at pH 9.

Keywords: Coagulation/Flocculation; Polymeric flocculant; Sulfonation; Waste plastic washing wastewater (WPWW)

ÖZET

YÜKSEK LİSANS TEZİ

ATIK PLASTİKLERDEN SÜLFOLAMA İLE FLOKÜLANT SENTEZİ VE PLASTİK YIKAMA ATIKSUYU ARITIMINDA ETKİNLİĞİNİN BELİRLENMESİ

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Plastik talebin sürekli artması, her yıl çevrede atık birikiminin artmasına neden olmuştur. Plastiklerin sadece %2'si kapalı devre geri dönüşümlüdür, ancak sektördeki teknolojik ilerlemelerle tüm polimer türleri geri dönüştürülebilir. Sülfonasyon, polimerlerin istenen su emme, biyouyumluluk, iyon değiştirme kapasitesi, şişme, vb. gibi belirli yüzey özelliklerin elde edilmesi için en yaygın yöntemlerden biridir. Plastik geri dönüşüm endüstrisinde, toplanan atık plastikler küçük parçalara kesilerek üzerindeki kirliliklerin giderilmesi için genellikle yıkanması gerekmektedir.Yıkama işleminde ortaya çıkan su atıksu olarak toplanmaktadır. Bu tür atıksularda ana kirletici parametreler, kimyasal oksijen ihtiyacı (KOİ), askıda katı madde (AKM) ve yüksek pH'dır. Böylece yıkama suyunun deşarj edilmeden önce arıtılması gerekmektedir. Bu çalışmada, geleneksel polistiren (PS) sülfonasyon işleminde modifikasyon yapılarak atık PS ve atık PET ile polimerik flokülantlar sentezlenmiştir. Sentezlenen flokülantların yapısı karakterize edilmiştir. Daha sonra sentezlenmiş malzemelerin plastik yıkama atık sularının (WPWW) koagülasyon/flokülasyon ile arıtımında bulanıklık, KOİ ve AKM giderim etkinliği araştırılmıştır. Sentezlenmiş flokülantlar, aynı koşullar altında konvansiyonel PEL ile benzer, hatta daha yüksek performansa sahiptirler. HDPE WPWW'de 50 mg L^{-1} FSPET2 flokülant dozu ile orjinal pH'da en yüksek bulanıklık giderimi (%86) elde edildi. En yüksek KOİ ve AKM giderimleri (%79 ve %52) PS ve PET WPWW'lerde elde edildi. PS ve HDPE WPWW'lerin arıtma performansları orijinal pH'da yüksekken, LDPE ve PP atıksuları için pH 7'de en iyi arıtma, PET ve Karışık plastik atıksuları için pH 9'da yüksek arıtma işlemi gerçekleştirildi.

Anahtar Kelimeler: Koagülasyon/flokulasyon; Polimerik flokülant; Sülfonasyon; Atık plastik yıkama atıksuyu (WPWW)

PREFACE

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Sofia SAFİ
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CONTENTS

SYMBOLS AND ABBREVIATIONS

Symbols

Ag_2SO_4 : Silver sulfate
BOD_5 : 5-day Biochemical Oxygen Demand
C : Carbon
C_2H_4 : Ethylene
Ca : Calcium
$Ca(OH)_2$: Calcium hydroxide
$CaCO_3$: Calcium carbonate
Cd : Cadmium
CFCs : Chlorofluorocarbons
CO : Carbon monoxide
CO_2 : Carbon dioxide
Cr : Chromium
Fe : Iron
Fe_2SO_4 : Iron(III) sulfate
$FeCl_3$: Iron(III) chloride
H : Hydrogen
H_2O_2 : Hydrogen peroxide
H_2SO_4 : Sulfuric acid
HCl : Hydrochloric acid
HSO_3 : Hydrogen sulfite
K : Potassium
KOH : Potassium hydroxide
Mg : Magnesium
Mn : Manganese
Mo : Molybdate
N : Nitrogen
N_2O : Dinitrogen monoxide
Na : Sodium
Na_2CO_3 : Sodium carbonate
NaOH : Sodyum hidroksit
NH_3 : Ammonia
Ni : Nickel
NO_x : Nitrogen oxide
P : Phosphorus
P_2O_5 : Phosphorus pentoxide
PAHs : Polycyclic aromatic hydrocarbons
Pb : Lead
S : Sulfur
SO_2 : Sulfur dioxide
SO_3 : Sulfur trioxide
SO_3H : Sulfonic acid
SO_x : Sulfur oxide
Zn : Zinc

Abbreviations

ASPETs : Sulfonated PET flocculants
COD : Chemical oxygen demand
EPS : Expanded polystyrene
EU : European union
FSPS : Classic sufonated PS flocculant
FSPSs : Sufonated PS flocculants
FTIR : Fourier transform infrared
GPPS : General purpose polystyrene
HDPE : High density polyethylene
HIPS : High impact polystyrene
ICP : Inductively coupled plasma
LDPE : Low density polyethylene
PE : Polyethylene
PEL : Polyelectrolyte
PET : Polyethylene terephthalate
PP : Polypropylene
PS : Polystyrene
PSW : Plastic solid waste
PVC : Polyvinyl chloride
SCR : Specific cake resistance
SPS : Syndiotactic polystyrene
TS : Total solids
TSS : Total suspended solids
WPS : Waste polystyrene
WPWW : Waste plastic washing wastewater

1. INTRODUCTION

1.1. Meaning and Importance of the Study

The purpose of waste recycling methods is to prevent the disposable wastes from being released to the environment, to prevent the reduction of raw material resources and to provide an economic return from recovered substances. In this sense, it is important to increase and diversify the approaches and methods that provide recycling and/or recovery. Nowadays, instead of an integrated approach to zero/minimize waste or economic value maximization, the focus is on the single product that can be converted to the maximum amount of money. The importance of energy needs is clear. However, there is a need for raw materials in developing technology and increasing varieties of products. Raw materials are mostly made from natural products or synthesized by using natural materials. On the other hand, recyclable materials are considered as waste or garbage by the consumers and are removed with garbage. Generally, in Turkey and many other countries in the world landfill is preferred since it is an easy and economical method of disposal. This method actually means removing many valuable components from the system and burying them into the ground. While efforts to obtain valuable material are being carried out rapidly by processes that require considerable labor and cost, such as mining excavation and ore enrichment, burying precious wastes in the ground is actually a great contradiction. Therefore, it is important to develop and reproduce the methods that will evaluate the waste materials in a different way, to recycle or recover valuable components. In this way, the materials will remain in the system for a longer period, and landfill pollution and damage of valuable materials to the soil will be reduced.

Plastic plays a vital role in enhancing the living standard of human beings for years (Chaukura et al., 2016). It is a key innovation for many products in almost all sectors such as construction, healthcare, electronics, automotive, packaging and others. The demand for commodity plastics has been increased due to the rapid growth of the world population and to the increase in living standards. The worldwide plastic consumption has reached about 322 million tons in 2015, representing a 4% increase over 2014 (Plastics, 2016). The continuous rising of plastic demand has led to the growth in waste accumulation in the environment every year. Current methods for the disposal of plastic wastes include landfill, recycling, incineration, and energy production (Hopewell et al., 2009). Landfill and incineration have the most utilized applications for post-consumer plastic disposal (Merrild et al., 2012). The continuous production and disposal of plastic would definitely cause serious environmental problems. Firstly, as they are not biodegradable, they break into small particles harmful for human and wildlife. Secondly, 4% of the global oil production is used to manufacture plastics products, 50% of which have a short life in the system, such that, useable raw materials are disposed as waste in less than a year (Chaukura et al., 2016; Diaz Silvarrey and Phan, 2016; Hopewell et al., 2009). Likewise, incineration generates emissions of toxic fumes and fly ash that require further disposal (Siddique et al., 2008). Only 2% of all plastics are closed-loop recycled, although with technological advancements in the industry all types of polymers can be recycled (Hamad et al., 2013; Neufeld et al., 2016). Various plastic wastes recycling/recovery methods provide valuable raw materials and products or energy recovery.

In the plastics recycling industry the collected waste plastic has been cut into smaller pieces, or flakes and then the stock usually needs to be washed in order to remove lingering dirt or attachments. In the case of high oil content plastic wastes, NaOH is used for washing of wastes in recycling facilities. The water effluent that is produced in the washing process is collected as wastewater. The main pollutant parameters in this wastewater are turbidity, chemical oxygen demand (COD), total suspended solids (TSS), oil – grease and high pH (Iskender and Yel, 2016). Waste plastic washing consumes a high amount of water and a high pollution wastewater is exposed. For economical chemical recycling, plastics washing step is generally not applied, therefore the quality of recycling product will be low. Although the high NaOH concentration in water indicates that water needs treatment, there is not much work in the treatment methods of such wastewater. In Turkey, this wastewater is reused after clarified in a settling tank located in the recovery plant (Sahinkaya, 2017). After a while, the washing water becomes so polluted that it cannot be used for washing, and needs to be treated.

1.2. Purpose and Scope of the Study

The extent and main objectives of this study are shown on the flow chart in Figure 1.1.

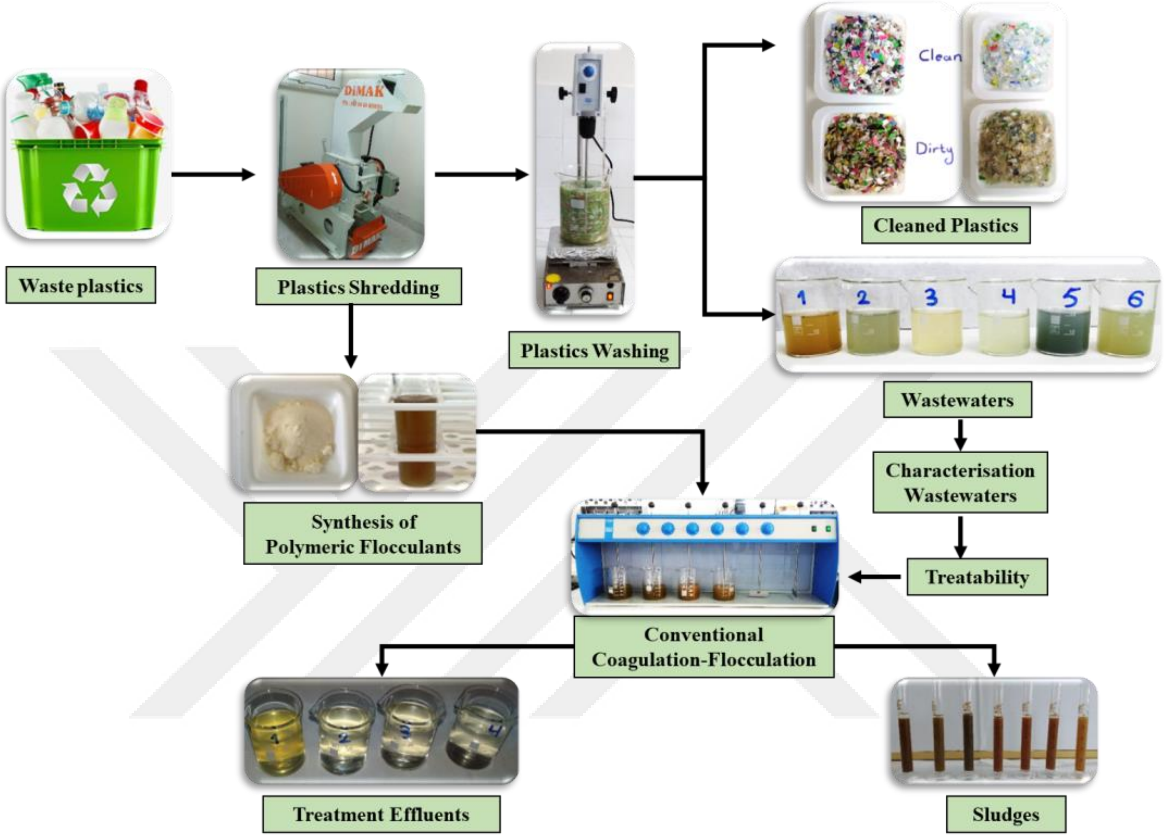


Figure 1.1. Flow chart of work and its main objectives

The objectives of the study:

- To synthesize flocculants with waste polystyrene (PS) by modifying the conventional PS sulfonation process
- To apply the conventional and modified PS sulfonation process to another aromatic plastic waste, polyethylene terephthalate (PET), to reveal the possibility of obtaining new flocculant material.
- To investigate the effectiveness of the synthesized sulfonated polymer flocculants on treatment of different waste plastic washing wastewaters (WPWW), which were the effluent of washing process of waste plastics samples at the laboratory scale by simulating the full-scale washing facility

Within the scope of treatability studies:

- Collection of waste plastics and preparation for the study
- Obtaining WPWW in a lab-scale system
- Characterization of WPWW
- Synthesis of alternating flocculants by modified sulfonation process
- Treatment of WPWW with synthesized polymeric materials
- Investigating the effectiveness of the synthesized materials in treatment
- comparing it with conventional flocculant, polyelectrolyte (PEL)

2. LITERATURE SURVEY

2.1. Plastics

The word plastic comes from the Greek word Plastikos, meaning “able to be shaped and molded.” Plastics are derived from crude oil, natural gas, coal, salt, sand, and a number of other possible additives. They are made from lighter hydrocarbons are the main fractions of cracked natural fuels which is the product of distillation process (Crawford, 1998). Most plastics are produced by either polymerization or polycondensation. In the two cases, oil distillates are joined with explicit impetuses to make novel, normally bigger, atoms (Seymour and Carraher, 1981). The two procedures happen in a reactor where heat is added making little atoms consolidate into bigger ones. A polymerization reaction begins with an essential fixing (monomer, for example, ethylene or propylene. Ethylene (C2H4) is an inactive particle with two carbon molecules and a double bond. Polyethylene (PE) is a made by the reaction of numerous ethylene particles within the sight of catalyst to break the twofold bond and associate the carbon atoms into a chain (Figure 2.1). The produced large molecules have specific properties depending on the process (Kuran, 2002).

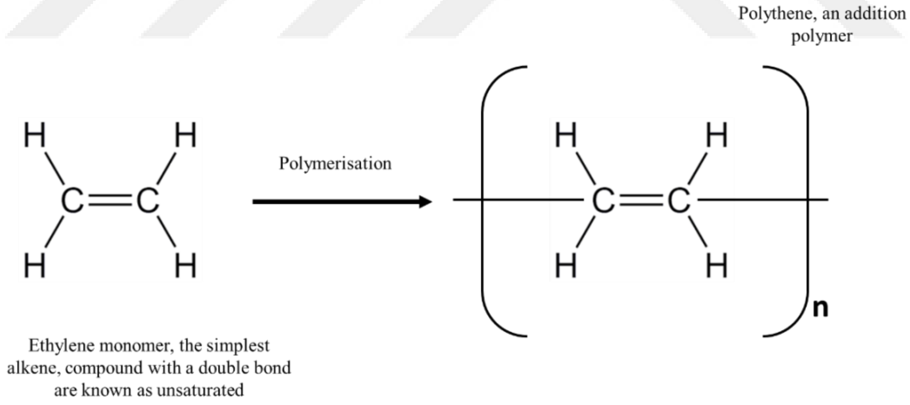


Figure 2.1. Polyethylene is made by the reaction of multiple ethylene molecules in the polymerization process

Two major classes of plastics based on their chemical structure are thermoplastics and thermosetting plastics (Table 2.1).

Thermosets: Are plastics that can be melted only once. When thermoset materials first heated, this cause them to set and chemical structure changes such that it cannot be reversed and the second heating cause its burning which makes thermoset materials poor contender for reusing. Their two- or three dimensional molecular structure differs frim one-dimensional linear chain (Figure 2.2). The different types of thermosets are silicons, phenol- or urea-formaldehydes, vinyl esters, Polyester, and Bakelite that are showed in Table 2.1 (Dodiuk and Goodman, 2013).

Thermoplastics: Are plastics that can be re-heated to their melting point several times without significant degradation. This property enables them to be effectively shaped by injection and afterward reused. Models include two plastics typical to injection shaping. Thermoplastics are much more common than thermosets. Their structure includes a progression of rehashing units joined into a solitary particle sorted out in a straight arrangement (Figure 2.2). The atomic structure of thermoplastics has an impact on the resistance against various chemicals and natural impacts like UV. The significant properties of the thermoplastics are hardness, thoughness, chemical resistance, durability and waterproofing. The six main families of thermoplastics are High/Low Density Polyethylene (HDPE/LDPE), Polyethylene Terephthalate (PET), Polypropylene (PP), Polystyrene (PS), and Polyvinyl chloride (PVC).

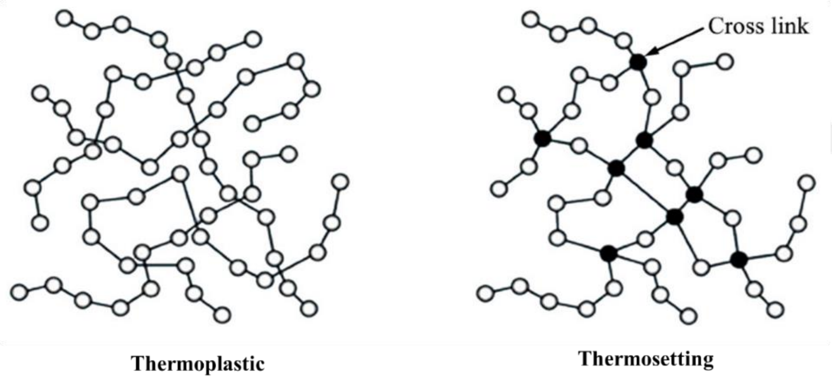
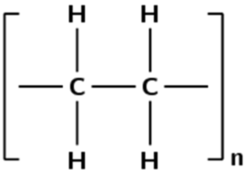
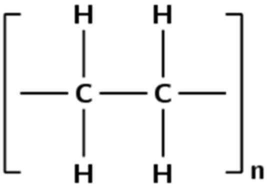
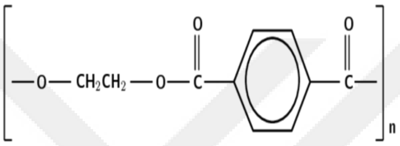
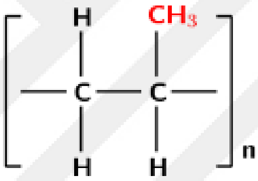
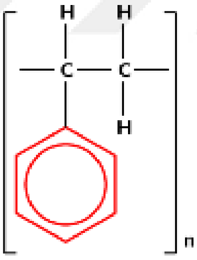
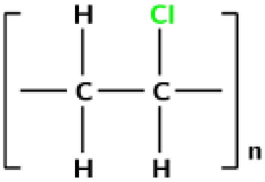


Figure 2.2. Molecular structures of thermosetting and thermoplastic

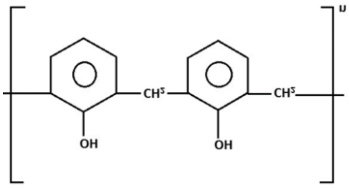
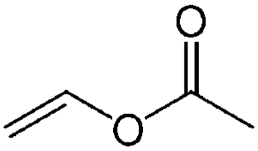
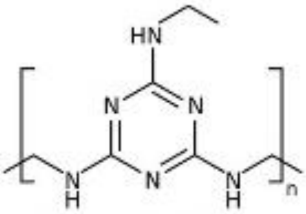
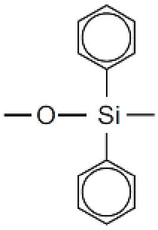
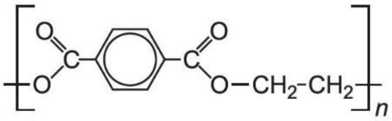
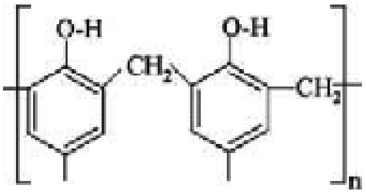
- **HDPE** has a density of 935-965 kg.m^{-3} composed of carbon and hydrogen atoms bonded to form a high molecular weight product (Hamad et al., 2013). It is slightly more expensive but strong and stiffer and have good mechanical properties. Therefore, it finds numerous applications such as general-purpose fluid containers, dustbins, pipes and bottle crates as well as various industrial applications (Jaggi et al., 2014). It has higher strength than LDPE. It is easy to recycle and its contribution in home products or commodities is maximum (Sommerhuber et al., 2015).

Table 2.1. Available thermoplastic polymers and their application (Crawford, 1998; 2013; Janajreh et al., 2015; Karger-Kocsis, 2012; Research, 2015; Yu et al., 2016)

Thermoplastic	Structure	Application Examples
HDPE		Bottles, toys, utensils, pipes, films, wire / cable insulations
LDPE		General-purpose containers, shopping bags, packaging, greenhouse covers, etc
PET		Bottles, engineering plastics, packaging films, filaments, staple fibers, carpet yarn
PP		Pipes, bags, carpets, rugs, mats, food packages
PS		License plate frames, cd cases, dinnerware, disposable plastic cutlery, detectors, housings
PVC		Window frames, clothing, roofing sheets, floor coverings, cables, medical, automobile, construction, electrical, etc…

- **LDPE** is produced under extremely high pressures, which result in polymerization creating branched polyethylene. The utility of LDPE is limited because of high number of branches. This property results in poor strength and requirement of extreme pressure condition for production (Kumar et al., 2011). Recycling of LDPE takes high energy to make LDPE as compared to HDPE.

Table 2.1. (Continued)

Thermosetting	**Structure**	**Application**
Phenol-formaldehyde resins		Circuit boards, laboratory utensils, coatings, fiberglass cloths, billiard balls, adhesives, etc.
Vinyl esters		Vessels, fiberglass reinforced plastics, tanks, laminating process, Marine industry, etc.
Urea-Formaldehyde		Agriculture, wrinkle resistant fabrics, cavity filler, paper, textiles, decorative laminates, cotton blends, rayon, etc.
Silicon		Lubricants, adhesives, cooking utensils, medicine, sealants, thermal and electrical insulation, etc.
Polyester		Bottles, staple fiber,drinks or detergents packages, technical yarn and tire cord
Bakelite		non-conducting parts of electrical and electronic devices, insulators and insulating parts of kitchenware, electrical component supports, billard balls, automobile parts etc.

- **PET** is semicrystalline thermoplastic resin. It is a fiber and film forming saturated polymer. In addition, it is the commercially popular polymer used in liquid and food containers and fibers for clothing. Furthermore, PET has good tensile and tear strength, insulation, oxygen carbon dioxide, aroma, anhydride compounds barrier property, etc.

(Mandal and Dey, 2019). It can be used in the thermoformed structure production as well as used in combination of glass fiber as composite.

- **PP** is used in the production of injection-molded objects such as food containers, washing up bowls, car bumpers, packaging, fibers for carpets and clothing and can be extruded into pipe. It can also be used as composite fillers, pigments and elastomers. PP has remarkable properties, making it suitable to replace glass, metals, cardboards and other polymers (Karger-Kocsis, 2012).
- **PS** is stiff, transparent, high strength, solvent resistant polymer formed from styrene monomer. It is widely used thermoplastic in food packaging and storage, appliances, automotive and foam industry. Its good process ability and good machinability are some of the favorable characteristics of PS (W. F. Smith, 1996).

2.1.1. Plastics as a Global Issue

After the introduction of synthetic polymers into industry in 1940s, plastic products gained importance in industrial history (Al-Salem, 2009b). Then material researches and applications that incorporating plastics become popular, so many commodities have started to be manufactured with plastics. The reason for this increase is some characteristics of plastics including their flexibility, corrosion resistance and low manufacturing cost. Plastics has been used in decoration, electronics industry, construction, automotive, healthcare, packaging, shopping bags, bottles, pipes and others (Subramanian, 2000).

Global plastics production has steadily increased, reaching a global annual production of 322 Mtons in 2015 (Lopez et al., 2018). Due to the traditional plastics and the new composites, plastics consumption increases (Lopez et al., 2018). Europe’s sector-based and plastic types-based distribution of plastics demand are indicated in Figure 2.3 a and b respectively. Accordingly, polyolefins (HDPE, LDPE, and PP) account for half of the produced plastics, but PS, PET and PVC are also produced in considerable amounts. Increasing population in the world increases the demand of commodity plastics. Plastics became a vital a part of life style and plastic production in the world has increased since 1960s (Gu and Ozbakkaloglu, 2016). The plastic consumption in the world reached about 322 million tons in 2015 and it increased 4% over 2014 (Plastics, 2016). Disposal of polymer is a worldwide issue because of high production and consumption of plastics, which will definitely result in the accumulation of plastic waste. It is to say that no authentic estimation is on the market on the full generation of plastic waste.

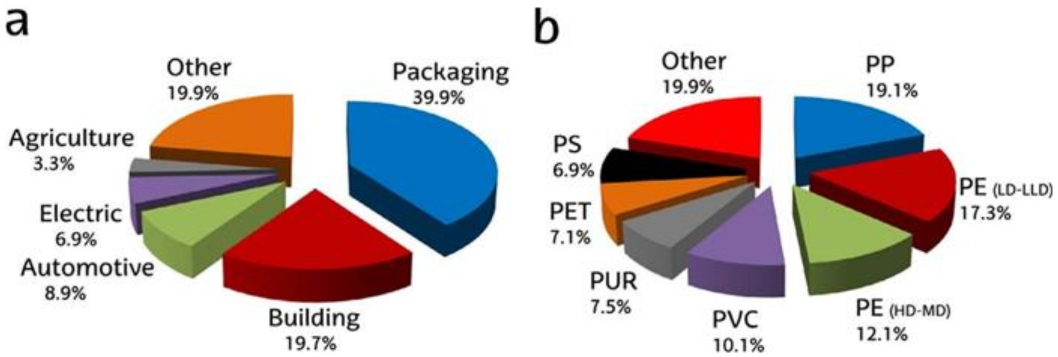


Figure 2.3. Plastic distribution demand in Europe according to sector (a) and type of polymer (b) (Lopez et al., 2018).

However, 70% of consumed plastics is assumed to be collected as waste (approx.5.6 million tons per year). In United States, the amount of plastic waste in 2014 was 39.3 million tons, indicating a 13% increase over 2011 (N. Themelis et al., 2011; N. J. Themelis and Mussche, 2014). Developing countries such as Malaysia experiencing a growth in plastic waste by 18% in 5 years(Abnisa et al., 2014). The current amount of plastic in use is about 30% of produced plastics. Moreover, by 2015, only 9% of the plastic wastes were recycled, and 12% was incinerated, 79% has engineered up in landfills or elsewhere within the environment. The global plastics additives market market is expected to grow at a rate of 4.5% per year from 2015 to 2022 to reach a value of US$ 62.50 billion in 2022 (Research, 2015).

It is a fact that plastics will never degrade and remains on landscape for hundreds of years (Pol and Thiyagarajan, 2010). Pigments of plastic waste contains many trace elements that are highly toxic (Gondal and Siddiqui, 2007) and they have been identified as a huge difficulty (Zheng et al., 2005). After each recycling, plastic material strength reduces as a result of thermal degradation. within the thermal degradation of polymers solvents with a hydrogen donor capability participate, this affects the hydrocarbon yield and distribution (Vicente et al., 2009).

Carvalho et al, (2007) investigated the rate of mineralization for non-pre-treated, UV irradiated and additive-free LDPE samples under long-term biodegradation conditions in natural soils, and they indicated that mineralization takes more than 100 years (Carvalho et al., 2007). US and the EU try to introduce new legislation for waste reduction in order to reduce landfill capacities together with some general environmental concerns (Muthu et al., 2011; Subramanian, 2000).

There are some advantages of reusing/recycling wastes. The first one is protection of natural resources while the second one is disposing the wastes in effective, safe and environmentally friendly manner. These solutions have inspired an impressive volume of research and development. Work is being conducted worldwide on the use of recycled materials, particularly on recycled plastics.

2.1.2. Plastic Solid Waste (PSW) Recycling/Recovery

Manufacture of virgin plastics with the conventional methods is easy but energy consuming. Manufacturing virgin plastics needs four-dimensional of the world's drilling corresponding to 1.3 billion barrels a year (Kreiger et al., 2014).Therefore, it is always advisable to reuse and recycle plastic waste.

Recycling/recovery and proper management of PSW is a major contributing factor to reduce the waste generated on a global level. Waste generation level of countries based on their income level. PSW management is a complex process because of the requirement of various information from different sources and forecasts of vast quantities and reliable data (Grazhdani, 2016).

Four main approaches for recycling of PSW were defined as primary (re-extrusion), secondary (mechanical), tertiary (chemical) and quaternary (energy recovery) recycling (Figure 2.4). Polymer recycling techniques play important role in the generation of the new polymer. However, recycling methods have some advantages and disadvantages. When the material undergoes a recycling process it starts losing some of properties in terms of tensile strength, wear properties and dimensional accuracy (Singh et al., 2017).

Primary recycling, (re-extrusion) utilizes scrap plastics that have similar options to the first products. Scrap, industrial or single-polymer plastics are introduced to the extrusion cycle and products of similar material are produced (Al-Salem, 2009a). Primary recycling is only feasible with semi-clean scrap otherwise it is an unpopular choice. Injection molding of LDPE is a good example of primary recycling (Barlow, 2008). In the United Kingdom, approximately 95% of 250,000 tons of the process scrap PSW is primary recycled (Parfitt, 2002). Generally, the greatest portion of this wastes are households. The main problem is the need for selective and segregated collection.

Secondary recycling (Mechanical recycling) is manufacturing plastic products via mechanical means. This can only be performed on single-polymer plastic, PE, PP, PS, etc(Mastellone, 1999). Separation, washing, and preparation of PSW are essential to produce clean, clear, high quality, and homogenous end-products. The quality is the main issue in managing the mechanically recycled product. Mechanical recycling is well suited for the use

PSW as a raw material in case of low level of impurities and clear separation of different types of plastics (Al-Salem, 2009b).

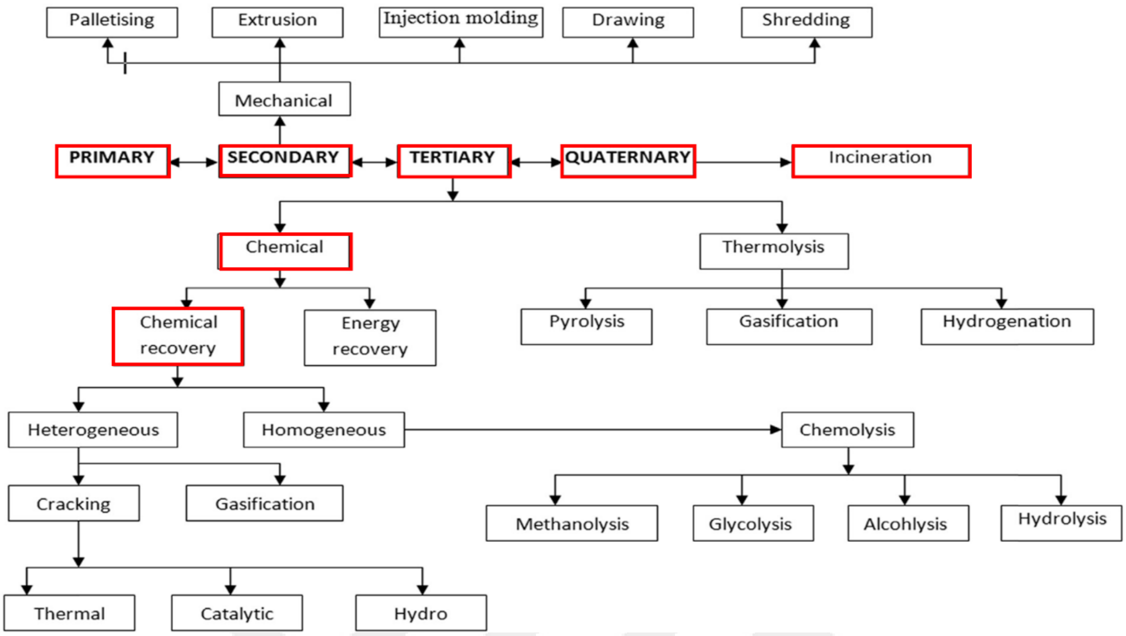


Figure 2.4. Various approaches for PSW recycling (Singh et al., 2017).

Tertiary recycling is a term accustomed with advanced technology processes that convert plastic materials into smaller molecules (through chemical reactions or thermolysis) sometimes liquids or gases that are appropriate to be used as a feedstock. Under this category advanced process appear such as liquid–gas hydrogenation, steam or catalytic cracking viscosity breaking, pyrolysis, gasification, and the use of PSW as a reducing agent in blast furnaces (Al-Salem, 2009b). This is also a method of producing various fuel fractions from PSW. The main advantage is the chance of treating heterogeneous and contaminated polymers with restricted use of pre-treatment is high.

Quarternary recovery implies burning PSW to provide energy within the kind of heat, steam, and electricity. When material recovery processes fail due to economic constraints, quarternary recovery is considered a sensible way of ultimate disposal. PSW possess a very high calorific value especially when considering that they are derived from crude oil. Producing water and carbon-dioxide upon combustion build them almost like different petroleum-based fuels (Dirks, 1996). Incineration of PSW results in 90–99%volume reduction, which reduces the reliability of landfilling. The destruction of foams and granules also destroys CFCs and other harmful blowing agents present (Al-Salem et al., 2009).

Some environmental concerns are associated with incineration PSW. One of these is the emission of air pollutants such as SO_x, NO_x, and CO_2 as well as smoke (particulate matter), volatile organic compounds, heavy metals, dioxins polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzofurans. Carcinogenic substances have been identified in airborne particles from incineration or combustion of synthetic polymers. Capture and removal of flue gases in thermal and combustion processes is a major issue dealt with by activated carbon addition, flue gas cooling, ammonia addition, filtration and/or acid neutralization (Yassin et al., 2005). In incineration, the temperature is an essential parameter that leads to a reduction in CO and N_2O accompanied by an increase in NO_x. 4-6% of fuel nitrogen is converted to NO_x and this is below what is usually observed in fluidized beds. Boavida et al. (2003), indicated that the conversion of sulfur in the fuel to SO_2 was almost complete during the co-incineration of PSW with coal.

2.2. Polystyrene (PS)

PS is a polymer of monomer styrene. PS was first developed by Eduard Simon in 1839 by distilling or pyrolysing liquid storax (Andrady and Neal, 2009). It is difficult to recycle, its code 6 also represents this (Imen Bekri-Abbes et al., 2006). The widely used common forms of PS (Figure 2.5) are general purpose PS (GPPS), high impact PS (HIPS), expanded PS (EPS) and syndiotactic PS (SPS) (Chaukura et al., 2016).

EPS and HIPS have outstanding mechanical and insulating properties. They are used in the resin-molded objects like TV cabinets and packing electric appliances (Brennan et al., 2002; Inagaki and Kiuchi, 2001; Inagaki et al., 1999). Large portion of waste EPS and HIPS are disposed of in landfills or by incineration in developed countries, through open burning and waste dumps in developing countries, and are almost never recycled since they are cheap and conventional recycling methods convert them into lower value materials (Chaukura et al., 2016).

One major disadvantage of PS that limits the engineering applications of it is its brittleness. Ramsteiner et al (2000) studied on developing toughening methods by using rubber particles as additives to PS (Ramsteiner et al., 2000). Rubber particles can facilitate crazing in PS, resulting in the material changing from brittle to ductile (Akbari and Bagheri, 2016).

Figure 2.5. The common types of polystyrene

2.2.1. The Polymerization Process of PS

Higher molecular weight aromatic vinyl polymers were generated by anionic polymerisation, in particular by polymers with an average mass of more than 300,000 (Figure 2,6). This is due to the slow polymerization speeds used to obtain elevated molecular weight polymers in free radical polymerization of styrene. However, anionic polymerization procedures involve costly initiators like organolithium compounds and, due to the existence of residual lithium-containing salts, tend to create discolored products. High molecular weight polymers from vinyl aromatic monomers are therefore generated using a free radical polymerization method that does not present these disadvantages, as well as to provide an enhanced method for the production of bimodal products comprising these high molecular weight polymers (Meister and Cummings, 2003). In case of styrene, polymerization in either a hydrocarbon or ether solvent with an organolithium initiator outcomes in a small molecular weight distribution atactic fluid (McIntyre et al., 1972; Worsfold and Bywater, 1963).

In general, elevated molecular weight vinyl aromatic plastics were also generated in the presence of a soluble organic acid with pKa of 0.5–2.5 by direct radical polymerization (Shero et al., 1992). In this phase, however, the acid does not attach to the polymer and can migrate during use from the polymer, which can lead mold surfaces to corrosion (Shero et al., 1992). All four separate polymerization processes polymerized styrene: anionic, cationic, free-radical and Ziegler (Soga et al., 1990). The most commercially common of these procedures is free-radical polymerization. This constitutes the most commonly used form of atactic PS in packaging and durable goods. In two distinct procedures, i.e. permanent (mass or bulk) and suspension polymerization, free-radical polymerization is used industrially.

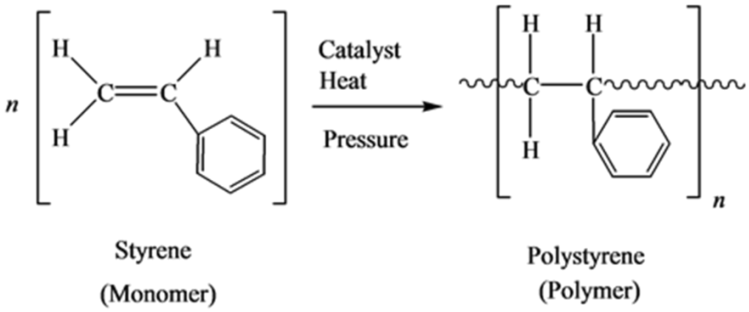


Figure 2.6. Polymerization of polystyrene

Some range of parameters such as initiator form and amount, surfactant, experimental circumstances such as polymerization temperature, and polymerization method may vary to synthesize and design PS with required characteristics. Taud (1993) studied styrene polymerization with various emulsifier systems including persulphate, 2,2-azoisobutyputyronitrile and Surface Active Initiators at ambient to 100 ºC temperatures. The activation energies showed a strong dependence on the systems used by the initiator-emulsifier. McIntyre et al. (1972) proved that tetrahydrofuran as the solvent and polystyryllithium in benzene as the initiator can be used to synthesize monodisperse PS with molecular weights up to 44/106. Several other styrene polymerization methods have been used. Bromoacetylated syndiotactic PS as macroinitiator and copper bromide coupled with N, N, N',N',N'-Pentamethyldiethylenetriamine as catalyst was used for atom exchange radical polymerization (Baker, 2011). In the presence of Fe_2SO_4 nanoparticles, ultrasonically initiated mini-emulsion polymerization of styrene was performed. The addition of Fe_2SO_4 nanoparticles significantly improved the polymerization frequency owing to increased acoustic intensity and the Fe^{2+} combined with H_2O_2 to generate hydroxyl radicals to increase free radical concentration. The increase in the quantity of co-surfactants also increased the polymerization speed (L. Qiu and Qu, 2006).

Other techniques for PS synthesis include the use of radical Blatter and its derivatives in controlled permanent free radical polymerization (Demetriou et al., 2014). This generates fresh possibilities for designing and developing radicals to optimize procedures of polymerization.

2.2.2 PS Processing

PS handling is an existing sector and as a consequence, advances are focused on additives that change the final product's characteristics. Although GPPS is the main business type, three other kinds of PS are intended through various polymerization processes, namely HIPS, EPS, and SPS. Continuous mass polymerization crops are used for GPPS and HIPS. A two-step method prepares EPS fabric beads. In an aqueous suspension, the blasting agent is impregnated in pre-prepared wood bottles. It can be placed in a method where the blowing agent is immediately impregnated into PS bottles created by polymerization of the suspension (Park et al., 2003). Mechanical strength of EPS products is small. To combat this, bead foams of polyolefin were developed (Kee, 2010). While polyolefin bottles are resilient, the blowing agent inserted during handling is not retained, so the polyester foam has been created. A blended blowing agent consisting of a high-solubility and low-permeability compound was used to synthesize the polyester foam that is both expandable and moldable. While the elevated solubility compound allows for a large degree of growth, secondary expandability is provided by the small permeability compound (Park et al., 2003). Recent study into injection foam handling using styrenemaleic anhydride copolymer has led in a significant and significant rise in foam efficiency in food packaging industries (Roberts and Kwok, 2007). By copolymerizing ethylene and styrene monomers, Dow Chemical Company's technology has enabled the development of ethylene-styrene interpolymers (Chaudhary et al., 2000). Interpolymers ' characteristics differ considerably with copolymer load.

2.2.3. Current Applications of PS

PS has a broad range from the production of products, design, medical devices, arts and crafts, to packaging (K. Marsh and Bugusu, 2007).

In food service and food packaging, PS foam containers are commonly used. If wrapped in PS, perishable food products may be avoided from spoiling. Electronic goods are placed in containers together with fabric produced of PS which isolates and protects against harm during shipping (Park et al., 2003). For trays, cups, coffees, bowls, cartons and for food containers, EPS, also recognized as lightweight Styrofoam, have been used (Issam et al., 2009; Thompsett et al., 1995).

PS is used for the manufacture of disposable plastic couch, household devices such as air conditioning, blenders, stoves, coolers, handheld aspirators, and microwaves. PS also imparts a flawless finish in addition to weight lightness. PS is also integrated into products, such as kitchen and bathroom equipment garden utensils, that create other household goods. It is also used in the construction of toys and homes for digital instruments, like smoke sensors, TVs, CD and DVD cases and a number of other tools. (Inagaki and Kiuchi, 2001; Inagaki et al., 1999). It is also used as a storage for cameras in smooth shell cycles (Mills, 2007) and can be interconnected in the production, for shoe components, of extruded plates and bun foams. Other PS uses include the building of ceilings, walls and surfaces for insulation (Pick and Knee, 1967). It also discovers usefulness in houses ' soundproofing walls. PS resins are used in fixtures, boards and sidings for lighting and plumbing. Laboratory products are produced from PS such as test tubes, petri dishes, tissue culture sample trays, diagnostic test facilities, medical cups, medical keyboards, plastic containers. For art and craft initiatives, architectural design drawings, window holders and Christmas trees decorations, EPS or styrofoam can be used (Chaukura et al., 2016).

2.2.4. Current Waste PS (WPS) and Disposal Practices

Because of the existence of phenyl groups and single C-C bonds, PS is extremely stable and resistant to decomposition. PS persistence creates multiple economic impacts including esthetic effects owing to high visibility, wildlife entanglement arising in decreased feeding effectiveness, strangulation, and ingestion (Davis, 2013). PS also produces a combination of polyaromatic hydrocarbons, known as carcinogens (Zhou et al., 2010). PAHs bioaccumulate once they reach the body due to poor volatility and biodegradability (Sese et al., 2009).

To minimize these economic and public health hazards, WPS is disposed of by landfilling or minimization procedures. PS is bulky due to poor density and decreases the ability and design life of landfills (Eckhardt, 1998). Moreover, landfilling is also a missed opportunity to recover the valuable energy resource from WPS. Predominantly CO_2, water, volatile hydrocarbons and heat are produced by high-temperature incineration. Compared to landfilling, 900 ° C incineration generates 65% carbon-shaped liquids and 35% solids, thus decreasing the quantity of the initial product (Durlak et al., 1998). The heat generated can be used for steam and hydroelectric generation due to the elevated calorific value. However, incineration was criticized for producing mixture of PAHs, especially at temperatures 800–900°C. (Durlak et al., 1998).

PAH exposure by inhalation, ingestion and dermal touch may result in cancer and genotoxicity (Zhou et al., 2010). Reactive polar products such as diol epoxides are produced by PAHs in body metabolism (Ramesh et al., 2004; Zhou et al., 2010). These metabolites are released or react with DNA, which leads to PAH-DNA cancer (Zhou et al., 2010).

2.2.5. WPS recycling and potential uses

PS recycling is also an established method. However, the use of recycled PS in food apps is restricted in most nations (Hocking, 1991). This confines the use of recycled PS for packaging, isolation, floating billets / boards, patio furniture and drainage materials (Aminudin et al., 2011; Hocking, 1991). The perfect alternatives for minimizing WPS appear to be reducing and recovering procedures. Direct recycling involves developing fresh WPS products, while indirect recycling involves changing the WPS to create fresh products. Typical instances of recycling include pyrolysis or catalytic splitting for the production of fuels volatile gases, styrene monomers, ion exchange resins and construction material (Aminudin et al., 2011; Kuhail and Shihada, 2015; Kuswanti, 2002; Mbadike and Osadebe, 2012; Williams and Bagri, 2004). Catalytic pyrolysis, for instance, was used to create recycled PS hydrocarbon oils and gases (Williams and Bagri, 2004). Mohammadi et al., (2012) used EPS as a diesel additive, while lowering emissions and improving engine efficiency. WPS has also been used for the development of low-cost and light-weight construction products such as brick and asphalt binders (Kuhail and Shihada, 2015; Mbadike and Osadebe, 2012). In order to create concrete matrix, Mbadike & Osadebe, 2012) integrated PS granules, while Kuhail and Shihada (2015) created PS lightweight concrete. A novel technique for transferring WPS to biodegradable plastic was created by Ward et al. (2006), namely polyhydroxyalkanoate.

WPS has also been used in disease and vector control. In sub-Saharan Africa, where malaria and other vector-borne illnesses prevail, this is particularly crucial. Low-cost control techniques are needed in this region that are inexpensive to bad homes. Studies have shown that WPS crystals are efficient in regulating illnesses and vectors of humans and animals (Chavasse et al., 1995; Sivagnaname et al., 2005). Following implementation of PS beads, 70–100 percent decrease in development, biting and microfilarial levels were noted in Kenya, Tanzania and India. For instance, using a flying coating of WPS beads to manage mosquitoes in Dares Salaam in Tanzania, Chavasse et al. (1995) found that mosquito densities in controlled locations fell by 76.7% but improved by 84.9% and 25.6% in two untreated control locations. Given the incidence of malaria in sub-Saharan Africa, the use of WPS was a rather underused technology in this respect.This implementation of WPS is primarily linked to its low density and floating capacity on water surfaces, and the elevated size allows it to cover big water bodies surfaces. However, owing to the WPS particles trapped in water, the broad use of this technique is probable to result in another type of water emissions (Nhapi et al., 2002). Using catalysts such as silica / alumina and ZSM5 zeolite, advanced thermo-chemical therapy techniques generate either fuel or petrochemical feedstock and power recycling. Zhang et al. (1995) recorded the use of barium oxide and its dimeric shape in the degradation of PS into the styrene monomer.

Noguchi et al. (1998) created a system for recycling waste EPS using d-limonene, a natural solvent that shrinks the EPS. It is suggested that reused PS has the same mechanical characteristics as virgin polymer and can therefore be used in processes comparable to those of virgin metal.

Adhesives production: The majority of research on WPS in adhesive production is carried out by scientists centered in Asia (Seluka et al., 2014) and is still quite an accessible topic. Issam et al. (2009) report that they have been using WPS in the production of adhesive emulsions.

Paints production: In the production of paints, WPS could also be used as a binder (Theiler, 1974). The odds of WPS being used in painting production were investigated by Osemeahon et al (2013). Faster dry and more resistant, with higher water, light and chemical resistance and poor yellowing in their film (Freitag and Stoye, 2008). Styrized alkyd resin covering It is therefore evident that a lot of WPS can be consumed by the paint sector.

Super-Absorbent production: It is also possible to modify WPS into good-value products like superabsorbents. Ismail and Zulkifli (2013) recorded the occurrence of a super-absorbent nanocomposite WPS-acrylic acid bentonite prepared by emulsion polymerization. For the nanocomposite containing 3% bentonite, the highest water absorption was obtained. Such super-adsorbents of nanocomposite may be used in diapers and may be used to remedy contaminated groundwater. But, the danger of remaining styrene monomers as well as other PAHs in these products needs to be assessed.

Flocculant and Ion exchanger production: Inagaki et al. (1999) researched the sulfonation regeneration of WPS. The WPS included PS with high-impact rubber or coloring agents. The method of sulfonation transformed the WPS into a polymeric flocculant. After using a mixture of the two polymer flocculants, the authors also noted some synergy. The manufacturing of flocculants from WPS is extremely appealing due to the elevated price and bad accessibility of water treatment chemicals. Also it is used as Cd^{2+} and Pb^{2+} adsorbent (Imen Bekri-Abbes et al., 2006); (Ruziwa et al., 2015). Although it has been discovered, for instance, that these products have superior extraction efficiencies to biosorbents, they have demonstrated helpful in separating chosen heavy metals from water considerably. To produce novel ion exchange resins, WPS was also used (Abrams, 1956). These resins have extensive agricultural applications in addition to water and wastewater treatment (Nasef and Güven, 2012), contaminated soil rectification, and also personal item purification such as bacteria and hormones (Azam and Dahman, 2008). Ozer et al. (2013) created a high-capacity cross-linked sulfonated PS ion exchange resin (up to 1,5–2 times that of business resins) and a fast ion exchange balance (i.e. less than 1 min). The transfer of ion resins was efficient in reducing divalent ions in water such as Ca^{2+}, Mg^{2+}, Ni^{2+} and Cu^{2+} particles (Ozer et al., 2013). PS-based exchangers can be low-cost water and wastewater treatment adsorbents in sub-Saharan Africa, where most individuals do not have access to safe drinking water. Another region of WPS implementation is the production for water purification of ion-exchange membranes after the needed chemical modification of the WPS. Sachdeva et al. (2008) recorded the chloride ion electrodialysis structure of extremely cross-linked anion exchange membranes. The composite ion exchange PS membrane was uniformly altered by gas component nitration followed by amination utilizing reductant hydrate and more responded to add quaternary ammonium fees on the membrane with dichloroethane and triethylamine. By electrodialysis, the chloride ions are separated. Tsyurupa et al. (1995) recorded the effective use of hyper-cross-linked PS sorbents (styrosorb) to remove phenol from water, with potential implementation in the therapy of agricultural effluent contaminated with phenol. Ion-exchange membranes can also be used in mineral processing with suitable selective chemical organizations after alteration of the membranes. As with all other feasible PS apps outlined by Tsyurupa et al. (1995), a cost-benefit analysis of feedstock compilation, washing and reprocessing is still required.

PS Nanofiber production: For catalysis as well as for the preparation of nanopore filters (water purification and air conditioning units), the high surface-to-volume property inherent in carbon nanofibers can be used. It is possible to prepare non-woven PS nanoporous filters from WPS. The nanoporous filters can be used to purify air and water. Marek et al. (2009), prepared regenerated PS electrospun PS nanofibers. To dissolve the WPS, solvents like tetrahydrofuran and dimethylformamide were used. Then the PS nanofibers were cross-linked using sulfuric acid accompanied by an ethylene diamine response. In quick water treatment, the cation and anion exchange PS nanofibers acquired were implemented. Such ion exchange nanofibers may be used for catalytically effective metal ions as matrix assistance. Rojas et al. (2009) designed WPS-loaded electrospun nanocomposites with nanowhiskers of cellulose. The PS nanofibers enhanced by cellulose whiskers have distinctive structural characteristics that allow for fresh characteristics and functionalities. It has been reported that Electrospun PS nanofibers thermally stabilize cyclodextrin inclusion complexes of volatile fragrances such as menthol up to 350 ° C (Uyar et al., 2009). Neoh and Yoshii (2008) revealed a distinct research in which an incorporation of 1-methyl cyclopropane cyclodextrin complex was electrospun in a PS nanofiber matrix. 1-Methyl cyclopropane inhibits and prolongs the shelf life of ethylene caused physiological modifications in different kinds of agricultural products.

2.2.6. Risks and challenges related to recycling WPS

The recycling of WPS involves several difficulties and hazards. Even though PS recycling technology is well recognized for producing a range of products, its recycling is restricted by transport issues because the volume ratio is small. This makes it unfavorable for lengthy ranges to capture, store and transport. In addition, owing to an absence of infrastructure investment, compacting machinery and logistic processes, there are restricted incentives to encourage recycling. The decomposition and depolymerization method into their monomers requires elevated energy-intensive temperatures and stress due to the elevated stabilization resulting from the existence of phenyl chains and single C-C links. Research shows that the pyrolysis of PS can take place at low temperatures of 400 ° C (J. A. Marsh et al., 1994) by using solvents like strong acids. In the presence of zeolites, the method concerned is comparable to catalytic pyrolysis (Williams and Bagri, 2004). PS usually has bad strain resistance, low strength, and extremely flammable features that restrict its use in the construction industry. For instance, Mbadike and Osadebe (2012) showed that their strength was reduced by incorporating PS into the concrete matrix. Similarly, Brennan et al. (2002) and Focke et al. (2009) indicated that mixing HIPS from external software hardware enclosures significantly decreased mechanical characteristics, especially stresses on material failure and effect strengths. Production of PAHs happens at temperatures below 500 ° C when combustion occurs. The next difficulty connected with WPS recycling has to do with sector and consumer views and behaviors. Using resins as an instance, Kuswanti (2002) showed that many recycling businesses are reluctant to use regrind and post-consumer resins due to comprehensive experimentation to define possible uses and handling parameters They also proved that labeling on recycled resins could be inaccurate and informative in determining molding and mechanical parameters (Kuswanti, 2002). Because used polymers are also degraded or misbranded, instead of tracking the first virgin compound properties, it is vital to characterize the used polymer. In addition, current polymer databases do not comprise data on resins for regrind or post-consumer resins. Such polymer databases are used to decrease the experimental time in order to determine molding and mechanical characteristics in addition to helping with the selection of productsAs a whole, Kuswanti's case study (2002) shows that adverse sector views stem from the economic hazards and expenses of extra material testing. Consumer risk may also contribute to the public health hazards connected with the use of recycled plastics. This is mainly because in the fields there are few academic establishments that offer curricula. The plastics, their disposal and recycling therefore constitute a fresh study region. Therefore, despite the various feasible implementations mentioned here, there is still restricted empirical evidence on such techniques ' wide-ranging agricultural implementation. However, as the public becomes more conscious of WPS ' economic effects, the need for recycling is expected to be regarded as one alternative for minimizing these effects.

2.2.7. Proposed use of WPS in the future

Although WPS recycling is gaining recognition in building materials and artifacts. For heavy metal extraction from solution, and for other uses such as paints and adhesives, future study is probable to follow the chemical conversion of WPS into flocculants. Although Hamad et al. (2013) have shown that mechanical recycling of WPS has been preferred to chemical recycling; flocculants are particularly helpful as drinking water is usually a issue in Zimbabwe. Water treatment costs are increasing, resulting in individuals consuming contaminated water in metropolitan regions and thus the spread of waterborne diseases such as cholera, typhoid, and the like is recurrent (Nhapi et al., 2002). While severe metal toxicity is not immediately apparent, severe metals in agricultural and mining effluent waters are constant pollutants (Pumure et al., 2011). To make the water appropriate for release into government rivers or to make it potable, these are often hard to remove. As a result, they discover their way into government rivers and to individuals straight or up to the food chain. It is therefore a concern to sequestrate heavy metals from water structures. In general, waste plastics, on the other side, pollute the soil. Current study is being carried out on studies into a chemical conversion of WPS into flocculants through sulfonation.

2.3. Polyethylene Terephthalate (PET)

PET is semi-cristalline, thermoplastic polyester with high strength, transparency and safety characteristics (Lopez-Fonseca et al., 2011). Pure terephthalic acid and ethylene glycol are obtained from crude petroleum for the production of PET. The first item when boiled together is a monomer Bis(2-hydroxyethyl) terephthalate blended with plastics (oligomers) of small molecular weight. The combination then responds further, distills surplus ethylene glycol and, as shown in Figure 2.7, shapes the PET. The PET is a viscous molten liquid at this point. It is extruded to create a glass-like amorphous substance, and water is quenched. In addition, some PETs are manufactured using technology based on the terephthalic acid dimethyl ester. Alternative responses, such as terephthaloyl carbonate response with antifreeze, often prepare PET. This response is simpler, but terephthaloyl chloride is more costly and more hazardous than terephthalic acid. (Sinha et al., 2010).

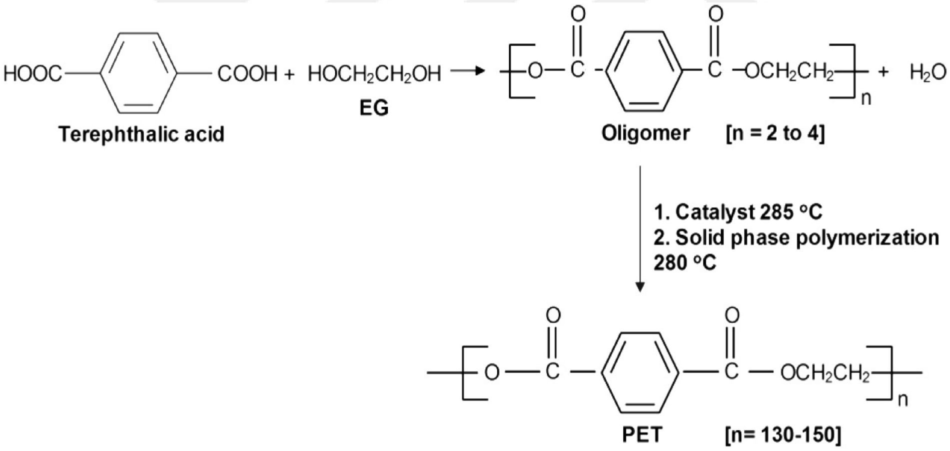


Figure 2.7. Manufacture of PET as described in (Sinha et al., 2010).

The necessary elevated molecular weight PET is produced at reduced temperatures through a second polymerization phase performed in the solid state. This prevents all volatile impurities, such as acetaldehyde, free glycols and water, efficiently. For excellent mechanical features, the elevated relative molecular mass is essential, providing rigidity, toughness and creep resistance while at the same moment offering adequate strength to withstand cracking and cracking under stress.

It is very hard to purify once the polymer is created and therefore the quality of the starting components is the main consideration. Processes of vacuum distillation readily purify ethylene glycol while continuous crystallization purifies terephthalic acid. For food packaging apps, such elevated purity and elevated relative molecular mass components are required.

2.3.1. Different Usage of Waste PET

For the construction industry, reuse of plastic bottles has been considered and studies exist on concrete (Siddique et al., 2008), mortar containing PET waste aggregates (Ge et al., 2014; Hannawi et al., 2010), use of rice husk and plastics (Choi et al., 2006), use as concrete composite (Marzouk et al., 2007), aggregate, Concrete substitution (Frigione, 2010; Z. Z. Ismail and Al-Hashmi, 2008), water-cement inquiry with PET containers (Albano et al., 2009) and ground strengthening (Babu and Chouksey, 2011). Rahman et al. (2013) discovered recycled PET in altered asphalt as a partial fine aggregate substitute. Klimek et al. (2016) manufactured particleboard using PET materials treated as raw material from air-plasma waste.

The use of plastic bricks has recently been regarded by Eco-bricks (Taaffe et al., 2014). There are a few instances, particularly in Latin American nations where an eco-brick-like idea was used as part of a volunteer project and to detail eco-parks or some architectural characteristics.

When removing (super-cleaning) the recollected post-consumer PET bottles were reused either to plastics or to fresh packaging apps. The primary task of super-clean use procedures is to get rid of traces of recycled contaminants. In most cases, polycondensation processes of the solid-state are supported by super-clean processes.

2.3.2. Waste PET Recycling

Due to economically scale away PET disposal, recycling procedures are the most efficient. As the cost of virgin PET stays, consistent, fresh and affordable PET recycling techniques are offering comparatively affordable PET to the PET recycling sector. The world's first post-consumed recycling attempt of PET bottles was in 1977. (Al-Sabagh et al., 2016). The amount and type of contaminants current in the flakes is the main variable influencing the suitability of post-consumed PET flake for recycling. Post-consumed PET contamination is the main cause of decayduring re-processing of its physical and chemical properties. Minimizing the quantity of these contaminants improves the performance of PET

(Giannotta et al., 1994). Post-consumed PET is polluted with many materials, such as pollutants that produce acid, water, pollutants that color, acetaldehyde, and many others.
Studies indicated that all four main recycling approasches can be applied for recycling post-consumer PET products: Primary recycling: waste or scrap is either combined with virgin metal to ensure product quality or used as a second grade material (Neale et al., 1983). Secondary recycling: involves physical reprocessing, drying and melt reprocessing (Al-Sabagh et al., 2016). Tertiary recycling: includes polymer chain conversion. Through distillation and drying, monomers are purified and used for polymer production. (Sinha et al., 2010). Quaternary recycling: incineration can recover the energy content (Sinha et al., 2010). Researchers have discovered methods to individually fix each issue; there is still no way to fix them all at the same time. The primary problem is to provide an effective and environmentally friendly manner to recycle PET.

There are some challenges with PET recycling. Colored PET bottles have limitations for their reuse and therefore a much lower value. Washed PET flakes are usually not suitable for the application in direct food contact. Super-clean processes for PET bottle recycling are using further deep-cleansing steps to clean-up flakes to contamination levels similar to virgin PET pellets (Welle, 2011).

2.4. Sulfonation

Sulfonation is among the most popular techniques of modifying polymers ' surface characteristics in order to attain certain industry-wanted features such as greater conductance, thermal resistance, water retention, biocompatibility, ion exchange ability, inflammation, etc. Sulfonated polymers with all these different features have a broad variety of applications from methods of chemical and water-wastewater treatment to tracking / detecting technology (Ergenekon et al., 2011).

Sulfonation is an exchange response observed in an organic compound and sulfonic acid between carbon (or sometimes nitrogen). Oleum, sulfuric acid, free sulfur trioxide, and halogen derivatives of sulfuric acid are the most commonly used sulfonation reagents for aromatic compounds. (Ergenekon et al., 2011).

Benzene is a hexagonal planer shape aromatic compound. With hybridization and planer geometry, there are six carbon atoms in benzene. In the benzene ring, the pi-bonds are arranged alternately, which delocalized the pi-electrons over six carbons. Benzene ring delocalization of pi-electrons makes it more robust relative to easy alkenes (P. W. G. Smith and Tatchell, 1969). This benzene trait that gives the molecule additional strength is called aromaticity.

An electrophile can readily assault the benzene ring due to the existence of elevated electron density in the molecule. The electrophile includes positive charge and benzene ring assaults to create an arenium ion that resonance stabilizes. An electrophilic replacement response includes replacing one of the aromatic ring's oxygen atoms with an electrophile.

2.4.1. Sulfonation of Benzene

Changing the benzene hydrogen atom by a set of sulfonic acids (SO_3H) is called benzene sulfonation. The response takes place in the presence of focused sulfuric acid that contains dissolved sulfur trioxide, also recognized as sulfuric acid fuming. Benzene sulfonation results in benzene sulfonic acid creation (Figure 2.8).

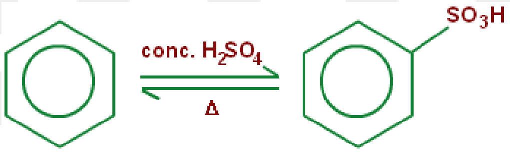


Figure 2.8. Benzene sulfonation scheme

In benzene sulfonation, sulfur trioxide functions as a focused sulfuric acid electrophile (Figure 2.8). In essence, the response is reversible; therefore, the reaction rate may improve as the electrophile material increases. Benzene sulfonation can be done in two ways, either by refluxing the benzene for numerous hours with concentrated sulfuric acid or by refluxing the warm benzene for 20-30 min at 40 ° C heat (Vink, 1981).

Benzene sulfonation is a multi-step response finished in four stages by forming an intermediate sigma complex. Sulfur trioxide functions as a reaction intermediate generated by sulfuric acid auto-protolysis. In the following measures, the reaction is done (Moors et al., 2017).

Step 1- Electrophile creation: Sulfuric acid auto-protolysis outcomes in the creation of sulfur trioxide that functions as an electrophile owing to a positive sulfur atom in the molecule of polar sulfur trioxide and responds with benzene (Figure 2.9). (Shi, 2017).

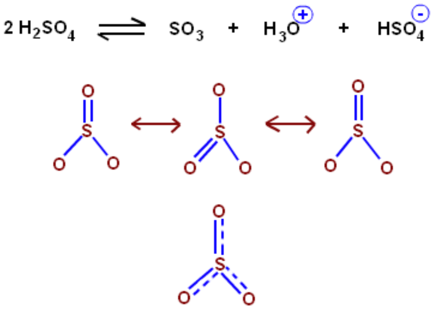


Figure 2.9. Step one of sulfonation, Formation of electrophile

Step 2 - Next move involves an electrophile assault on the benzene ring to create a sigma structure that in this response is a zwitterion owing to the existence of reverse load on the same molecule (Figure 2.10.) (Shi, 2017).

Step 3 - The intermediate is maintained by the benzene chain charge delocalization (Figure 2.10).(Shi, 2017).

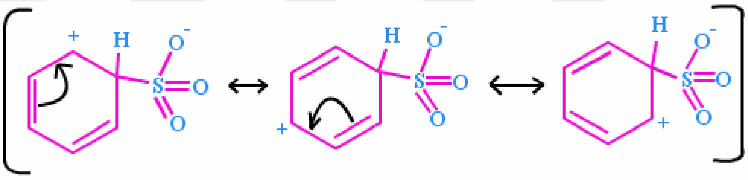


Figure 2.10. Steps two and three of sulfonatio

Step 4 - Last two stages, the dissolved SO_3 nucleus removes proton from the sigma structure to create an aromatic sulfonate that is protonated by $HSO_3{}^{+}$ to create benzene sulfonic acid and sulfur trioxide (Figure 2.11).(Shi, 2017).

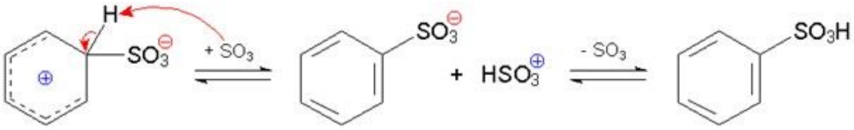


Figure 2.11. Step four of Sulfonation

2.4.2. Applications of Sulfonated PS

Application of sulfonated HIPS and EPS were effective in the removal of Zn^{2+} and Pb^{2+} from aqueous solution at 37 to 84% efficiency (Ruziwa et al., 2015). Rubinger et al. (2007)used sulfonated PS to prepare humidity sensor films by the dip coating on insulating ceramic substrates**.** PS sulfonation allows producing cationic exchanger resin (L. Qiu and Qu, 2006; Q. Qiu et al., 2017), polyelectrolyte to use it for the removal of turbidity from wastewater (Imene Bekri-Abbes et al., 2007) and fuel cell membranes (Golubenko et al., 2017). Al-Sabagh et al. (2018) have used sulfonated PS for organic dye adsorption. EPS waste was utilized for the production of partially sulfonated PS, which is used as catalyst for the esterification of rubber seed oil and free fatty acid (Suresh et al., 2017).

2.4.3. Sulfonated PS Polyelectrolytes

Polyelectrolytes in their repeat units are polymers with dissociating bands. They can be split into polycations, polyanions and polysalts. They dissociate in water like ordinary electrolytes (acids, bases and salts) and carry one or more charges depending on the pH value. Thus, polyelectrolyte features are similar to electrolytes as well as polymers. The sort of dissociating organizations in the polyelectrolyte determines their solubility in water and other liquids (alcohols etc.) that are polar and hydrogen bonding. A sulfonated linear PS, for instance, dissolves easily in water, while PS itself is one of the most water-resistant polymers. PS sulfonic acid is a compound that can be easily produced from PS and used in polyelectrolyte chemistry (Vink, 1981). PS sulfonic acid attracts attention with its ion exchange characteristics and low cost (Bozkurt, 2005). The sulfonation of PS began in the 1960s (Turbak, 1962), and the patent of Makowski (1975)has been rapidly spreading (Kucera and Jancar, 1996) and continues to be studied (I. Bekri-Abbes et al., 2008).

The first PS sulfonation method in homogenous phase was developed by Turbak (1962). In this method, triethyl phosphate and sulfur trioxide complexes in dichloroethane are reacted with PS. In the Makowski patent (1975) acetyl sulfate complexes were used as sulfating. The most basic form of the present work was the Vink method (Vink, 1981) and it was prepared in PS sulfonic acid inert cyclohexane with using Ag_2SO_4 or P_2O_5 as accelerator. The PS sulfonation process in the heterogeneous phase was developed by Kucera and Jancar (Kucera and Jancar, 1996). Along with other studies, Vink is the most widely used method. Over time, the Vink method has been examined and various modifications have been developed in various studies (Imene Bekri-Abbes et al., 2007; I. Bekri-Abbes et al., 2008; Holley, 2009; Vandevoorde, 1996).

When sulfonation studies in the literature are examined, the main rationale of the synthesis method seems to be the same but the details are influential on the structure of the synthesis material or applications. In the studies, PS was sulfonated to obtain flocculant and adsorbent material. However, PET is one of the versatile semi-aromatic polymer, which can be sulfonated because of presence of benzene ring in the PET structure; however, it has not been studied yet. Therefore, in this study the procedure will be applied as a modified sulfonation to PET.

2.5. Washing of Waste Plastics and Treatment of Its Wastewater

2.5.1 Washing of Waste Plastics

When the waste plastics are sorted, the waste needs to be washed properly to remove impurities such as dirt, labels, adhesives, etc. Washig enhances the quality of the recycled product**.** Different washing techniques are described below:

Dry Brushing: When the product is too soiled, particularly as a result of sand, soil or waste from roads, parks and landfills, a first dry scouring does not allow the washing water to become too polluted. Usually scouring is performed with rigid brushes.

Manual Wash: performed in big reservoirs or half-barrels with a capability of at least 100 liters. Different methods can be used according to the tenacity of the mud:

1. Washing in cold water is adequate for comparatively smooth waste, which is only soiled by dirt or dust. Plastics are rubbed with bristles strongly.
2. The washing should be performed in warm water with the aid of soaps or detergents for extremely soiled and greased waste. The temperature of water stays restricted due to manual washing of the waste.
3. If detergents are not adequate, sodium hydroxide (NaOH) or potassium hydroxide (KOH) may also be used, particularly to remove oil and grease residues. A several-hour bathing period enables the waste to be scoured properly. Then they are cleaned and rinsed correctly. Nevertheless, this method is not recommended for hand washing as these are comparatively hazardous to handling.

In addition, water management is to use a "against the current" wash. This includes transferring the waste into a sequence of consecutive bins in which the water is gradually becoming warmer. Clean water flows from the other direction, i.e. from the cleaner reservoir to the foulest reservoir. As such, dirty water is rubbing against cold waste and smooth water is used to finish the job. The bins are placed in steps so that the water can circulate due to gravity. The waste is taken out from the basins until they have attained the required cleanliness.

Washing of Flakes: It's very simple if they've been grinded already. In cooking water tanks, the plastic flakes can be put in which detergent or soda is added. Frequent mixing of plastic and dust creates friction. The flakes are collected using bins with big skimmers after a more or less lengthy settling time (several hours for soda baths). They may be washed after rinsing with transparent water.

2.5.2. Characteristic of Waste Plastics Washing Wastewater (WPWW)

The washing water used in the recycling of plastics is the basic waste from the recycling process. The main pollutant parameters in such wastewaters are COD, SS and turbidity with high pH. In Turkey, this wastewater is reused after clarified in a settling tank located in the recovery plant (Sahinkaya, 2017) but it is at lower quality. Thus, an environmentally friendly recycling activity is achieved by consuming less water. After a while, the washing water becomes soiled that it cannot be used for washing, and this water needs to be treated. The pollution character of wastewater during the cleaning of plastic wastes varies according to the type of plastic to be recycled.

Table 2.2 presents the characteristics of wastewater from cleaning of PET plastics (A. S. F Santos et al., 2005) . However, these values in the Table vary according to the origin of the plastic and the properties of the material used in packaging. Hence, studies related to this type of wastewaters characteristics are needed.

Discharge criteria in Turkey are defined by The Water Pollution Control Regulation (WPCR, 2004). The pollution parameter values of plastic washing wastewater characteristics in Table 2.2 are above Water Pollution Control Regulation's "Criteria for plastic materials processing and production" and they are risky for the environment. These parameters in the washing wastewater are caused by the plastic waste itself and contaminates at the outside of container. As a result of cleaning process, wastewater with high pollution and cleaned waste plastic are obtained. There is no study or practice to treat this wastewater in the recycling facilities of Turkey. Generally these wastewaters are being reused several times after primary settling for solids removal. Then they are being discharged into sewerage. This causes an increase in sewage pollution load and water consumption.

The water framework Directive aims to prevent the negative effects of wastewater from urban settlements and industries on the environment (IPPC, 2003). The following BAT for water pollutants presume the optimization of BAT for environmental management and prevention/ minimization. Wastewater streams containing heavy metals or toxic or non-biodegradable organic compounds are treated or recovery separately. Individual waste streams containing toxic or inhibitory organic compounds or having low bio-degradability are treated separately e.g. by chemical oxidation, adoption, filtration, extraction, stripping, hydrolysis or anaerobic pretreatment. Effluent from individually treated waste stream are discharged to the combined biological treatment plant for further treatment. In particular metals and heavy metals are treated as a individual waste streams before mixing with non-metal containing streams.

Table 2.2. Washing wastewater character for PET, PE and PP plastic waste

Parameter	**PET***	**PE and PP***	**Turkish Regulation****
COD, mg.L^{-1}	897	190	250
BOD$_5$, mg.L^{-1}	-	-	-
Oil-grease, mg.L^{-1}	53	97	25
TSS, mg.L^{-1}	5338	7975	65
Turbidity, NTU	303	127	-
pH	11.9	12.4	6-9
Total Coliform, 10^8 MPN/100 mL	48	2.5	-
Fe, mg.L^{-1}	7.46	4.37	-
Pb, mg.L^{-1}	1.29	1.10	-
Mn, mg.L^{-1}	0.08	0.07	-
Cd, mg.L^{-1}	-	0.05	-

*(A. S. F.; Santos et al., 2005) **WPCR,Table 14.8 (2004)
BOD$_5$: 5-day Biochemical Oxygen Demand

2.5.3 Treatment of WPWW

Chemical treatment of wastewater pollutants was researched and established, but owing to the high expenses of chemicals, its complete application was postponed in favour of biological treatment techniques. (Semerjian and Ayoub, 2003). Coagulation / flocculation is a frequently used physico-chemical treatment method in which coagulants and/or polymeric flocculants are dosed to wastewater to destabilize colloids and agglomerate them into bigger settleable flocks. Several surveys recorded examining this method for industrial wastewater treatment, in particular with regard to efficiency optimization of coagulant /

flocculant, determination of experimental circumstances, pH evaluation and evaluation of flocculant supplementation (Abdel-Shafy and Emam, 1991). However, biological treatment may not always be appropriate, particularly for particular circumstances such as intermittent waste streams, waste containing materials that are poisonous to biological growth, or wastewater comprising non-biodegradable impurities and elevated pH. Coagulation and flocculation take an important place in chemical treatment and may be used as a pretreatment prior to biological treatment to enhance biodegradability of wastewater during secondary treatment (Amuda et al., 2006).

Coagulation is typically done by adding and mixing chemicals. The method is used in main storage centres to improve the degree of suppression of TSS, BOD, COD, and bacterial population, as well as to improve the efficiency of secondary treatment procedures. Coagulation utilizes salts such as aluminum sulfate or ferric (iron) substances that bind to the suspended objects, making them less stable, i.e. more probably to drop out (Amuda and Amoo, 2007).

Flocculation is the physical method of putting into touch the destabilized objects to create bigger flocks that can be separated from suspension more readily. Flocculation is normally used in combination with coagulation and preceding it. Generally speaking, the method is achieved by smooth blending of the destabilized suspension to provide the particles with an chance to meet and bridge. Flocculation therefore enhances subsequent sedimentation or filtration system efficiency by enhancing particle size, leading in higher settling and filter capture rates. Flocculation agents are natural synthetic polymers used to create the flocculant and synthetic organic materials. Efficient extraction of solids, colloids and certain soluble substances in wastewater is achieved by flocculation at elevated pH.

In this study, first sulfonation process was applied to both PS and PET type of plastics, which have aromatic structures, then the effectiveness of those synthesized materials on coagulation/flocculation treatment of WPWW in terms of turbidity, COD, and SS removals was investigated.

3. MATERIALS AND METHOD

Experimental configuration of this study was shown in Figure 3.1 as a flow chart. The scope of the whole study and the analysis performed at each step are clearly shown in this flow chart. The steps are described in the following order:

- Collection of waste plastics and preparation for the study
- Washing of waste plastics to obtain six different WPWW
- Synthesis of eight alternating polymeric flocculants by modified sulfonation process
- FTIR (Fourier Transform Infrared) analysis for sufonated PS flocculants (FSPSs) and sulfonated PET flocculants (ASPETs)
- Characterization of WPWW
- Investigating the effectiveness of the eight synthesized polymeric flocculants in treatment of six WPWW with coagulation/flocculation process
- Comparing synthesized polymeric flocculants in treatment WPWW with classic sufonated PS flocculant (FSPS) and conventional flocculant PEL
- Selection of the two most successful flocculants for each wastewater and analysis of the effluents and treatment sludges produced as a result of treatments
- According to the results of effluent analysis, selecting the most effective flocculant for each wastewater and dose optimization of the selected flocculants
- Analysis of the effluents and treatment sludges produced as a result of dose optimization process
- Optimizing the pH by selecting the optimum dose from dose optimized with four different pHs
- Analysis of the effluents and treatment sludges produced as a result of pH optimization process
- According to effluents quality of dose and pH optimization, characterization of the treatment sludge of the most efficient dose and pH

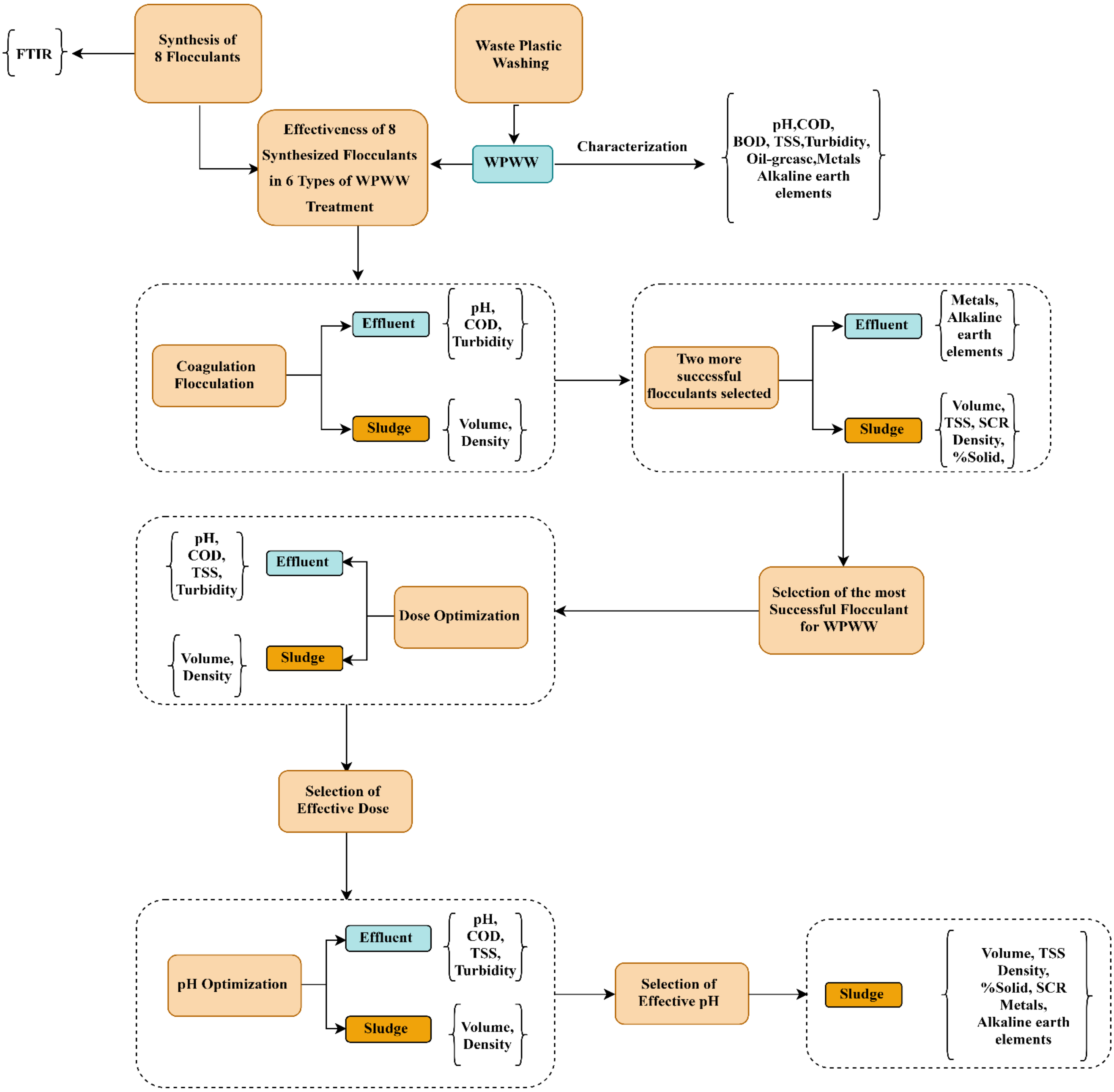


Figure 3.1. Flow chart of works in this study

3.1. Procurement of Waste, Shredding, Washing and Specification of Properties

The HDPE, LDPE, PET, PP, and PS thermoplastic wastes used in the study were obtained from the municipal solid waste separation center in Konya-Turkey. After the preliminary examination of the wastes, the impurities (paper, glass, etc.) were removed. Then, they were shredded up to less than 8 mm in size. Due to the flexible structure of the plastic, the shredding process was carried out by using a specially designed plastic crushing machine (Figure 2.1).

Figure 3.2. Laboratory scale plastic crushing machine and shredded plastics

The eight mm shredded HDPE, LDPE, PET, PP, and PS thermoplastic wastes were washed. Coustic washing is the most common plastic washing bath method applied in Turkey and suggested in the literature. Washing was performed in a lab-scale system by using NaOH in a completely stirred batch system in three stages. In the first stage, washing was carried out using 42% NaOH (A. S. F.; Santos et al., 2005) solution in which 126 g/1500 mL NaOH was dissolved. 250 g plastic waste was washed in this solution (Figure 3.3). The first stage washing process was finished after keeping the mixture at 90°C for 10 min, the wastes were filtered, and first step plastic wastewater was obtained. In the second stage, waste plastics were transferred to 1500 mL tap water, rinsed at 90°C for 10 min, and then filtered. In the third stage, the same rinsing process was carried out as the second stage. The washed and rinsed waste plastic sample was allowed to dry, and the wastewater obtained from of those three stages of washing process were collected and mixed to obtain WPWW. This is the same as the one discharged to the sewer system in field applications. This procedure is repeated for each type of plastic.

3.2. Synthesis of Sulfonated Polymeric Flocculant from PS and PET Plastics

First, literature method (I. Bekri-Abbes et al., 2008; Grossi et al., 2010; 2006; Sulkowski et al., 2005) were applied to the WPS obtained from the waste center to synthesize conventional sulfonated PS and these synthesized material were used for comparison. The adsorbent synthesized in the literature was insoluble (Bekri-Abbes et al., 2008) and the flocculant was water soluble (Bekri-Abbes et al., 2007). There are described small differences in the synthesis methods in the literature (Table 3.1). The main logic of the synthesis method seems to be the same, but the details of the synthesis, effect on the structure or the activity of the place it is used of the synthesized substance. As an example, application steps of classic sulfonated PS synthesis by Vink (1981) method in Table 3.1 are indicated in Figure 3.4.

Figure 3.3. Waste plastic washing process

The synthesis of sulfonated PS is based on the addition of the sulfo group to the aromatic ring structures of PS. It is necessary to have an aromatic structure to obtain the sulfonated structure. In the study, the method of obtaining flocculants by PS sulfonation was a modification of methods of Table 3.1 where new flocculants were synthesized. The same modified method was used to synthesize flocculants material using other aromatic structured plastic, PET. The plastics studied in the thesis since PS, as well as PET, has aromatic rings in their structure similar methods with small modifications was carried out for both PS and PET. These modification applications and the resulting materials are explained in Table 3.2. The Grossi method presented in Table 3.1 was actually the method for obtaining adsorbent from PS by sulfonation. When applying this method to PET plastic, since PET is dissolved in acid, two materials obtained by this method were not in the form of insoluble adsorbents. Therefore, these two materials have also been classified as flocculants in the experiments.

Table 3.1. Some PS sulfonation methods in literature

Method	Material	Reference
➢ Mix 50 mL H_2SO_4 with 11 g P_2O_5, cool it to 40°C ➢ Dissolve 1,5 g PS and 75 mL cyclohexane in separate container ➢ Mix both (while mixing one add other slowly) ➢ Mix for 30 min in 40°C ➢ Wait for 1 hour without mixing ➢ Add 25 g ice, cool it immediately, form 3 phases ➢ Take the middle sticky phase, add 150 mL distilled water, discharge the formed solvent phase and dry (Figure 3.3)	Flocculant	(Vink, 1981)
➢ Mix 50 mL H_2SO_4 with 3 g P_2O_5 for 30 min, cool it to 40°C ➢ Dissolve 0,25 g PS and 25 mL cyclohexane in a separate container ➢ Mix both (while mixing one add other slowly) ➢ Mix for 120 min in 45°C ➢ Take it into separation funnel, form 3 phases ➢ Discharge the bottom acid phase, add 150 mL distilled water, mix the polymer for 15-30 min ➢ Separate the wet part, bring to basic pH with NaOH pellet ➢ Distill and dry	Flocculant	(Imene Bekri-Abbes et al., 2007)
➢ Mix 50 mL H_2SO_4 with 10 g P_2O_5, cool it down to 40°C ➢ Dissolve 1,5 g PS and 25 mL cyclohexane in a separate container ➢ Mix both (while mixing one add other slowly) ➢ Mix it at 40°C and wait 60 min ➢ Add 25 g ice, cool it immediately, form 3 phases ➢ Take the sticky yellow substance, dialysis it with 100 mL water ➢ Dry	Flocculant	(Bozkurt, 2005)
➢ Mix 200 mL H_2SO_4 with 20 g P_2O_5, cool it down to 40°C ➢ Dissolve 1,5 g PS and 300 mL cyclohexane in a separate container ➢ Mix both (while mixing one add other slowly) ➢ Mix it at 40°C and wait 60 min ➢ Add 50 g ice, cool it immediately, form 3 phases ➢ Take the middle sticky phase, mix it with 500 mL deionized water ➢ Add NaOH pellet until pH 9 ➢ Separate the salts with dialysis ➢ Dry	Flocculant	(Holley, 2009; Vandevoorde, 1996)
➢ Mix 6 mL acetic anhydride with 50 mL 1,2-Dichloroethane and 3 mL H_2SO_4 ➢ Cool it down to 5-10°C ➢ Mix 10,4 g PS with 50 mL 1,2-Dichloroethane , bring it to 50±2°C ➢ Mix both (while mixing one add other slowly) ➢ Mix it at 50°C and wait 60 min ➢ Start mixing with a large amount of water or methanol, add the solvent mixture drop by drop ➢ Rinse the precipitate formed in water several times ➢ Filter its water and dry it in vacuum at 50°C	Flocculant	(Kucera and Jancar, 1996)
➢ Mix ratios X g PS with 5X g H_2SO_4 and 0,01X g Ag_2SO_4 ➢ First mix the chemicals in vertical condenser ➢ Add PS when reached 80°C, mix for 1,5 hours in constant temperature ➢ Filter the solid product, dissolve it in deionized water ➢ Precipitate it with Na_2CO_3	Flocculant	(2006; Sulkowski et al., 2005)
➢ Mix 5 g PS with 100 mL H_2SO_4 ➢ Mix at 40°C for 4 hours or at 60°C for 1,5 hours ➢ Filter PS and wash with distilled water until the pH is neutralized ➢ Dry at 40°C for 30 min	Adsorbent	(I. Bekri-Abbes et al., 2008)

Table 3.1. (Continued)

Method	Material	Reference
➢ Mix 5 g PS with 100 mL 1,2-Dichloroethane ➢ After dissolving add silica-sulfuric acid in 1 by 2 ratio ➢ Mix for 7 hours at 60°C ➢ The coarse grains are acid and the fine grains are SPS ➢ First filter it, then dry ➢ Rinse with water and wash with%10(w/w) HCl ➢ Rinse with deionized water, dry ➢ Porcelain can be grinded in grinder if necessary	Adsorbent	(Sułkowski et al., 2012)
➢ Mix 1 g PS with 20 mL H_2SO_4 ➢ Mix at 105°C for 3 hours ➢ Wash it first with 0.1M NaOH, then with deionized water until it reaches pH7 ➢ Wash with 1/50 HCl solution, rinse with water ➢ Dry it for 24 hours in vacuum at 70°C	Adsorbent	(Grossi et al., 2010)

Figure 3.4. Steps of FSPS synthesis by classical method (Vink, 1981)

Totally, eight flocculants were synthesized (Table 3.2). Three of them were obtained by PS sulfonation (FSPS1, FSPS2, and FSPS3) and three by PET sulfonation (FSPET1, FSPET2, and FSPET3). The last two of them were obtained by using waste PET material in the method of synthesizing the adsorbent by sulfonation. A water-soluble product was obtained since the PET material was dissolved in the acid, because, the side chain aromatic groups of PS are placed in the main chemical structure chain of PET. Therefore, H_2SO_4 has affected the chain structure of PET and probably broken the PET's aromatic ring on the main chain, lower molecular compounds were formed. So, the product is not insoluble. Hence, these products are named ASPET1 and ASPET2 and have been tested as flocculants.

Table 3.2. Synthesized flocculant materials and synthesis methods

Abbreviation	Form	Reference	Method
FSPS1	Solid Powder 	(Bekri-Abbes et al.(2007)	WPS plates were used, applied without modifying the method.
FSPS2	Fluid 	Modified from Sulkowski et al. (2006; 2005)	1.2 g PS foam + 0.05g Ag_2SO_4 + 20 mL H_2SO_4 PS foam waste was used. First materials were stirred at 80°C for 4 hours in the top cooling system. Then, when 20 mL deionized water was added, a pink solid phase sticky material was formed. The pink solid phase was taken and dissolved by adding 30 mL deionized water. Finally, 12 g Na_2CO_3 was added to form a precipitate. However, when it was separated from its fluid, since that fluid is its wastewater, it was stored and dosed as fluid in experiments.
FSPS3	Solid Powder 	Modified from Sulkowski et al. (2006; 2005)	1.2 g PS plate + 0.05 g Ag_2SO_4 + 20 mL H_2SO_4 A similar method to FSPS2 was applied, but PS plates were used. It was precipitated with $CaCO_3$, and the final precipitate was dried by filtration and used in powder form. 1 g PS and 20 ml H_2SO_4 was stirred at 60-80˚C for 4 hours. When 20 mL deionized water was added to the dark brown slurry, a sticky solid phase material was formed. The material was dissolved in 30 mL deionized water and the mixture was stirred while adding $CaCO_3$ powder slowly. The resulting yellow precipitate was filtered off and dried at 40°C.
FSPET1	Solid Powder 	Modified from Sulkowski et al. (2006; 2005)	2 g PET + 0.02 g Ag_2SO_4 + 10 mL H_2SO_4 The method was performed using PET instead of PS. First, Ag_2SO_4 and H_2SO_4 were mixed at 60°C in the top cooling system. When 50 mL of deionized water was added, a pink and sticky solid material was formed. Then, it was filtrated and the fluid was spilled. The process up to here for FSPET 1, 2 and 3 is the same and is differentiated after this. In FSPET 1 : The solid was dissolved by adding 200 mL deionized water. Then, it was precipitated with adding 58 g Na_2CO_3 by followed 1.6 g $CaCO_3$. In FSPET 2 : The solid was dissolved by adding 200 mL deionized water. Then it was precipitated with 2.3 g $CaCO_3$. In FSPET 3 : The solid was dissolved by adding 75 mL deionized water. Then NaOH solution (5N) was added dropwise until the precipitate was formed. (The amount of NaOH used was about 80 g when calculated totally).
FSPET2	Solid Powder 	Modified from Sulkowski et al. (2006; 2005)	
FSPET3	Solid Powder 	Modified from Sulkowski et al. (2006; 2005)	

Table 3.2. (Continued)

Abbreviation	Form	Reference	Method
ASPET1	Solid Powder 	Modified from Grossi et al. (2010)	1 g PET and 20 ml H_2SO_4 was stirred at 105°C for 3 hours. First, it was brought to pH7 with 50 mL 0.2M NaOH and then with 130 mL deionized water was added. At this stage, it was decided that the sample could not be an adsorbent, because the sample had been dissolved. It was precipitated with 10.6 g NaOH and then with 2.5 g $Ca(OH)_2$. Half of the synthesized material was filtered and dried at 70°C for 24 hours and was tested as a powder material. As the filtrate water was wastewater, the other half was tested without filtration. The results will be compared. If the treatment efficiency is achieved without the need for filtration so the liquid part will be removed with the treated wastewater and the costs of the filtration, drying, and wastewater removal during the production of the substance will be saved.
ASPET2	Fluid 	Modified from Grossi et al. (2010)	

The results presented by Ozdemir et al (2018; 2017) revealed that the coagulation/flocculation process applied to WPWW has been performing very well especially in the treatment of some parameters under particular conditions. The treatment performance was observed to be dependent on the flocculant used and experimental conditions such as pH. Based on these results, it was aimed to investigate the efficacy of flocculants, which are synthesized by the same logic but with different methods in improving the treatment performance. Therefore, in this study, by using the synthesized eight types of new polymeric flocculants, the performance of each plastic species in the washing wastewater was investigated by performing coagulation/flocculation experiments. Treatment performances were compared to both the conventional flocculant PEL and classical FSPS by conventional Vink method. In this comparison, the wastewater obtained for each plastic type has been tested separately.

3.3. Characterization and Treatability of WPWW

For each type of waste plastic, raw wastewater (Figure 3.5) collected during washing was firstly characterized. The characterization of the wastewater from washing process was performed in accordance to Water Pollution Control Regulations (WPCR, 2004) and EU's Development of the Urban Waste Water Treatment Directive (DIRECTIVE, 2003) regarding TSS (mg L^{-1}), COD (mg L^{-1}), BOD_5 (mg L^{-1}), Turbidity (NTU), pH, oil-grease (mg L^{-1}), Pb (mg L^{-1}), Cd (mg L^{-1}), Mn (mg L^{-1}) and Fe (mg L^{-1}). However, when the wastewater samples were subjected to Inductively Coupled Plasma (ICP) analysis, multiple parameters were selected and further parameter values were obtained. The analysis of parameters other than those read in ICP was performed as specified in Standard Methods (APHA, 2005).

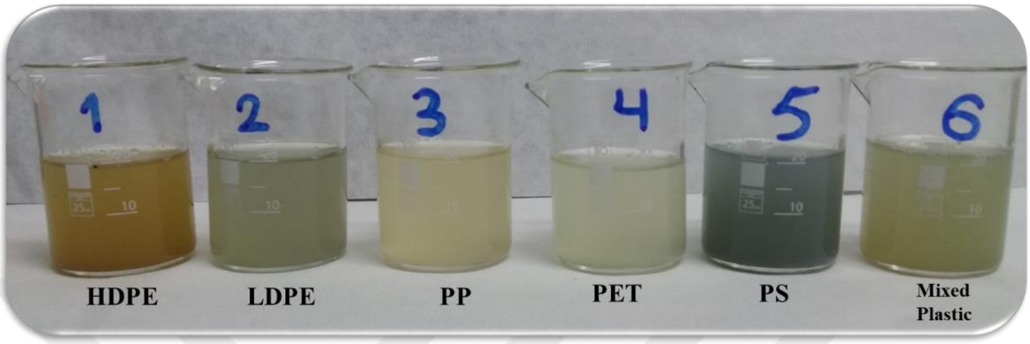


Figure 3.5. Plastics washing raw wastewaters

Treatability tests were carried out on the washing wastewater by using synthesized polymeric materials. In the literature, it has been reported that soluble and insoluble forms of this material are used in the treatment of synthetic wastewater as flocculant and adsorbent-ion exchanger, but not in real wastewater and industrial wastewaters such as those in this study. That is why; coagulation/flocculation experiments were carried out with this material. The same experiments with conventional flocculants PEL (Euroflock8440 cationic) and classic FSPS were repeated for comparison.

In the studies of Özdemir (2019), Iron(III) chloride ($FeCl_3$) and aluminum sulfate were tested as coagulant in plastics wastewater treatment. According to that study, the most efficient treatment with FeCl3 1000 mg L^{-1} dose was performed. Thus, $FeCl_3$ was used as a coagulant at dose of 1000 mg L^{-1} in this study.

The coagulation/flocculation process flow diagram is presented in Figure 3.6 (Reynolds and Richards, 2005). Experiments were performed with Jar-test apparatus in 500 mL beakers. Before coagulation/flocculation process, wastewater sample was thoroughly shaken to avoid possibility of settling solids. At first, each beaker was filled with 250 ml of wastewater. Then 1000 mg L^{-1} $FeCl_3$ coaglant was added to each beaker and rapid mixing of 90 seconds at 125 rpm were done. After rapid mixing, different doses of flocculant were added and slow mixing was applied at 25 rpm for 20 min. The mixture was allowed to settling for one hour (Figure 3.7). After 1 hour settling period, samples were withdrawn from supernatant for analyses. In all wastewater treatment studies experimental conditions such as coagulant dose, duration and speed of slow and rapid mixings, and settling time were kept constant.

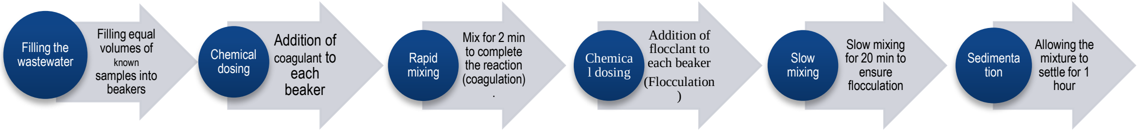


Figure 3.6. Coagulation/Flocculation experiments flow chart

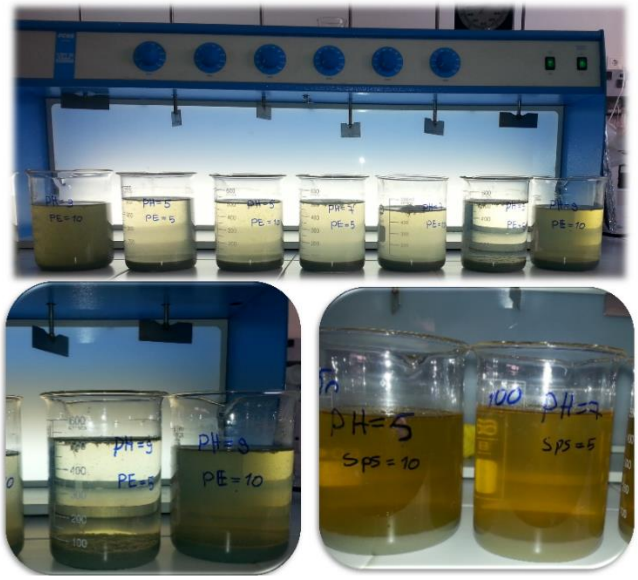


Figure 3.7. Jar-test experiments

Initially, eight synthesized flocculants were tested at a fixed dose (50 mg L^{-1} for solid flocculants and 50 mL L^{-1} liquid flocculants) at six WPWW. After these tests, two successful flocculants were selected according to COD and turbidity values in each wastewater. Alkaline earth elements and some metals were observed in the treatment effluents of selected flocculants, and Volume, TSS, Density, %Solid, and specific cake resistance (SCR) were observed in their treatment sludge.

For each WPWW, dose optimization was performed on one of the flocculants, selected according to high turbidity removal efficiency. In the flocculants doses optimizations, experiments were done on doses of 10, 30, 50, 70, and 90 mg L^{-1} for solid

(Figure 3.8) flocculants and 5, 10, 20, 30, 40, 50, 60, and 70 mL L^{-1} for liquid flocculants at the original pH of the raw wastewaters (about 13). The original pH of the washing wastewater is high because the washing is done with a high proportion of NaOH. After sedimentation, as a result of optimization, pH, turbidity, COD, and TSS parameters were analyzed in the supernatant, volume and density parameters were examined in the treatment sludge. In dose optimization, optimum dose of flocculant was selected for each WPWW according to COD and turbidity parameters.

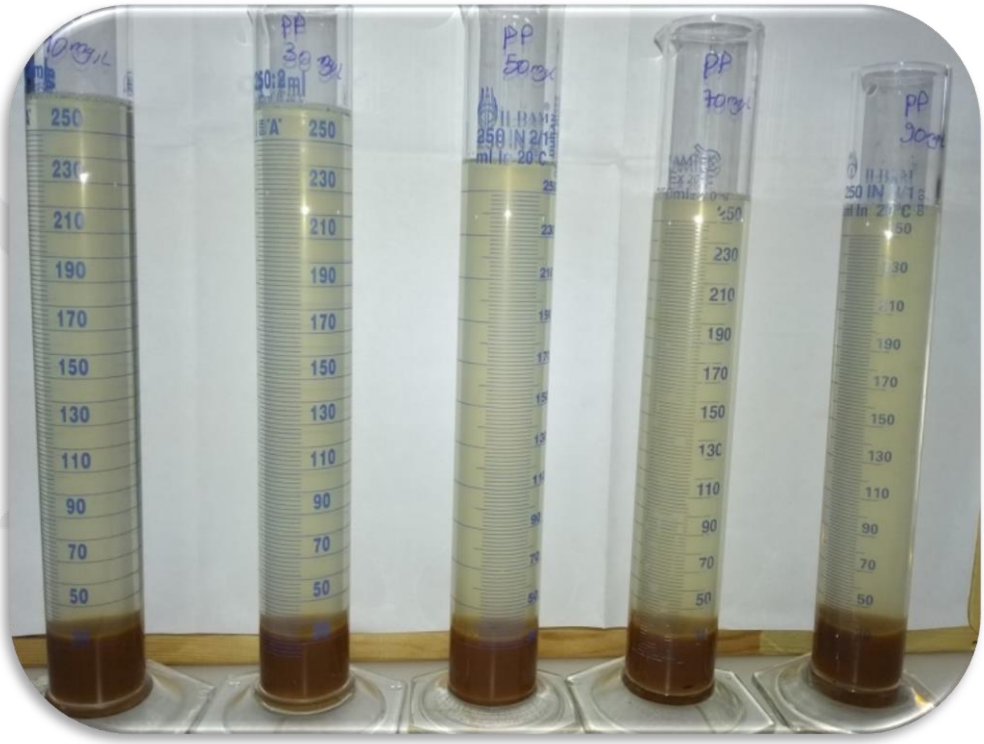


Figure 3.8. Solid flocculants doses optimizations experiments

Optimization of pH was performed at 3, 5, 7, and 9 different pHs using the optimum dose of each selected flocculant (Figure 3.9). The sample pH was adjusted from 3 to 9 by adding 50% HCl solutions .Turbidity, pH, COD, and TSS parameters in the supernatant; volume, and density in the treatment sludge were analyzed. After selecting the optimum pH of optimum dose for each WPWW, Volume, TSS, density, % Solid, SCR, metals, and alkaline earth elements in their treatment sludge were examined.

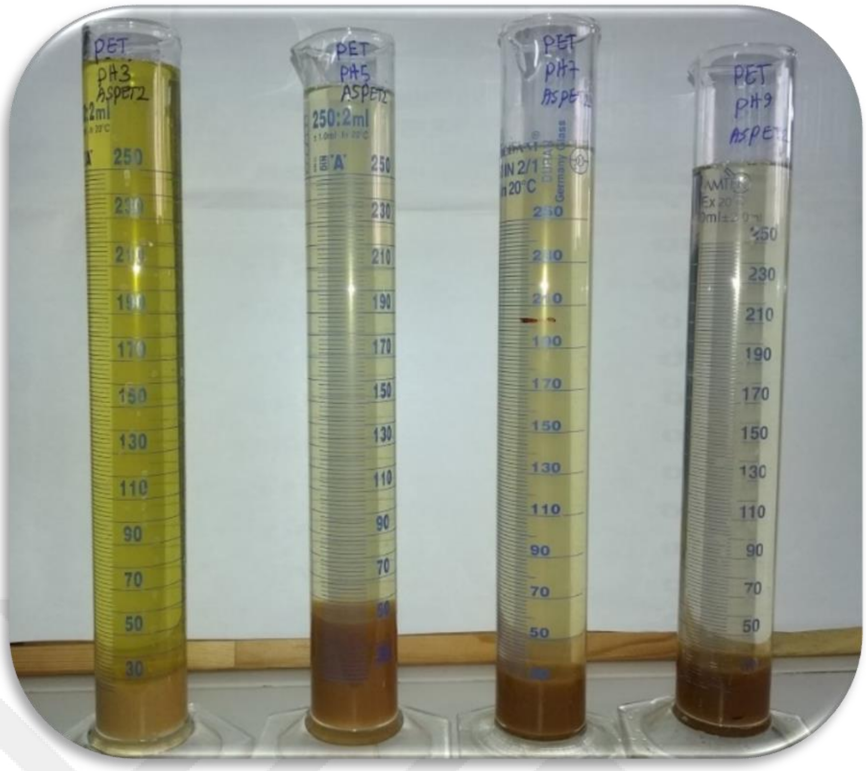


Figure 3.9. Liquid flocculants pH optimizations experiments

3.4. Analyses

3.4.1. FTIR Analysis

For synthesized FSPSs and ASPETs polymer materials was used FTIR analysis. FTIR Spectrum Device is used to identify the organic structure. Apart from optical isomers, the IR spectrum of all compounds is different from each other. The IR region is located between the visible region of the electromagnetic spectrum and the microwave zone between 4000-450 cm^{-1} wavelengths. The IR spectrum provides direct information on the structure of organic matter. However, it does not give information about whether a substance is pure or not. The IR spectrum is obtained by pressing the granules with KBr to a certain extent. In this study, Bruker brand FTIR Spectrophotometer was used to determine the sulfonate group in the flocculants obtained from the synthesis process. The analyses were carried out at Selcuk University central laboratory upon service.

3.4.2. Wastewater Characterization Analyses

In Characterization of WPWW and treatability of studies turbidity, COD, BOD, SS, oil-grease, pH, some metals, alkaline and alkaline earth elements, sludge density, solids content and SCR were analyzed according to Standard Methods (APHA, 2005). The standard 4000 NTU solution for turbidity was prepared and diluted in varying proportions. The spectrophotometer was initially calibrated through wavelength. After 375 nm was determined as the most suitable wavelength, the absorbance of each standard solution was read at this wavelength. Calibration equation with linear regression was determined as ABS375 = 0.00175 * NTU Corresponding to standard NTU value. For analysis of turbidity, the absorbance values were read by spectrophotometer device in 375 nm wavelength and the turbidity value was calculated by means of this equation.

COD: 5220C and 5220D, TSS: 2540D, Oil-Grease: 5520B were measured by standard methods (APHA, 2005), pH was measured by Hach pH meter.

The concentrations of other elements, metals, alkali and alkaline earth elements in liquid samples were determined by the ICP-AES device (Inductively Coupled Plasma Atomic Emission Spectrometer, Vista-Pro Axial, Varian Pty Ltd, Australia). The device determines the element concentrations in 2 mL liquid sample at different wavelengths with SSP detector in the atmosphere of inert argon gas at a temperature of 1000°C.

In the produced treatment sludge characterization analyses sludge density, solids content, and SCR were determined. In an empty weighed graduated cylinder, 10 mL of treatment sludge samples were weighed. The density of the sludge was calculated by dividing the difference of empty and full graduated cylinder weights by the volume of the sludge sample. In order to measure sludge TSS contents, filter papers were first brought to constant weight at 105°C in the drying-oven. 10 mL treatment sludge samples were filtered through weighed filter papers and during vacuum filtration the filtrate volume was recorded against time (5,10,15,20,30,40,50,60 ..... seconds) (Figure 3.10). After filtration, the filter papers were dried at 105°C for 1 hour, cooled down in desiccator and then weighed. TSS concentrations of the treatment sludges were calculated by dividing the differences in weight between the initial weighing and final weighing of the filter papers by the sample volume (Figure 3.11).

Figure 3.10. Treatment sludges characterization analyses

Figure 3.11.TSS concentrations of the six different WPWW sludges

For the calculation of the SCR of the treatment sludges, time/volume (t/V) graphs were plotted against the filtered volumes (V) corresponding to the time during the filtration of samples. Then, linear regression was performed to determine slope, intercept, and R^2 values of the linear regression trend lines. By using the slope value, SCR was calculated using formula (3.1) (Reynolds and Richards, 2005).

$$\mathrm{SCR}=\frac{2\triangle p A^{2} m}{\mu w} \tag{3.1}$$

Where;

SCR = Specific cake resistance of sludge (m.kg^{-1})

A = Filter area (0.00173 m^{2})

$\triangle$p = Negative pressure difference (49000 N.m^{-2})

w = Weight of dry sludge solids per unit volume of filtered sludge (kg.m^{-3}, calculated by dividing the weight values of solids by the volume of water fixed during the filtration process)

m = t/V -V Slope, from the linear regression of the graph (s.m^{-6})

μ = Absolute viscosity of the filtered (Ambient temperature 20°C to 0.001002 N.S.m^{-2})

4. RESULTS AND DISCUSSION

4.1. Characteristics of WPWW

Table 4.1 shows the characteristics of wastewater obtained by caustic washing of waste plastics. The washing process was carried out repeatedly at different times during the working period. Just after obtaining the wastewater from the washing process it was used for other studies in the same period and when it got consumed the washing process repeated by using new waste plastic sample. Each wastewater's characteristic was used as the input value for the study where that wastewater was used. That is why different input values can be observed for washing wastewater characteristics of the same kind of plastic in the study. Since this application provides more than one characterization, statistical analysis for each parameter of wastewater was also possible. Thus, in Table 4.1, each parameter is presented with the mean value and the standard deviation.

Wastewater characteristics are similar between the plastic types in terms of the proximity in the parameters, but in terms of their size, they are different. For example, in PS washing wastewater COD and BOD_5 were higher than others. The parameters in the WPWW are caused by the plastic waste itself, the contaminated outer surface and/or the product residues contained therein. The more foodstuffs in PS containers and the presence of cleaning agents in HDPE containers, etc., resulted in high COD and BOD_5 values in both. Although the wastewater composition varies according to the origin of the plastic and the properties of the material in which it is used as packaging, it is not possible to mention a specific pollutant related to the origin when the level of pollution is too high as reported here. As the washing process is carried out with a highly concentrated caustic solution, pH and Na were high in all wastewater samples.

While no significant metal pollution was observed in wastewater, it was observed that alkaline elements were present at different levels.

BOD_5/COD ratios are given as interval values. The smallest and the highest values of these parameters were used in this calculation. The BOD_5/COD ratio was observed to be highest in LDPE and PS WPWWs and lowest in PET washing wastewater. As BOD_5 is a measure of the biochemically degradable part of organic compounds in wastewater, the BOD_5/COD ratio also provides information on the biological degradability of wastewater. When the biological degradability is less, it is assumed that the organic compounds cannot be degraded by microorganisms. Even if the biological treatment will be applied in wastewater with a low rate, it is interpreted that chemical or physicochemical processing is necessary to remove non-biodegradable components. In this study, it will be determined whether the coagulation/flocculation processes will meet the need for this physicochemical treatment or not.

Table 4.1. Washing wastewater characterization for different plastic types

Parameters	**Wastewaters**					
	HDPE	**LDPE**	**PET**	**PP**	**PS**	**Mixed**
pH	13.94	13.76	13.87	13.75	13.69	13.67
Turbidity, NTU	1597±180	650±100	655±100	770±60	3240±480	1245±400
COD, mg L^{-1}	2310±650	1350±800	2450±210	2030±210	6870±2190	2170±250
BOD, mg L^{-1}	1095±650	840±500	840±280	795±320	4560±750	1300±550
BOD/COD	0.20-0.49	0.44-0.57	0.22-0.37	0.25-0.48	0.56-0.84	0.28-0.58
TSS, mg L^{-1}	1560±215	650±160	1100±170	1340±190	2020±160	1070±170
Oil-Grease mg L^{-1}	4270±240	2275±650	3758±2200	3308±980	4621±960	8320±2600
Ca, mg L^{-1}	33.5±15	6.7±3	18.4±5	15.3±3	10.2±1	11.0±2
Cr, mg L^{-1}	2.01±0.5	0.65±0.05	0.16±0.05	0.16±0.05	0.12±0.05	0.09±0.01
Cu, mg L^{-1}	0.13±0.001	0.08±0.001	0.09±0.001	0.05±0.001	0.01±0.001	0.05±0.001
Fe, mg L^{-1}	7.70±1	0.66±0.2	2.12±0.5	1.53±0.5	16.78±1.4	4.83±1
K, mg L^{-1}	34.85±14	73.16±30	27.48±12	25.56±9	92.37±40	66.35±20
Mg, mg L^{-1}	2.27±1	1.66±0.7	3.74±1.8	2.24±1	2.32±1	1±0.04
Mn, mg L^{-1}	0.13±0.06	0.04±0.02	0.06±0.03	0.15±0.07	0.17±0.08	0.00±0.00
Mo, mg L^{-1}	0.55±0.00	0.18±0.00	0.04±0.00	0.03±0.00	0.03±0.00	0.04±0.00
Na, mg L^{-1}	17300±171	17250±171	17380±172	17225±171	17550±173	17500±174
Ni, mg L^{-1}	0.13±0.00	0.04±0.00	0.01±0.00	0.02±0.00	0.06±0.00	0.05±0.00
P, mg L^{-1}	7.01±1.6	13.54±2	3.7±0.4	5.05±1.4	16.35±5	12.0±3
Pb, mgL^{-1}	0.03±0.02	0.76±0.03	0.1±0.09	0.05±0.02	0.01±0.009	0.2±0,01
S, mg L^{-1}	435,9±164	78,3±20	73,0±31	89,7±36	103,3±45	103±80
Zn, mg L^{-1}	0.82±0.01	0.33±0.01	0.38±0.01	0.36±0.01	1.23±0.1	0.49±0.01

When comparing the old and new version of Water Pollution Control Regulation “Discharge Criteria of Mixed Industrial Wastewater” (SWQR, 2012; WPCR, 2004) it is observed that TS parameter was changed to SS (suspended solids) while the numerical values remain the same, oil-grease, Pb was increased to twice the limit, and Cd was increased to four times the limit. In this case, the upper limits are slightly more flexible. Other metals added to the list also have high limits. On the other hand, the European Union Directive on Urban Wastewater Treatment (DIRECTIVE, 2003) provides only BOD$_5$ and COD limits and does not define limits for heavy metals. BOD$_5$, COD, suspended solids, Turbidity and Oil-grease levels of the wastewater in this study were higher than the other WPWW in the literature as well as the criteria in the mentioned regulation. There is no criterion for some measured ions, whereas, for others, the wastewater values were below the limit. Therefore, in evaluating the treatability of the WPWW in this study, organic matter (BOD_5-COD) and turbidity will be considered primarily.

4.2. Structures of Synthesized Materials

FTIR spectrums of synthesized flocculants are given in Figure 4.1-4.8. In the FTIR spectrum of FSPS1 at the 1082 cm^{-1} aromatic C-H plane bending; at 855 cm^{-1} disubstitue benzene; at 608 cm^{-1} sulfonic acid S-O stress bands were observed (Figure 4.1). In the FTIR spectrum of FSPS2 at 3326 cm^{-1} O-H stress; at 1638 cm^{-1} stress of C = C alkene; at 1379 cm^{-1} sulfonate group SO_2 asymmetric stress; at 1092 cm^{-1} aromatic C-H plane bending; at 1037 cm^{-1} sulfonic acid SO_2 symmetrical stress bands were observed (Figure 4.2).

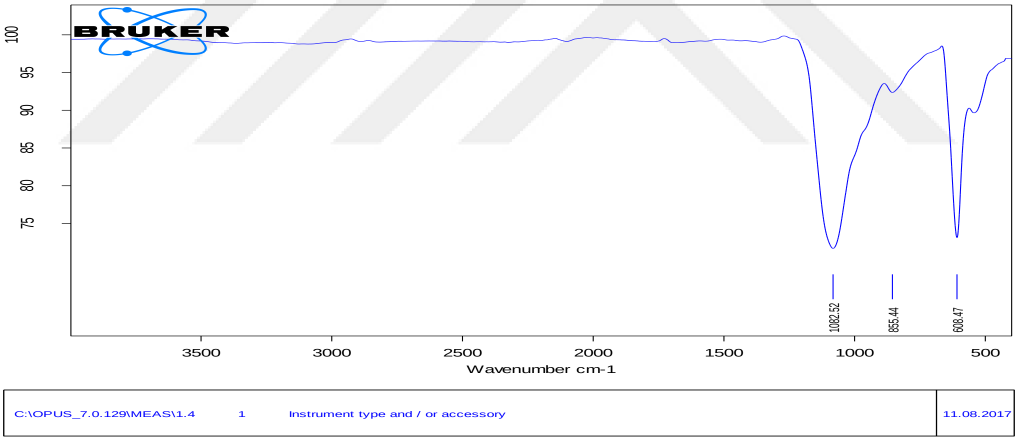


Figure 4.1. FTIR spectrum of FSPS1 flocculant

In the FTIR spectrum of FSPS3 at 3523 and 3399 cm^{-1} O-H strain; at 1620-1453 cm^{-1} aromatic C = C; at 1113 cm^{-1} sulfonate SO_2; at 853 cm^{-1} disubstituted benzene; at 700-600 cm^{-1} S-O stress bands were observed (Figure 4.3).

In the FSPET1 structure, at 3396 cm^{-1} acid O-H; at 1740 cm^{-1} ester C = O; at 1616-1450 cm^{-1} aromatic C = C stress; at 1132 cm^{-1} sulfonate; at in 861 cm^{-1} disubstituted benzene; at 599 cm^{-1} sulfonic acid S-O stress bands were observed (Figure 4.4).

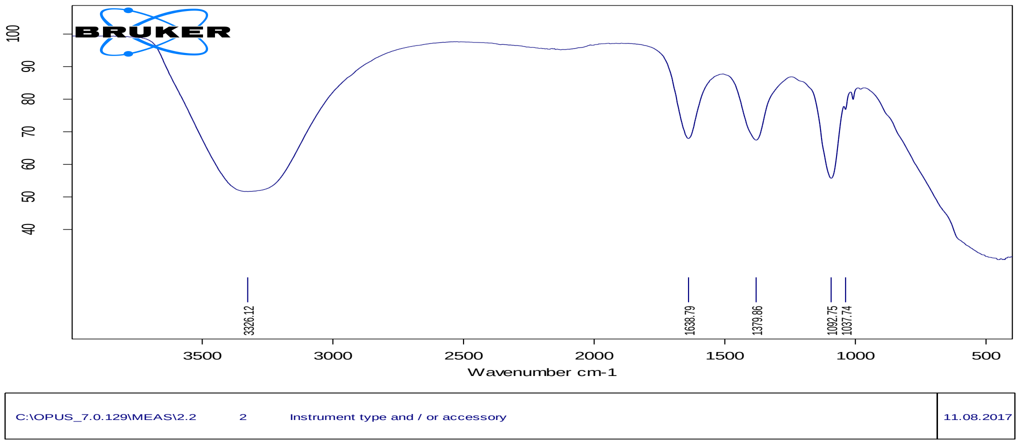


Figure 4.2. FTIR spectrum of FSPS2 flocculant

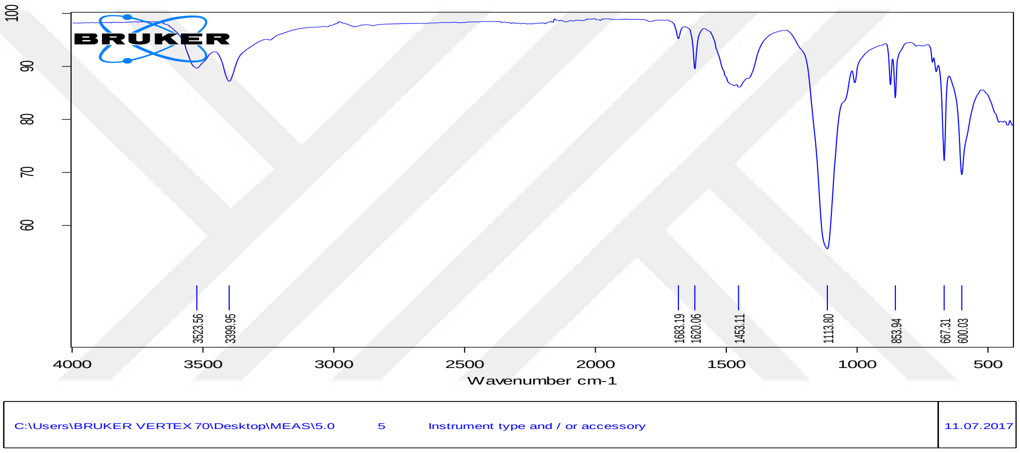


Figure 4.3. FTIR spectrum of FSPS3 flocculant

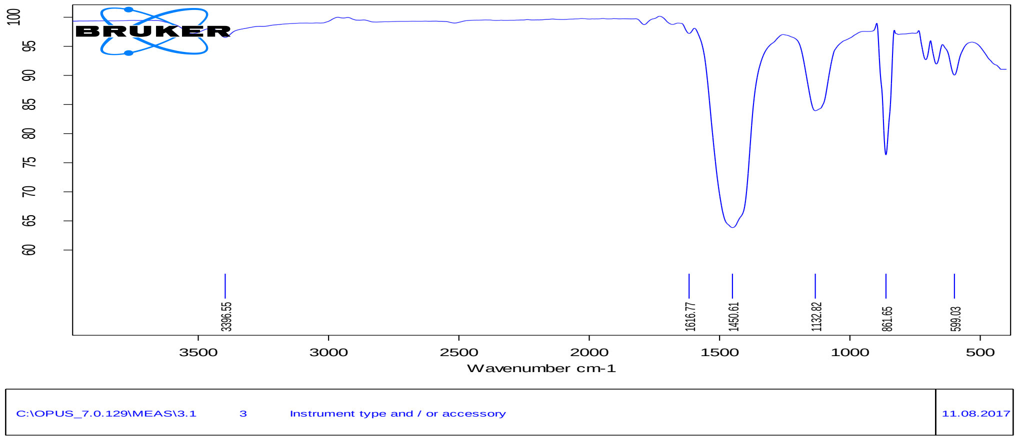


Figure 4.4. FTIR spectrum of FSPET1 flocculant

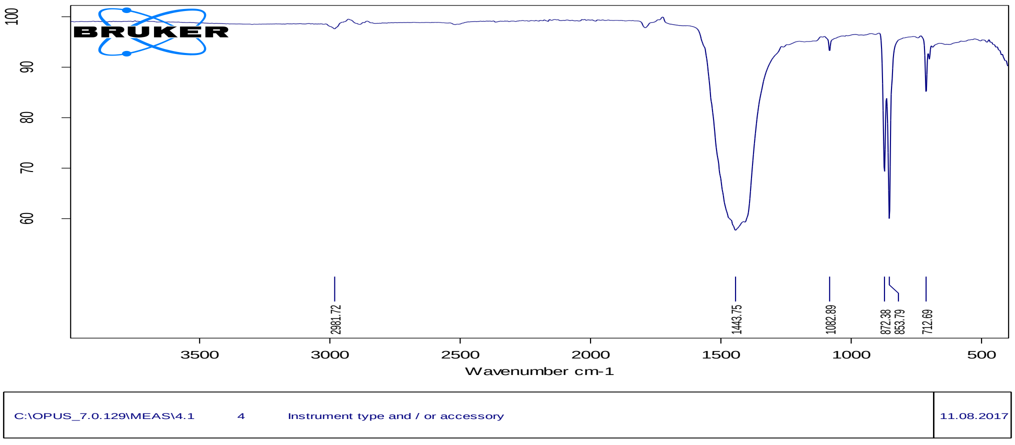


Figure 4.5. FTIR spectrum of FSPET2 flocculant

In the FTIR spectrum of FSPET2 at 2981 cm^{-1} the aliphatic C-H stress; at 1740 cm -1 ester C = O; at 1600-1443 cm^{-1} aromatic C = C stress; at 1082 cm^{-1} sulfonic acid SO_2 symmetric strain; at 872 and 853 cm^{-1} disubstituted benzene; at 712 cm^{-1} aromatic C-H bending bands were observed (Figure 4.5). In the FTIR spectrum of FSPET3 at 3063 cm^{-1} aromatic C-H; at 2547 cm^{-1} acid O-H; at 1679 cm^{-1} C=C alkene; at1574-1424 cm^{-1} aromatic C = C stress; at 1277 and 1106 cm^{-1} acid and ester C-O bonds; at 726 cm^{-1} aliphatic C-H bending; at 612 cm^{-1} sulfonic acid S-O stress bands were observed (Figure 4.6).

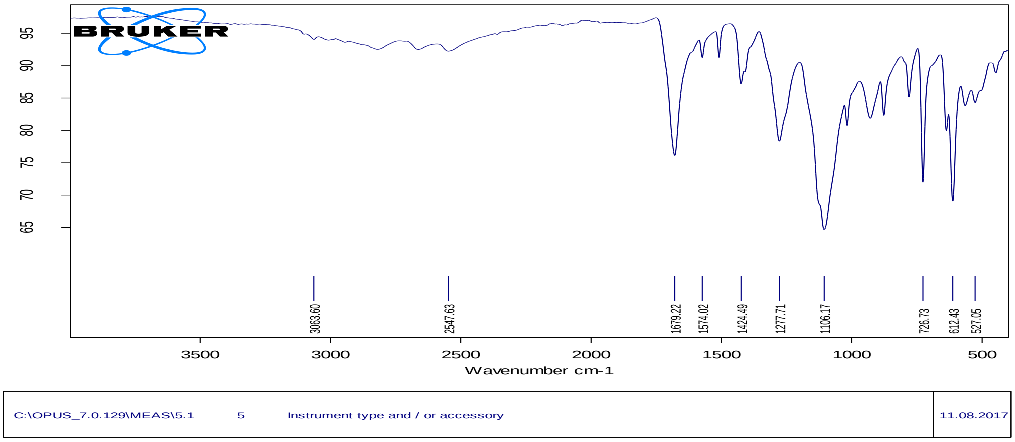


Figure 4.6. FTIR spectrum of FSPET3 flocculant

In the FTIR spectrum of ASPET1 at 3339 cm^{-1} O-H strain; at 1638 cm^{-1} acid–salt COO; at 1383 cm^{-1} aliphatic C-H; at 1087 cm^{-1} sulfonic acid SO_2 symmetrical stress bands were observed (Figure 4.7). In the FTIR spectrum of ASPET2 at 3300 cm^{-1} O-H stress; at

1600-1450 cm^{-1} aromatic C = C stress, at 1105 cm^{-1} ester C-O bond; at 744 cm^{-1} aliphatic C-H; at 609 cm^{-1} sulfonic acid S-O stress bands were observed (Figure 4.8).

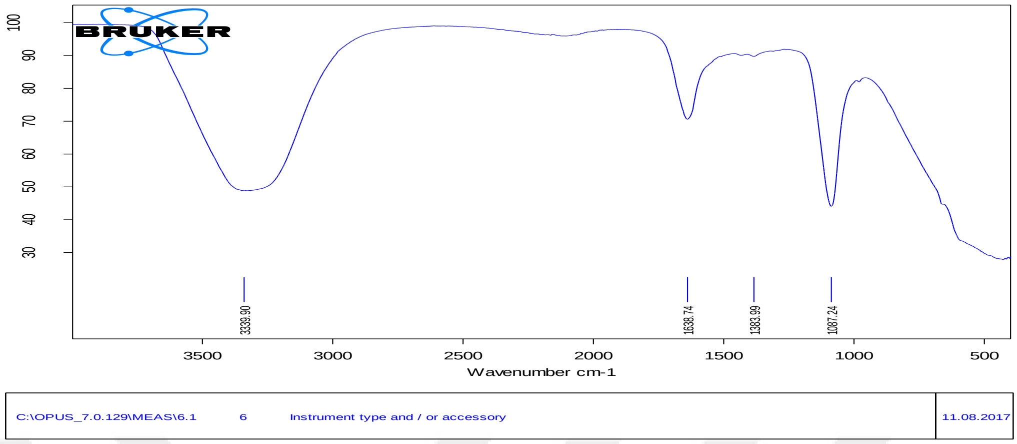


Figure 4.7. FTIR spectrum of ASPET1 flocculant

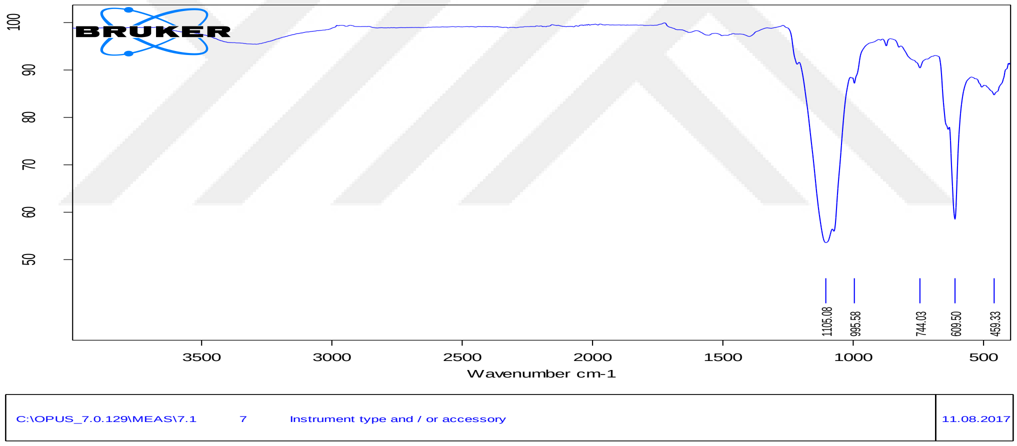


Figure 4.8. FTIR spectrum of ASPET2 flocculant

The FTIR spectrum of untreated polystyrene foam flakes is shown in Figure 4.9(a). The absorption bands at 3895 indicate O-H bond stretching, 3434 cm^{-1}, 2613 cm^{-1}, 2509 cm^{-1} and 1876 cm^{-1} has been attributed to C=O bond stretching (carbonyl group), 2351 to O-C-O bond stretching, 2095 cm^{-1} to C=C bond stretching, 2195 cm^{-1} to O-C-O bond stretching,1876 cm^{-1} to C=O bond stretching, 1800 cm^{-1}, and 1728 cm^{-1} to C=O bond stretching (carbonyl group),1607 cm^{-1} to C=C bond stretching (benzene ring), 1447 cm^{-1},1369 cm^{-1},1023 cm^{-1},913 cm^{-1} and 756 cm^{-1}, has been assigned to C-H bond stretching (Umamaheswari and Murali, 2013).

FTIR spectrum of PET flakes is presented in Figure 4.9(b). The absorption bands at 3431 cm^{-1}, 2357 cm^{-1} and 1729 cm^{-1} has been assigned to C=O bond stretching (Carbonyl group), 1631 cm^{-1} to C=C bond stretching (Benzene ring), 1459 cm^{-1} and 1379 cm^{-1}, 1073 cm^{-1} and 744 cm^{-1} to C-H bond stretching (Methylene group),1938 cm^{-1} to C=C=C= bond stretching (Umamaheswari and Murali, 2013) .

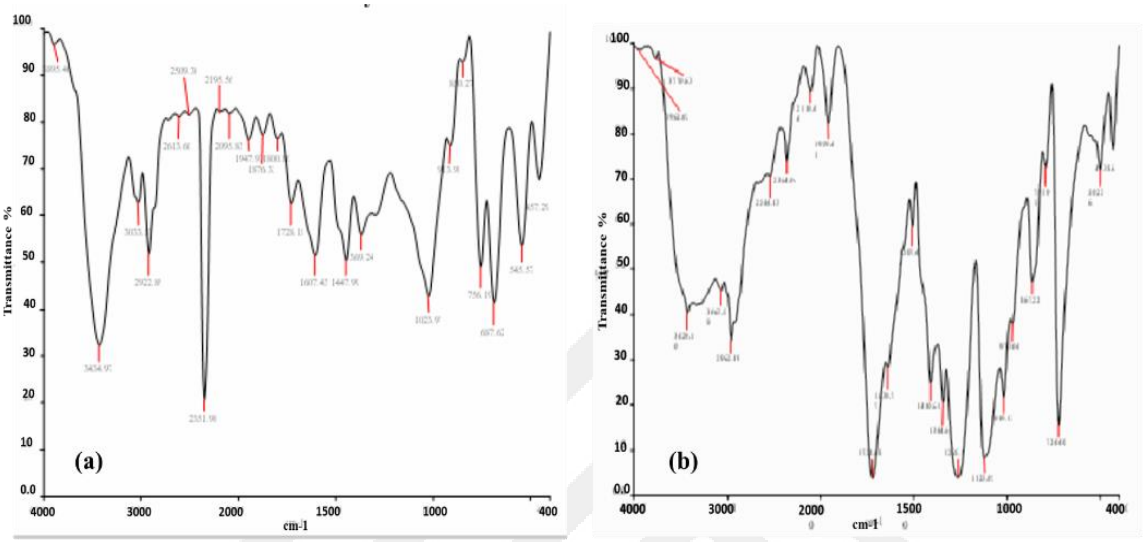


Figure 4.9. FTIR spectra of PS foam flakes (a) and PET flakes (b) (Umamaheswari and Murali, 2013)

The spectra obtained for the synthesized polymeric flocculants confirmed the presence of sulfonic groups in the materials structure as outlined in Table 4.2. FSPS1 was synthesized without modifying the method of Bekri-Abbes (2007). Thus, changes in the structure of other flocculants were compared with FSPS1. In the structure of FSPS2 that was sulfonated by modifying Sulkowski (2006; 2005) method (using PS foam and precipitating resulting mixture solution with Na_2CO_3) Carboxylic acid O-H, C=C alkene, sulfonate SO_2 asymmetric, Sulfonic acid SO_2 symmetric appears to be added and benzene is disrupted. In FSPS3 that was synthesize by modifying Sulkowski (2006; 2005) using PS plate, sulfonic acid S-O stress bands were observed at 500-700 cm^{-1} and sulfonate SO_2 at 1000-1400 cm^{-1}. In structures of FSPS1, FSPET3 and ASPET2 only sulfonic acid group was observed. In the FSPET2 and ASPET1 structures, only sulfonic acid SO_2 is asymmetrically bound. However, in the structure of FSPS2, FSPS3 and FSPET1, both sulfonic acid S-O group and sulfonate SO_2 are observed. The aromatic structure was preserved and present in all materials except ASPET1.

Table 4.2. FTIR spectrum peaks of synthesized polymeric flocculants

Synthesized Polymeric Flocculant	Wavenumber (cm^{-1})	Kind of Vibration
FSPS1	1082	Aromatic C-H
	608	**Sulfonic acid S-O**
	855	Disubstituted benzene
FSPS2	3326	Carboxylic acid O-H
	1638	C = C Alkene
	1379	**Sulfonate SO_2 (Asymmetric)**
	1037	**Sulfonic acid SO_2 (Symmetric)**
	1092	Aromatic C-H
FSPS3	3399	Carboxylic acid O-H
	1620-1453	Aromatic C = C
	1113	**Sulfonate SO_2**
	700-600	**Sulfonic acid S-O**
	853	Disubstituted benzene
FSPET1	3396	Carboxylic acid O-H
	1740	Ester C = O
	1616-1450	Aromatic C = C
	1132	**Sulfonate SO_2**
	599	**Sulfonic acid S-O**
	861	Disubstituted benzene
FSPET2	2981	Aliphatic C-H
	1740	Ester C = O
	1600-1443	Aromatic C = C
	712	Aromatic C-H
	1082	**Sulfonic acid SO_2** (Symmetric)
	872	Disubstituted benzene
FSPET3	2574	Carboxylic acid O-H
	3063	Aromatic C-H
	1679	Aromatic alkene C=C
	726	Aliphatic C-H
	1424	Aromatic C = C
	1277	Ester C = O
	612	**Sulfonic acid S-O**
ASPET1	3339	Carboxylic acid O-H
	1638	Acid–salt COO
	18	Aliphatic C-H
	1037	**Sulfonic acid SO_2 (Symmetric)**
ASPET2	3306	Carboxylic acid O-H
	1600-1450	Aromatic C = C
	744	Aliphatic C-H
	1105	Ester C = O
	609	**Sulfonic acid S-O**

4.3. Effectiveness of Synthesized Flocculants in WPWW Treatment

4.3.1. Effectiveness of Flocculants on Removal of Turbidity and COD

Experiments were performed at the 1000 mg L^{-1} coagulant dose for each modifying flocculant at the same mixing and sedimentation times and under the same ambient conditions. In addition to these eight substances for comparison, a conventional flocculant PEL was dosed as the ninth reactor and treatment was performed. After adding (50 mg L^{-1} for solids and 50 mL L^{-1} for liquids) flocculants to 250 mL of raw wastewaters, 20 min slow mixing was applied. After one hour sedimentation, the supernatant was collected and analyzed. At first, wastewater turbidity and COD changes were examined (Table 4.3) because the main target in coagulation is turbidity removal, the flocs may also remove some organics while precipitating.

Table 4.3. Effects of Synthesized Materials in Turbidity and COD Removal from WPWW

Parameters	**Raw WW**	**FSPS1**	**FSPS2**	**FSPS3**	**FSPET1**	**FSPET 2**	**FSPET3**	**ASPET1**	**ASPET2**	**PEL**
HDPE Washing Wastewater										
pH	13,94	13,03	13,06	13,14	13,11	13,08	13,13	13,09	13,12	13,31
Turbidity, NTU	1664	282	233	223	253	**232**	252	**240**	231	230
COD, mg L^{-1}	2202	1504	1805	1705	1805	**1094**	1905	**1504**	1604	1153
LDPE Washing Wastewater										
pH	13,76	13,12	13,13	13,13	13,7	13,13	13,07	13,1	13,09	13,11
Turbidity, NTU	830	289	259	241	230	289	225	**207**	**150**	232
COD, mg L^{-1}	1354	1388	1889	1288	1589	1589	1488	**1388**	**1188**	1037
PET Washing Wastewater										
pH	13,87	13,2	13,2	13,15	13,16	13,18	13,16	13,16	13,15	13,26
Turbidity, NTU	877	215	**202**	187	217	208	185	188	**158**	169
COD, mg L^{-1}	3021	2807	**1902**	2707	2457	2406	2807	2306	**2156**	1654
PP Washing Wastewater										
pH	13,75	13,21	13,23	13,25	13,24	13,24	13,24	13,23	13,23	13,27
Turbidity, NTU	889	**205**	228	237	**179**	202	227	251	284	212
COD, mg L^{-1}	2304	**1021**	1623	1422	**1422**	1623	1372	1623	1222	2174
PS Washing Wastewater										
pH	13,69	13,26	13,23	13,18	13,22	13,23	13,2	13,18	13,18	13,22
Turbidity, NTU	3323	714	733	653	**650**	**549**	672	659	577	671
COD, mg L^{-1}	4864	3008	3108	3108	**2507**	**2958**	3509	2707	3610	4562
Mixed plastic Washing Wastewater										
pH	13,67	13,17	13,15	13,1	13,13	13,14	13,13	13,11	13,11	13,19
Turbidity, NTU	1955	578	577	577	**567**	575	725	**783**	1091	579
COD, mg L^{-1}	2918	1704	1905	1955	**1103**	3509	1805	**1504**	1705	1654

From the results of the coagulation experiments in Table 4.3, two flocculants with the best treatment performance were selected for each wastewater. Other parameters in the treatment effluents of these were analyzed with ICP. The ICP results of the raw wastewater from previous sections were compared with these treatment effluents and for removed parameters, efficiency calculations have been done. Detailed data obtained from ICP analyses are given in Appendix A. As seen in Table 4.3, FSPET2 and ASPET1 in the coagulation/flocculation of HDPE wastewater provided the most efficient treatment. Performance of both materials, which are derived from PET plastic, were close to each other: 86% turbidity, approximately 20% SS, 25% COD, and over 90% removal of Cr, Mg, Mo, and S were observed (Figure 4.9). In addition, removal of Ni, Cu, Fe, and in low quantities Ca, K, and Zn were also provided.

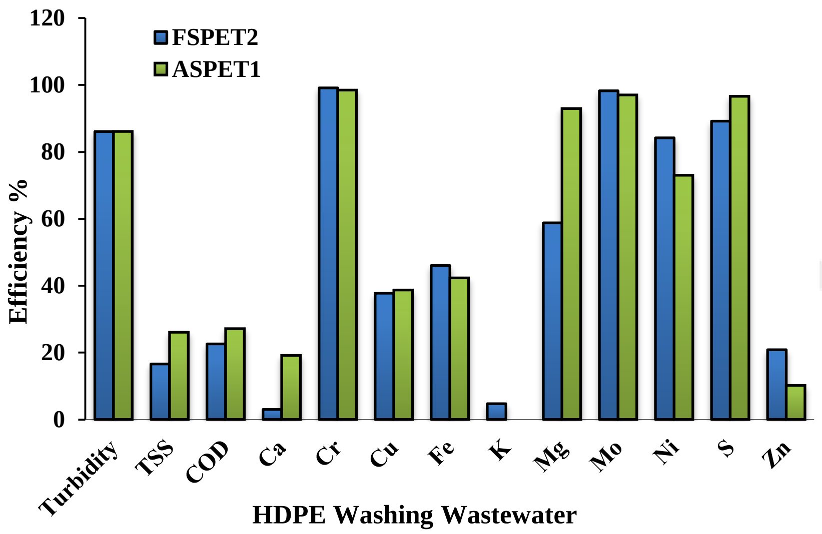


Figure 4.9. Removal efficiencies of parameters in the treatment of HDPE washing wastewater with two selected flocculants

ASPET1 and ASPET2 syntheses materials were more successful in the treatment of LDPE washing wastewater (Table 4.3). In fact, the materials were obtained by the same method, but at the last step of synthesis, one was filtered and dried, and the other was used with its liquid. It can be observed that 75-82% turbidity, 93-95% Cr, 77% Mo, 70-88% Ni, 94-99% Pb, 24% K and 15-20% P removal could be achieved. The parameters that were not successfully treated in its fluid sample but were treated in their dried sample are COD, Ca, Cu, Fe, and Mg (Figure 4.10). As a single dose (50 mg L^{-1} or 50 mL L^{-1}) is tried, the doses of the liquid and the solid varies.

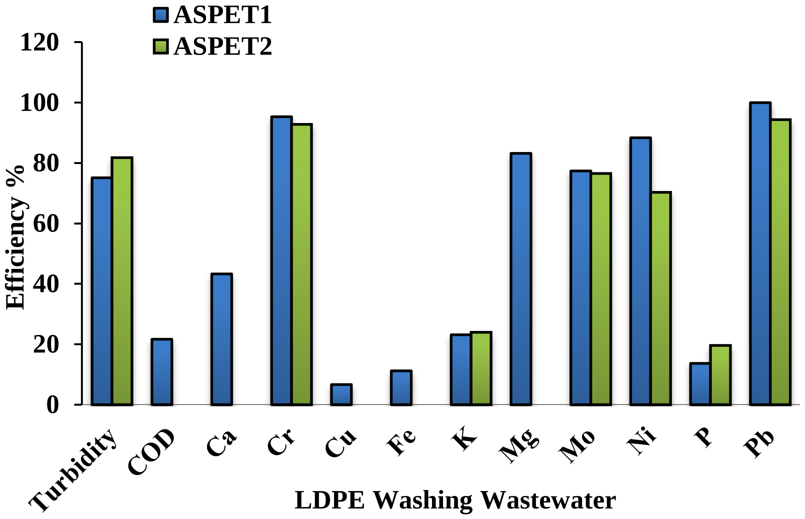


Figure 4.10. Removal efficiencies of parameters in the treatment of LDPE washing wastewater with two selected flocculants

Two synthesis agents, which were more effective than others in waste PET washing wastewater treatment, are FSPS2 and ASPET2 (Figure 4.11). One of them was synthesized by using WPS and the other was by using waste PET, but the common point was that they were stored as liquids after synthesis. In addition, FSPS2 was obtained from the foam-shaped PS material (styrofoam). In some studies in the literature, it was reported that obtaining synthesis material from both plate PS and foam PS material had different properties (Sulkowski et al., 2006). Here too, the synthesized material from the foam PS material provided more successful treatment than other PSs. In the liquid state synthesis material, the liquid part contains the carbonate precipitation process after the dissolution of the intermediate product formed in the final stage of the synthesis in deionized water. In this case, the content of the liquid already contains deionized water, excess of the added carbonate and the precipitated sulfonated PS precipitates. In this instance, the liquid part is a carbonate solution that predicted to contribute to the treatment. For this reason, samples have been tested as liquid and the success in PET washing wastewater has shown the accuracy of this prediction. The performance of the two synthesis materials in the removal of turbidity, Cr, Mg, Mo was very close to each other. FSPS2 resulted in higher COD, Cu, Fe, K and Pb removals (Figure 4.11) than others. Considering that other parameters except turbidity and COD were low in the effluent, FSPS2 material obtained from foam PS can be said to be more effective in PET washing wastewater treatment.

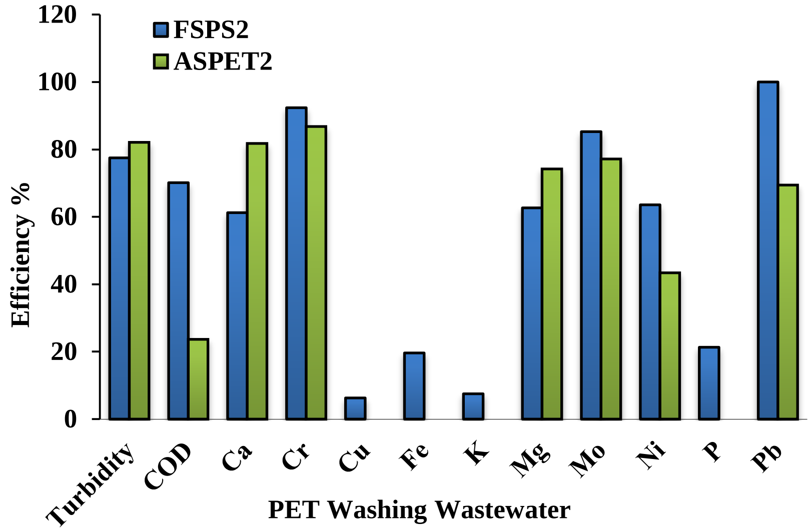


Figure 4.11. Removal efficiencies of parameters in the treatment of PET washing wastewater with two selected flocculants

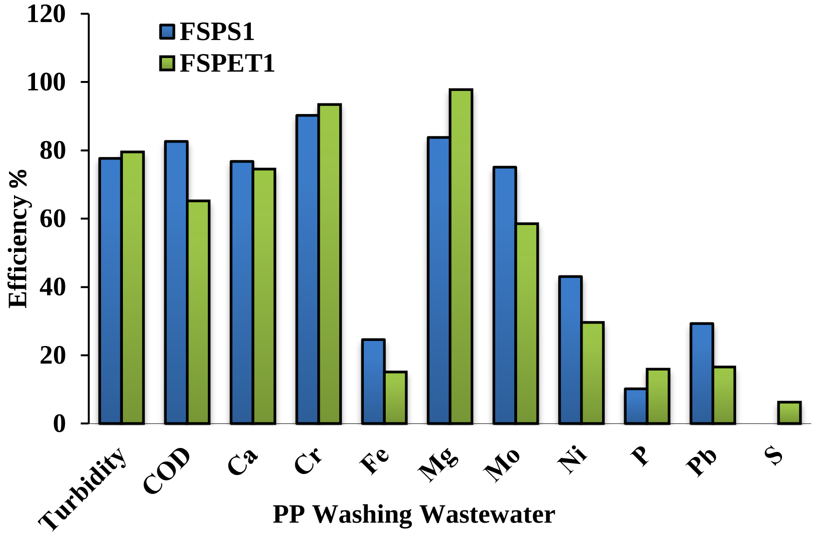


Figure 4.12. Removal efficiencies of parameters in the treatment of PP washing wastewater with two selected flocculants

FSPS1 and FSPET1 were more successful in coagulation/flocculation of PP washing wastewater. FSPS1 was the flocculant obtained by Bekri-Abbes (2007) sulfonation method. FSPET1 was obtained by modifying the Sulkowski (2005) method. Waste PET was used instead of WPS. This flocculant was precipitated by using Na_2CO_3 and $CaCO_3$ in synthesis. As shown in Figure 4.12, the efficacy of two flocculants in the removal efficiency of parameters is close to each other. About 80% of the turbidity and COD removal and about

90% removal of Cr and Mg were observed. Here too, the highest valued parameters are turbidity and COD and the concentrations of other parameters in the wastewater are very low.

FSPET1 and FSPET2 could treated PS washing wastewater more efficiently than other flocculants. These two materials were synthesized in the same way using waste PET. At the final precipitation stage, FSPET2 was precipitated using $CaCO_3$ while FSPET1 was precipitated using both Na_2CO_3 and $CaCO_3$. It is thought that calcium used in the synthesis plays a role in the treatment. Because there is no synthesized flocculant using Ca except for these two materials of this study. In all parameters, the two materials provided close removal efficiencies for all parameters (Figure 4.13). 80-81% turbidity, 39-48% COD, 54-58% Ca, 72-79% Cr, 40% Fe, 29% K 63% Mg, 76% Mo, 60% Ni removal was calculated (Figure 4.13).

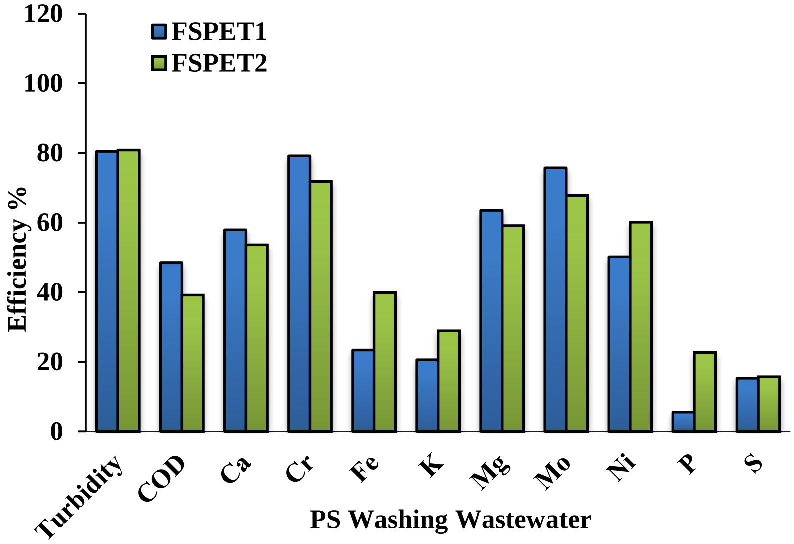


Figure 4.13. Removal efficiencies of parameters in the treatment of PS washing wastewater with two selected flocculants

Synthesized materials that provide the most successful coagulation/flocculation treatment in mixed waste plastic washing wastewater were FSPET1 and ASPET1. Again, the flocculants synthesized by PET are more successful here. The lowest turbidity removal efficiency compared to other WPWW was observed in this wastewater. The removal of COD and other parameters is not very different from the other wastewaters (Figure 4.14). ASPET1 was obtained by adsorbent synthesis method. However, due to the fact that PET can dissolve in the acid, an insoluble material such as adsorbent could not be obtained. Thus, ASPET1 was used in the treatment as flocculants. That is why, ASPET1 was more effective than FSPET1 on extensively removable parameters such as Ca, Fe, Mg, Ni, P, and Pb by ion exchange (Figure 4.14).

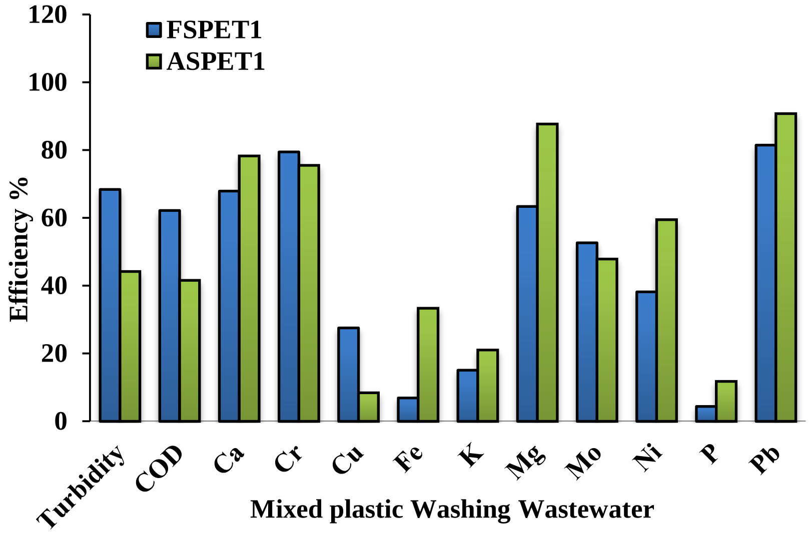


Figure 4.14. Removal efficiencies of parameters in the treatment of Mixed plastic washing wastewater with two selected flocculants

4.3.2. Comparison of Turbidity Removal Performance of Selected Synthesized Flocculants with PEL and Classic FSPS

Table 4.4 compares the turbidity removal of selected successfully synthesized flocculants from all studied WPWW with the classic FSPS and conventional flocculant PEL. FSPS was synthesized by Vink (1981) which is a classic method. Turbidity has been selected as the base comparison parameter for coagulation/flocculation process. However, it is known that some other pollutant parameters in the wastewater can also be removed with the turbidity, and during the reaction, the sediment depending on the ambient conditions settle with the flocs. FSPS2, which was obtained by using foam PS in the catalyzed medium by modification of first developed sulfonated PS method and FSPS1, has been found to be more successful only in the treatment of PET and PP washing wastewater. In addition, the successful synthesis material selected for six types of wastewater were materials obtained from the majority PET sulfonation process (Table 4.4). When compared to classic FSPS, similar and even higher efficiencies have been observed in some wastewater. There are synthesis materials that show the same or even higher success compared to conventional flocculant PEL. For HDPE wastewater, PEL, which is known as the most effective flocculant and, classic FSPS have 86% and 83% removal turbidity efficiency respectively. In LDPE wastewater, ASPET1 has the same turbidity efficiency as conventional PEL and ASPET2 is higher than all. ASPET2 was also more effective in removing turbidity than both conventional PEL and classic FSPS in PET washing wastewater. FSPET2 and ASPET1 that were obtained in this study had achieved the same yield with the most common flocculant PEL. In PP wastewater treatment, 69% turbidity was removed with PEL, while an 80% yield was obtained with FSPET1. In this type of wastewater, even the conventional FSPS has a higher efficiency than PEL (Table 4.4). In PS wastewater, FSPET1 and FSPET2 achieved nearly the same turbidity removal (80%) with conventional PEL, while the highest yield (87%) was observed in conventional FSPS use. In Mixed plastic washing wastewater, 68% turbidity was removed with FSPET1 synthesized material, it is higher than PEL and classic FSPS removal efficiency (61%).

Table 4.4. Comparison of turbidity removal performance of selected synthesized flocculants (By using $FeCl_3$ as a coagulant and at the original pH of the wastewater)

Wastewater	**The More Effective Synthesized Flocculants in Treatment**	**Turbidity Removal,%**		
		Selected Flocculants	**Classic FSPS**	**PEL**
HDPE Washing Wastewater	FSPET2 ASPET1	86 85	83	86
LDPE Washing Wastewater	ASPET2 ASPET1	82 75	73	75
PET Washing Wastewater	FSPS2 ASPET2	77 82	80	81
PP Washing Wastewater	FSPS1 FSPET1	78 80	80	69
PS Washing Wastewater	FSPET2 FSPET1	83 80	87	80
Mixed plastic Washing Wastewater	FSPET1 ASPET1	71 60	61	61

FSPET3, precipitated by NaOH in the final synthesis process, had not been more successful in any treatment than others. After the reaction to obtain flocculants, FSPS2, FSPET1, and FSPET2, which were precipitated by Na_2CO_3 and $CaCO_3$, were successful in the treatment process. There is no significant difference in yield between the carbonate ion in Na_2CO_3 or $CaCO_3$ form that is used in the precipitation. However, $CaCO_3$ is more advantageous because it provides synthesis even when added in much lower amounts. In addition, when the commercial sales prices are compared, they are sold in close proximity to each other (6-10 TL/kg-Technic) or $CaCO_3$ even have a slightly lower price.

The synthesized flocculant materials successfully treated WPWW, both in liquid and in solid form. Furthermore, the liquid form of flocculant was more efficient (82%) in the treatment of LDPE and PET wastewaters. These results show that using them in liquid form is a proper decision as indicated in Table 3.2. In this way, both the dewatering and drying process is eliminated and the production of wastewater is prevented during the production of this material.

The efficiency of the coagulation/flocculation with classic FSPS was increased when pH and dose optimization had been performed previously (N.C. Özdemir, 2019). Similar optimization studies for each of the synthesis material can cause an increase in the yields presented in Table 4.4. Dose and pH optimization performed in the following sections were examined.

4.4. Dosage and pH Optimization

Flocculant dosages vary in a wide range aiming at maximum removal efficiency of pollutants using minimum doses at optimum pH (Watanabe et al., 1993). Accordingly, dose and pH optimizations were considered.

Totally 8 flocculants had been studied at 6 different types of WPWW. In the previous section, for each type of WPWW two synthesized flocculants were selected as more effective synthesized flocculants in the treatment. Among these two successful synthesized flocculant, the most effective one for each wastewater was selected according to turbidity removal (Table 4.4). FSPET2 flocculant for HDPE and PS wastewaters, ASPET2 flocculant for LDPE and PET washing wastewaters and FSPET1 for PP and Mixed plastic wastewater were selected as the most successful flocculants.

In this step of the study, first dosage optimization was performed for selected flocculants, and then by keeping the optimized dosage and other conditions constant, pH was optimized.

4.4.1. Dosage Optimization

In this part of the study, treatment performance at different doses of synthesis materials was evaluated. In dose optimization, 10, 30, 50, 70, and 90 mg L^{-1} doses for solid flocculants (FSPET1 and FSPET2) and 5, 10, 20, 30, 40, 50, 60, and 70 mL L^{-1} doses for liquid flocculants (ASPET2) were selected respectively. First, coagulation with 1000 mg L^{-1} $FeCl_3$ was carried out in 250 mL wastewater and then flocculation was performed by adding flocculants for each wastewater in original pH. The coagulant dose, rapid mixing, slow mixing and sedimentation time conditions were kept constant in all tests. Detailed data obtained for dosage optimization are given in Appendix B. In this section, removal performances for each parameter were compared.

4.4.1.1. Treatment Properties of optimized dosage in HDPE WPWW

FSPET2 synthesis material was selected as the most effective flocculant for HDPE washing wastewater. In dose optimization of this flocculant, turbidity removal efficiency increases as the dose increases, but decreases again when it reaches a dose of 70 mg L^{-1} (Figure 4.15). 50 mg L^{-1} dose achieved the highest yield of COD removal with 53%. TSS removal, yields are close to each other for all doses. In total, 50 mg L^{-1} dose can be selected as the optimum dose for treating HDPE wastewater in coagulation/ flocculation process.

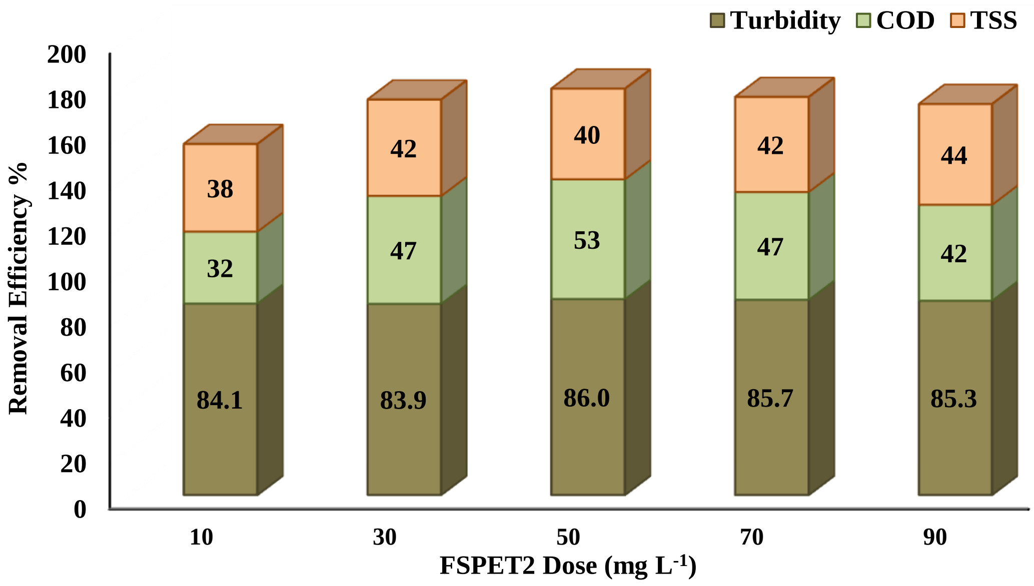


Figure 4.15. Effects of FSPET2 flocculant dosage on its performance in the treatment of HDPE washing wastewater (Initial Turbidity = 1597 NTU, Initial COD= 2310 mg L^{-1}, Initial TSS= 1560 mg L^{-1})

Figure 4.16 shows the visual comparison of treatment effluent of five different doses of FSPET2 for HDPE WPWW.

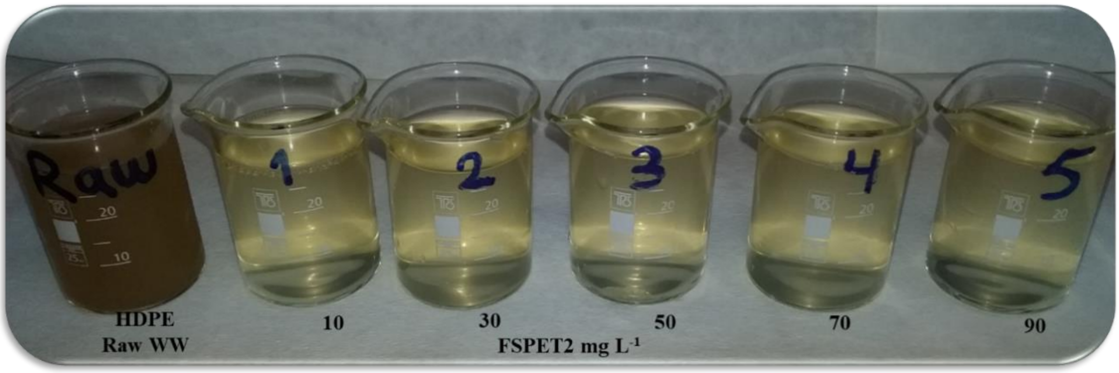


Figure 4.16. HDPE washing raw wastewater and effluent obtained from dosage optimization of FSPET2 in this wastewater

4.4.1.2. Treatment Properties of optimized dosage in LDPE WPWW

ASPET2 has yielded more successful results in LDPE washing wastewater treatment. Therefore, dose optimization of ASPET2 synthesis material was performed in LDPE washing wastewater. As shown in Figure 4.17 turbidity removal efficiency increases as ASPET2 concentration increases up to 40 mL L^{-1} dosage, but yield decreases again after 40 mL L^{-1} dose. COD removal decreases as the dose of the synthesis agent increases, and COD removal does not occur at all as the dose reaches 50 mL L^{-1} (Figure 4.17). This is due to the fact that as the dose of flocculant increases, the polymer in the liquid flocculant dissolves and does not settle, so instead of decreasing, it increases the COD concentration. NaOH and $CaCO_3$ were used during precipitation in ASPET2 synthesis. NaOH formed a large amount of salt in neutralization with sulfuric acid. These salts are the reason why the synthetic substance is white. Thus, there were abundant salts in the liquid synthesizer, these salts are forming small sediments with other minerals that they cannot precipitate and result in increased TSS. As shown in Figure 4.18, even if COD and TSS removal are low or zero, turbidity removal was successful in all doses as compared to raw wastewater. Based on turbidity removal (77.4%), 40 mL L^{-1} dose of ASPET2 was chosen as the optimum dose for LDPE WPWW.

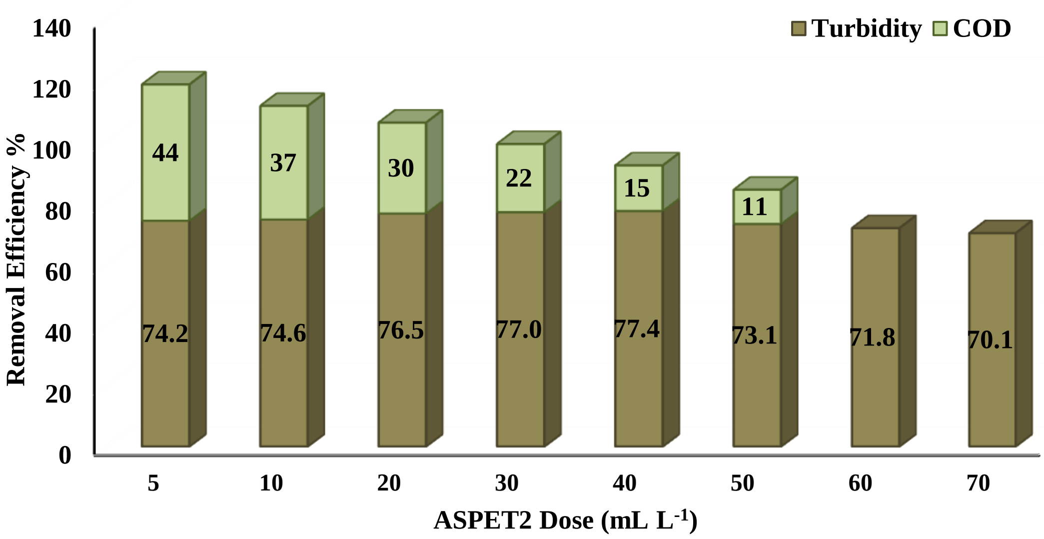


Figure 4.17. Effects of ASPET2 flocculant dosage on its performance in the treatment of LDPE washing wastewater (Initial Turbidity = 645 NTU, Initial COD = 1354 mg L^{-1}, Initial TSS = 650 mg L^{-1})

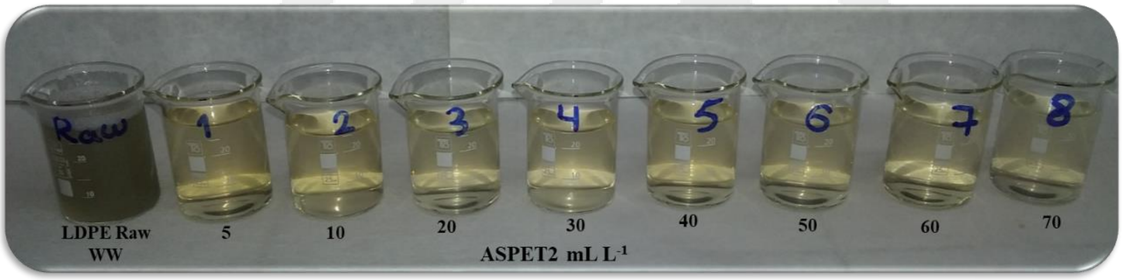


Figure 4.18. LDPE washing raw wastewater and effluent obtained from dosage optimization of ASPET2 in this wastewater

4.4.1.3. Treatment Properties of optimized dosage in PET WPWW

Coagulation with polymeric flocculants followed by sedimentation can clean up industrial effluent when the flocs formed are dense enough (Ozacar and Sengil, 2002). According to the results obtained from optimization experiments in PET washing wastewater, turbidity removal efficiency increases up to 30 mL L^{-1} dose and decreases after this. There was an increase in COD removal between doses 5 to 30 but after a dose of 30 mL L^{-1} the yield was reduced to 4% (Figure 4.19). Similarly, TSS removal efficiency up to 30 mL L-1 dose was very close to each other. After this dose, the TSS removal was reduced. As a result, 30 mL L^{-1} dose was chosen as the optimum dose with 76.8% turbidity, 29% COD and 14% TSS removal in PET washing wastewater (Figure 4.19). Figure 4.20 shows the effluent of 8 different treatment doses.

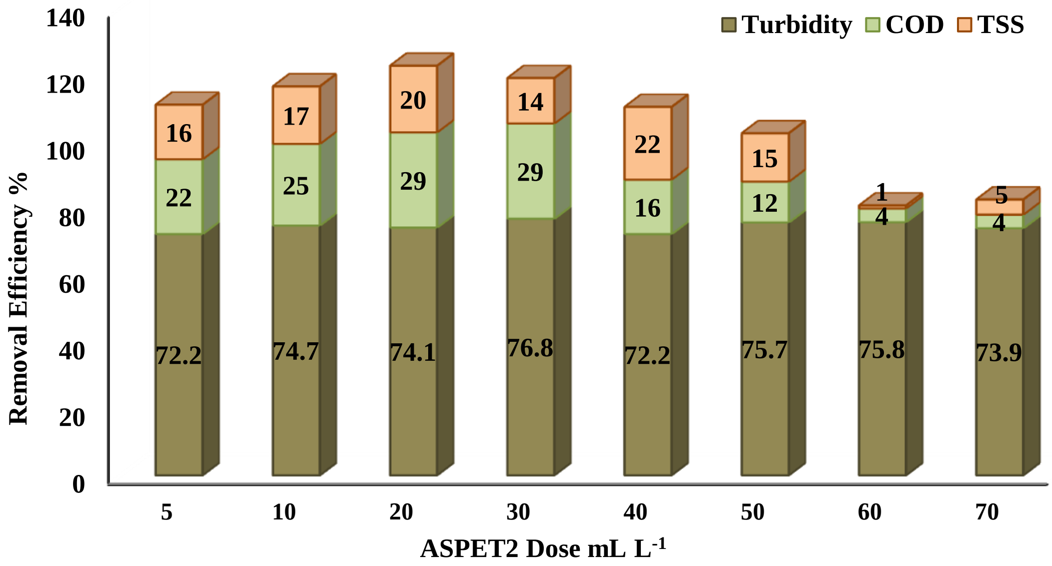


Figure 4.19. Effects of ASPET2 flocculant dosage on its performance in the treatment of PET washing wastewater (Initial Turbidity = 654 NTU, Initial COD = 2457 mg L^{-1}, Initial TSS = 1100 mg L^{-1})

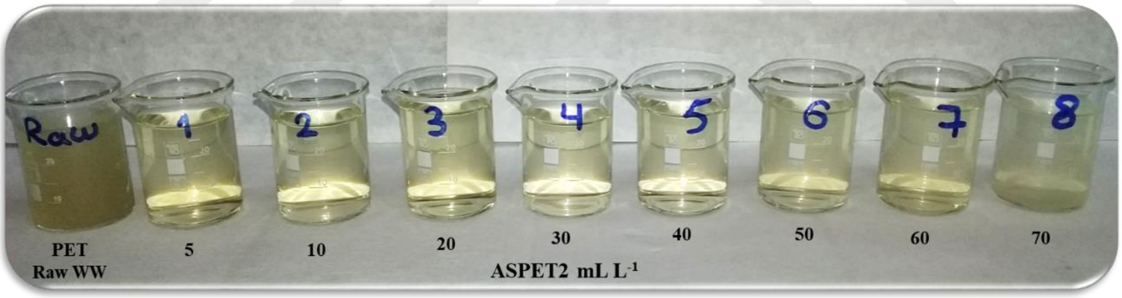


Figure 4.20. PET washing raw wastewater and effluent obtained from dosage optimization of ASPET2 in this wastewater

4.4.1.4. Treatment Properties of optimized dosage in PP WPWW

FPET1 that was synthesized from waste PET was selected as the most effective polymeric flocculant in PP washing wastewater and dose optimization was performed. In the dose optimization of PP washing wastewater, turbidity removal efficiencies were obtained between 70-74% in all doses. The highest COD removal was obtained at a dose of 30 mg L^{-1} (Figure 4.21). At other concentrations, except for 10 mg L^{-1}, COD and TSS removal efficiencies are almost identical. The optimum dose was selected as 30 mg L^{-1} with 73.7%

turbidity, 33.9% COD and 37.3% TSS removal efficiency. Figure 4.22 shows the effluent of five different treatment doses.

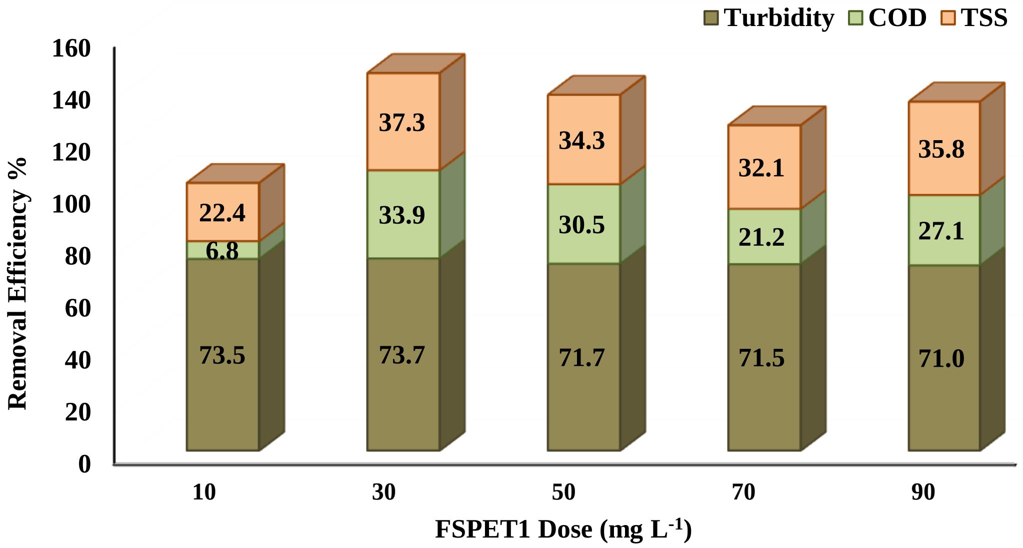


Figure 4.21. Effects of FSPET1 flocculant dosage on its performance in the treatment of PP washing wastewater (Initial Turbidity = 763 NTU, Initial COD = 2030 mg L^{-1}, Initial TSS = 1340 mg L^{-1})

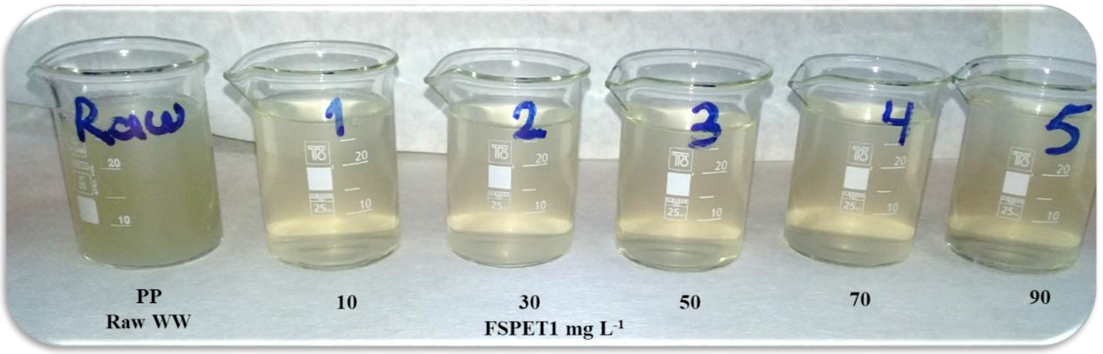


Figure 4.22. PP washing raw wastewater and effluent obtained from dosage optimization of FSPET1 in this wastewater

4.4.1.5. Treatment Properties of optimized dosage in PS WPWW

Based on the results of Table 4.4, FSPET2 was selected as the most effective flocculant for PS washing wastewater. Dose optimization of this flocculant material was performed and the results were shown in Figure 4.23. When this graph is examined, the removal efficiencies of turbidity, COD and TSS parameters are very close to each other at all concentrations of FSPET2. There is no obvious difference in removal efficiencies as the dose increases. Thus, 10 mg L^{-1} was chosen as the optimum dose. It may provide higher yields at doses lower than 10 mg L^{-1}. Figure 4.24 shows the extent to which the treatment of PS washing wastewater is successful in removing turbidity.

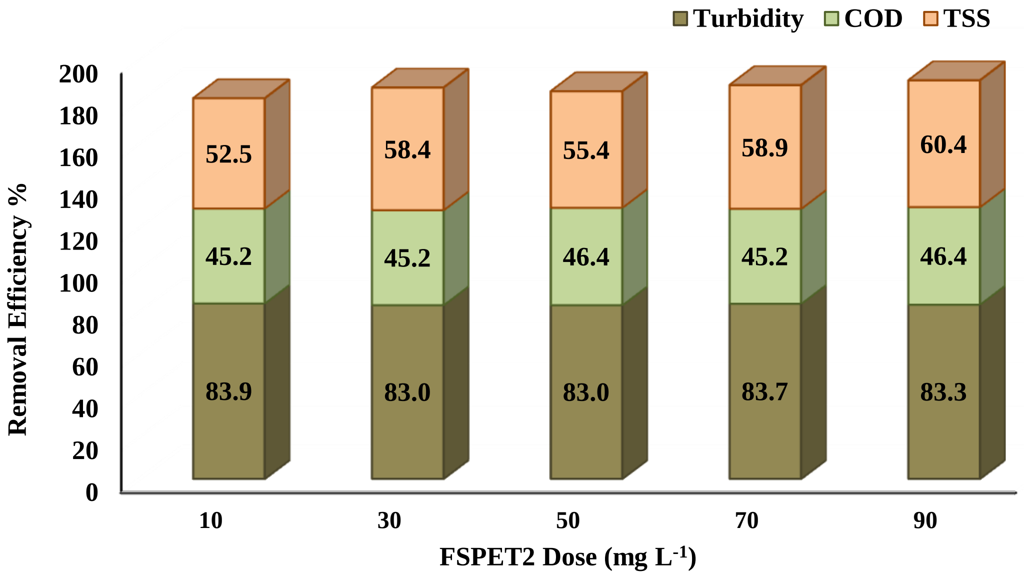


Figure 4.23. Effects of FSPET2 flocculant dosage on its performance in the treatment of PS washing wastewater (Initial Turbidity = 3240 NTU, Initial COD= 7661 mg L^{-1}, Initial TSS= 2020 mg L^{-1})

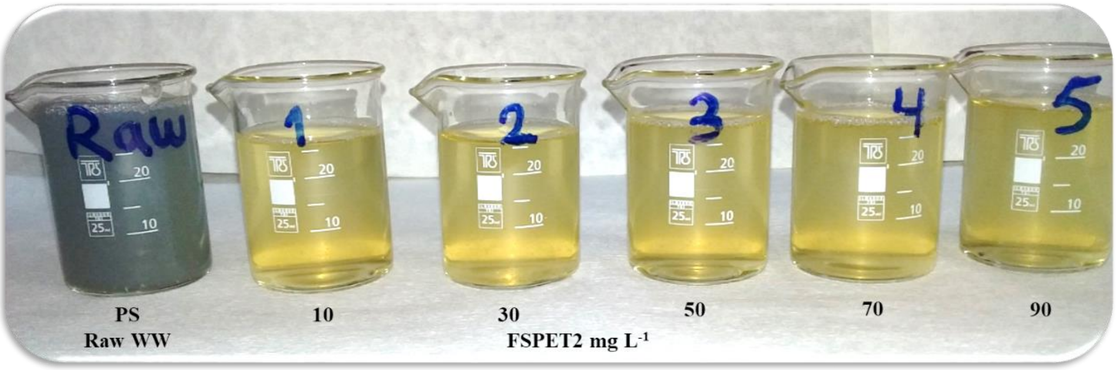


Figure 4.24. PS washing raw wastewater and effluent obtained from dosage optimization of FSPET2 in this wastewater

4.4.1.6. Treatment Properties of optimized dosage in Mixed plastic WPWW

FSPET1 flocculant was selected for dose optimization in Mixed plastic washing wastewater, as in PP wastewater. In this wastewater, turbidity removal efficiencies vary between 70-74% at 10-70 mg L^{-1} doses. However, after a dose of 70 mg L^{-1}, the yield decreases to 66.2% at 90 mg L^{-1} (Figure 4.25). Optimum concentration of polyelectrolyte forms a bridge between particles and cause good flocculation. However high concentration of polyelectrolyte forms an envelope on the suspending particles and causes them to remain in suspension thus removal efficiency decreases (Demırcı et al., 1998). Similar result was obtained from this study and when the FSPET1 polymeric flocculant concentration was increased, process performance was decreased.

The highest COD removal (44.4%) was achieved at dose of 10 mg L^{-1}. The removal efficiency of the TSS parameter is almost similar (31.8-35.5%) in all doses except for 70 mg L^{-1}. Therefore, 10 mg L^{-1} was chosen as the optimum dose, both in terms of efficiency and economics. Figure 4.26 shows the effluent of dose optimization visually.

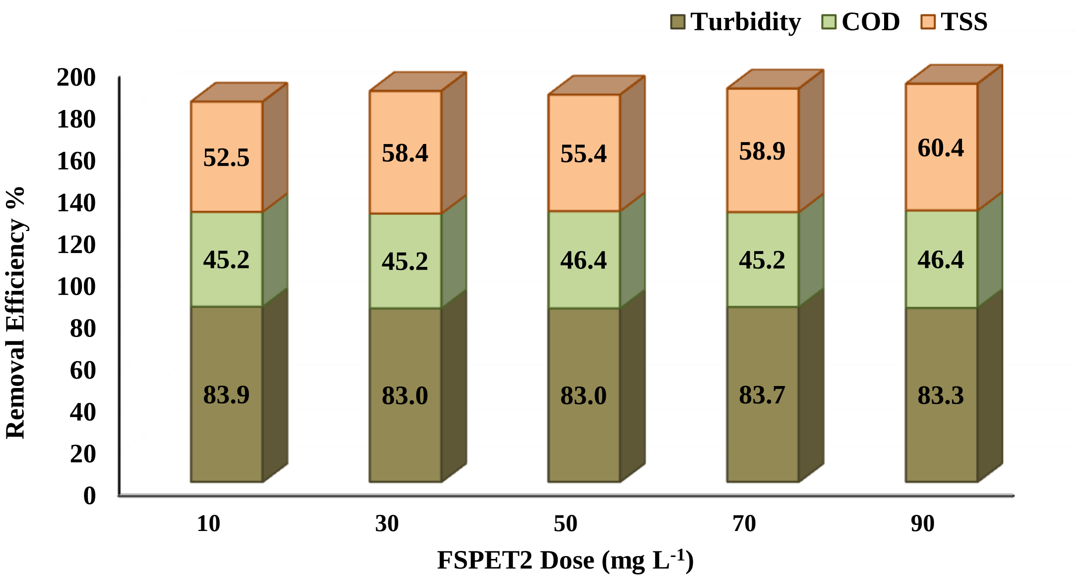


Figure 4.25. Effects of FSPET1 flocculant dosage on its performance in the treatment of Mixed plastic washing wastewater (Initial Turbidity= 1245 NTU, Initial COD= 2167 mg L^{-1}, Initial TSS= 1070 mg L^{-1})

Figure 4.26. Mixed plastic washing raw wastewater and effluent obtained from dosage optimization of FSPET1 in this wastewater

4.4.2. pH Optimization

Studying the effect of pH on coagulation/flocculation is essential in determining the optimum pH for treatment. In this part of the study, treatment performance at different pH of optimum dosage of selected synthesis flocculants was evaluated. In pH optimization, 3, 5, 7 and 9 pH values were studied. The pH optimization was performed with the optimum dose of the flocculant selected for each WPWW. As described in the material method section, during pH optimization, the coagulant dose, the selected optimum flocculant dose, the rapid and slow mixing times, and the precipitation time were kept constant for all experiments.

4.4.2.1. Effect of pH in HDPE WPWW Treatment

The effects of pH on turbidity, COD, and TSS removal, using FSPET2 are shown in Figure 4.27. The removal of turbidity using FSPET2 increased when pH increased from 3 to 9 (Figure 4.27a). The highest percentage of turbidity removal (85.5%) was achieved at an initial pH of 13.94. When pH increased from 3 to 9, COD and TSS removal efficiency increased from 39.5% and 49.4 to 71.1% and 52.6 respectively. COD and TSS concentration of effluent was 669 mg L^{-1} and 740 mg L^{-1} respectively. At higher pH value (pH 13.94), COD and TSS removal efficiency decreased (Figure 4.27a and b). It is clear that optimal pH was 9 for the coagulation/flocculation process at 50 mg $L^{-1}$of FSPET2 dosage. pH is an important parameter for coagulation process since it controls hydrolysis species. When a coagulant such as ferric salt is added to water, a series of soluble hydrolysis species are formed. These hydrolysis species have positive or negative charges depending on the water pH. They are positively charged at low pH (< 6) and negatively charged at high pH. The positively charged hydrolysis species can absorb onto the surface of colloidal particles and destabilize the stable colloidal particles. This mechanism is called ‘charge neutralization’ (Aygun and Yilmaz, 2010). A precipitate of ferric hydroxide is formed at sufficiently high coagulant dosage. These precipitates can physically sweep the colloidal particles from the suspension. This mechanism is called ‘sweep-floc coagulation’ (Kim et al., 2001). In this study, after FeCl3 addition as a coagulant, mechanism of coagulation showed properties of sweep-floc coagulation due to the high pH in operation. Thus, the highest turbidity removal at pH 13.94 and the highest COD and TSS removal at pH9 were obtained. The effluent waters of the pH optimization are given in Figure 4.28.

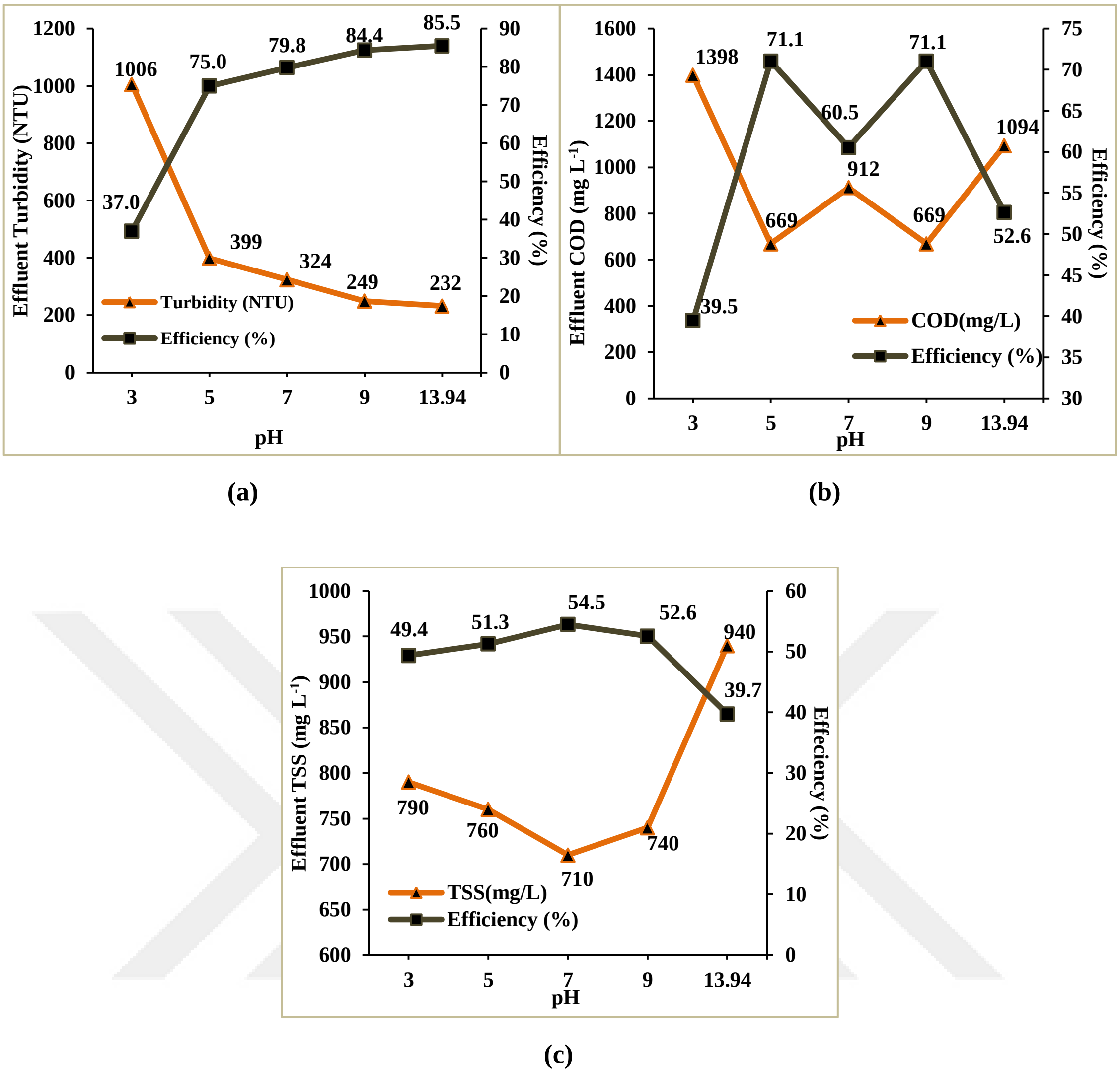


Figure 4.27. Change of FSPET2 flocculant performance with initial pH in the treatment of HDPE washing wastewater for (a) Turbidity, (b) COD and (c) TSS (Initial Turbidity = 1597 NTU, Initial COD = 2310 mg L^{-1}, Initial TSS = 1560 mg L^{-1})

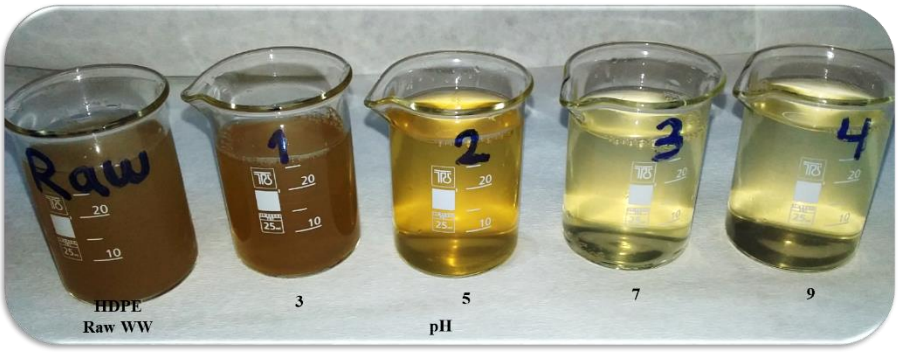
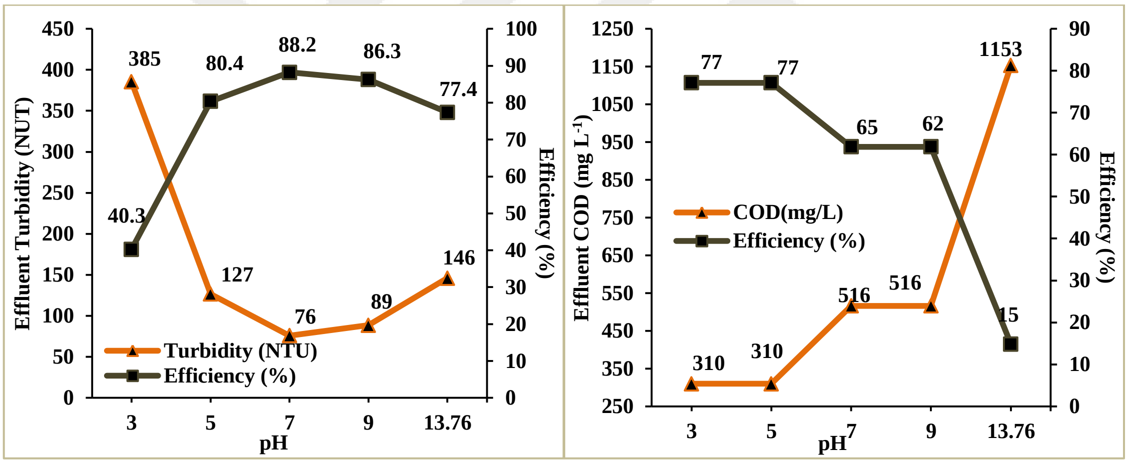


Figure 4.28. HDPE washing raw wastewater and effluent obtained from pH optimization with FSPET2 flocculant

4.4.2.5. Effect of pH in LDPE WPWW Treatment

pH optimization of LDPE washing wastewater was carried out with 40 mL L^{-1} dose of ASPET2 flocculant. The effluent obtained as a result of the coagulation/flocculation process is observed to be clear (not turbid) (Figure 4.34). Turbidity was removed up to 88% at pH 7. At lower and higher pHs, the removal efficiency was decreased (Figure 4.33a). at pH 3, turbidity removal has the lowest value (40.3%), but COD removal efficiency (77%) has the highest value (Figure 4.33b). COD removal has decreased to 62% in 7-9 pH range while at the original pH of the wastewater it was only 15%. The high COD removal at pH 3 may have eased the fragmentation of acid pH materials, but the increase in turbidity may have caused the absence of precipitation hence increasing the dissolution. According to turbidity and COD removal efficiencies, pH range 5-9 can be used for this wastewater treatment, but a pH of 7 can be selected as optimum pH.



(a) (b)

Figure 4.33. Change of ASPET2 flocculant performance with initial pH in the treatment of LDPE washing wastewater for (a) Turbidity and (b) COD (Initial Turbidity = 645 NTU, Initial COD = 1354 mg L^{-1}, Initial TSS = 650 mg L^{-1})

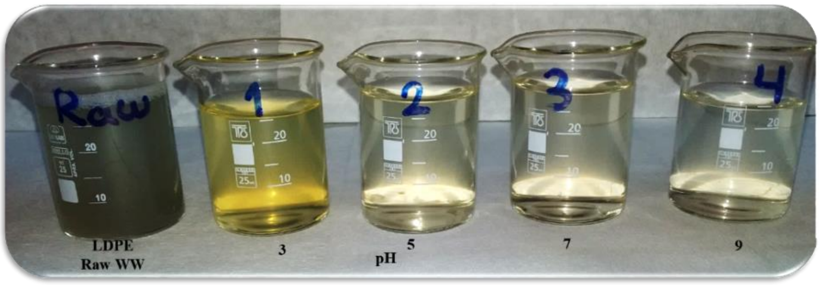
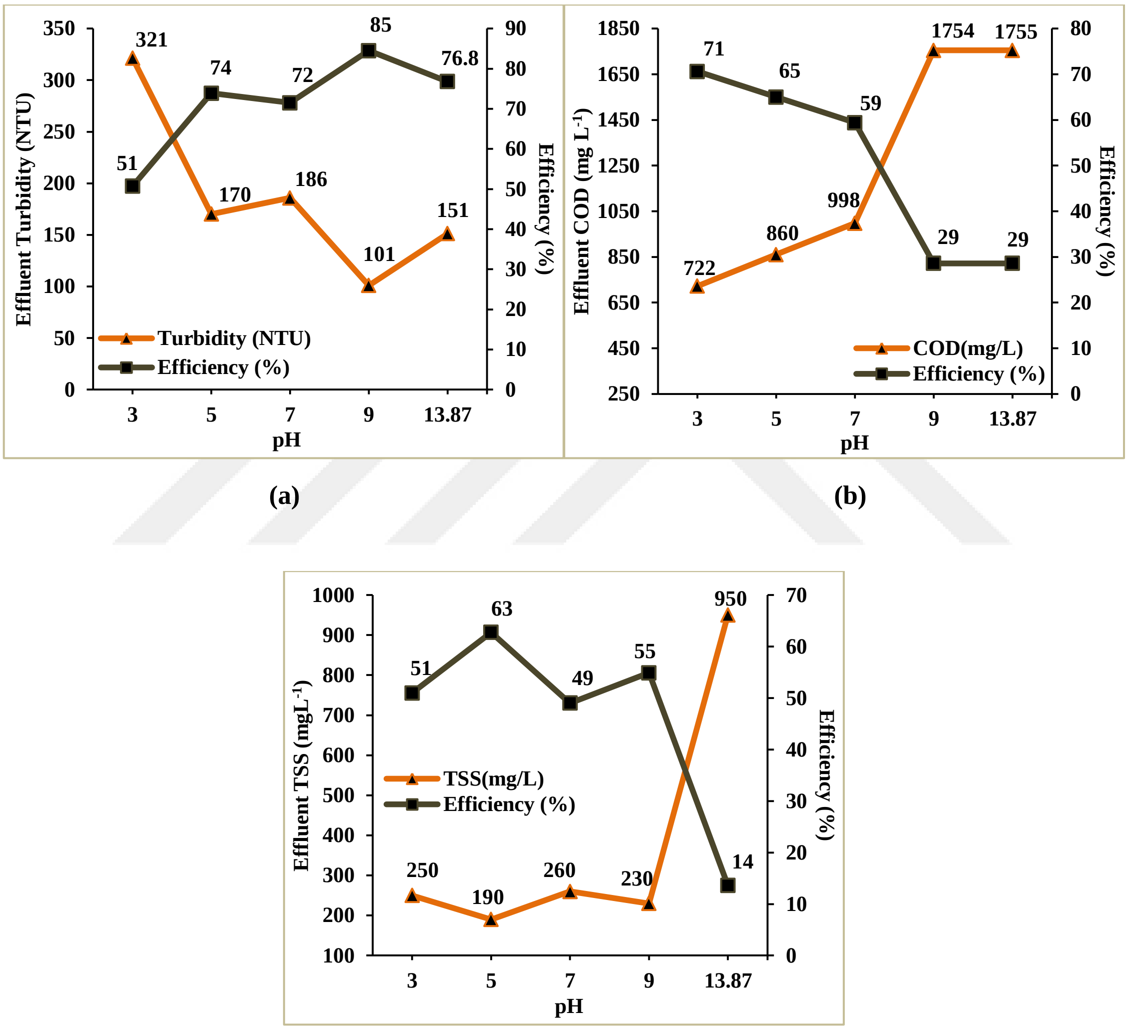


Figure 4.34. LDPE washing raw wastewater and effluent obtained from pH optimization with ASPET2 flocculant

4.4.2.4. Effect of pH in PET WPWW Treatment

pH was optimized at a dose of 30 mL L^{-1} ASPET2 in PET washing wastewater. When Figure 4.35 was examined, turbidity removal decreases as pH of wastewater decreases whereas COD removal increases. TSS removal efficiency in range of 3-9 pH has between 50-65%, while TSS removal is only 14% at initial pH of the wastewater. With respect to these results, the optimum pH was selected as 9 for PET WPWW.



(a)

(b)

(c)

Figure 4.35. Change of ASPET2 flocculant performance with initial pH in the treatment of PET washing wastewater for (a) Turbidity, (b) COD and (c) TSS (Initial Turbidity = 654 NTU, Initial COD = 2457 mg L^{-1}, Initial TSS = 1100 mg L^{-1})

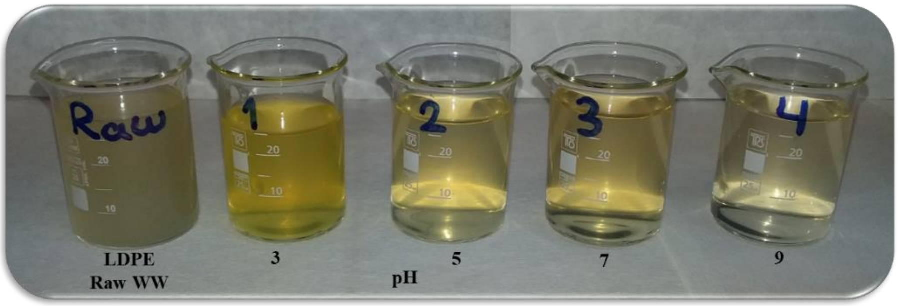


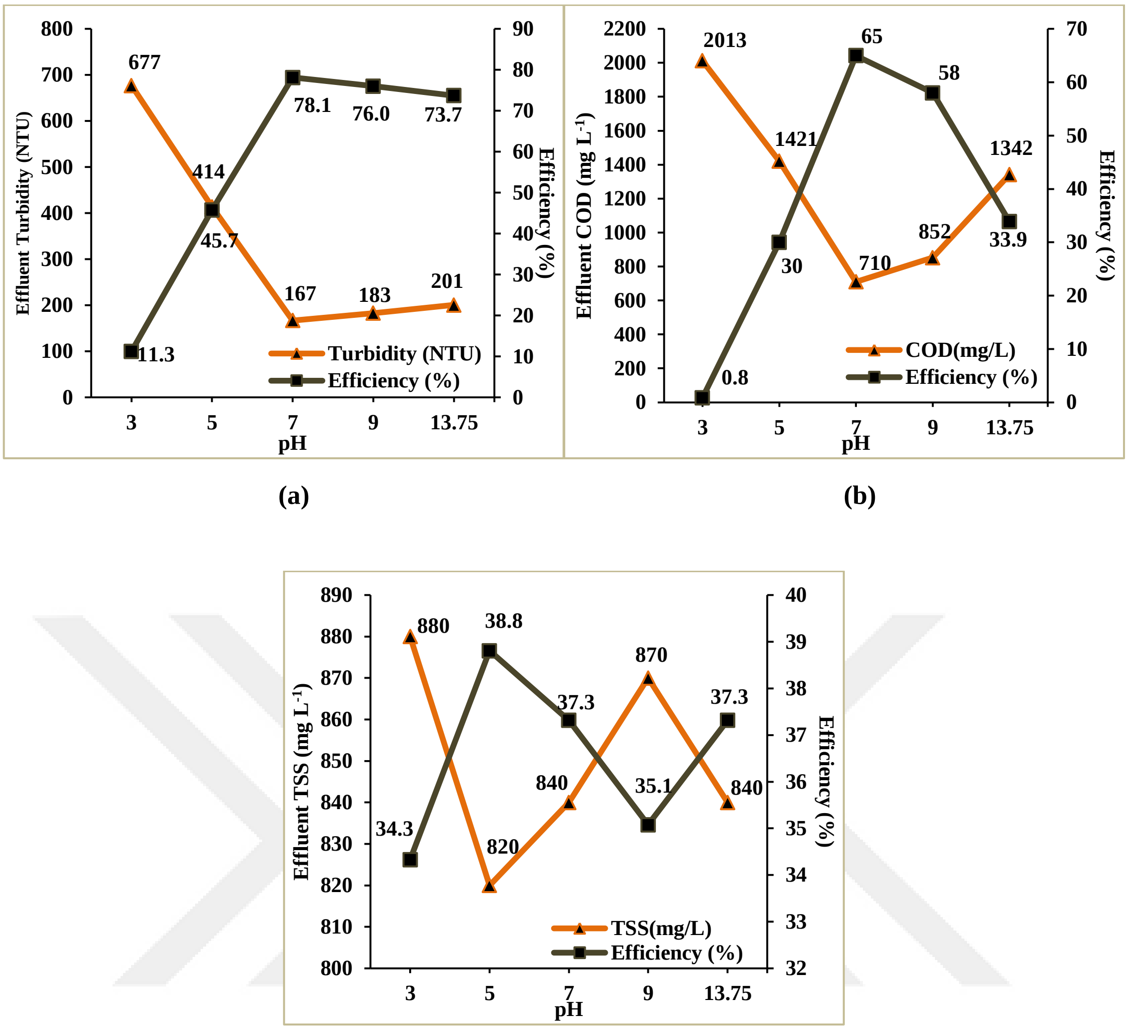
Figure 4.36. PET washing raw wastewater and effluent obtained from pH optimization with ASPET2 flocculant

4.4.2.3. Effect of pH in PP WPWW Treatment

In PP WPWW, pH optimization was performed with 30 mg L^{-1} FSPET1 flocculant. Turbidity and COD removal efficiencies increased from 11.3% and 0.8% to 78.1% and 65%, respectively, between in 7-9 pH range (Figure 4.29a and b). While TSS was removed 38.8% at pH 5 (Figure 4.29c). These removal achievements are clearly seen in Figure 4.30 visually for pH 7 and 9. Decreasing the pH below 7 markedly deteriorated the quality of the wastewater. In the pH range of 7–9, contaminants level decreased as pH increases. According to turbidity and COD removal, PP WPWW coagulation/flocculation process can be performed very efficiently between 7-9 pH. The optimal pH as the presenter of this study was chosen as 7 for PP washing wastewater.

4.4.2.2. Effect of pH in PS WPWW Treatment

In PS WPWW pH optimization, pH was varied within the range of 3-9 for fixed FSPET2 flocculant dose (10 mg L^{-1}). Effluent and removal efficiency of turbidity, COD, and TSS versus different pHs are given in Figure 4.28. When pH increased from 3 to 5, turbidity removal efficiency increased from 74.6% to 76.4% and TSS removal efficiency was also increased (Figure 4.29a and c). COD concentration of effluent was decreased from 4211 to 3309 mg $L^{-}1$ in 3-7 pH range (Figure 4.29b). Turbidity and TSS removal are reduced when the pH is increased from 5 to 9, but the highest pH (initial pH) yields the highest efficiency. On the contrary, at higher pH value, COD removal efficiency decreased. It is clear that optimum pH was initial pH for the coagulation/flocculation process at 10 mg L^{-1} of FSPET2 dosage. The effluent waters of the pH optimization are given in Figure 4.30.



(a)

(b)

(c)

Figure 4.29. Change of FSPET1 flocculant performance with initial pH in the treatment of PP washing wastewater for (a) Turbidity, (b) COD and (c) TSS (Initial Turbidity = 763 NTU, Initial COD = 2030 mg L^{-1}, Initial TSS = 1340 mg L^{-1})

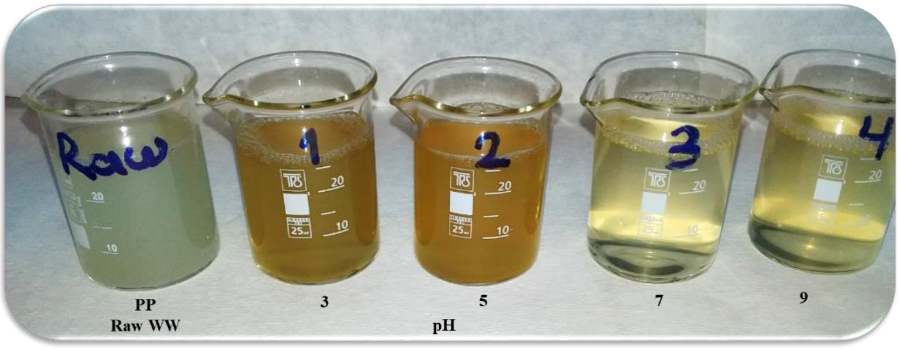
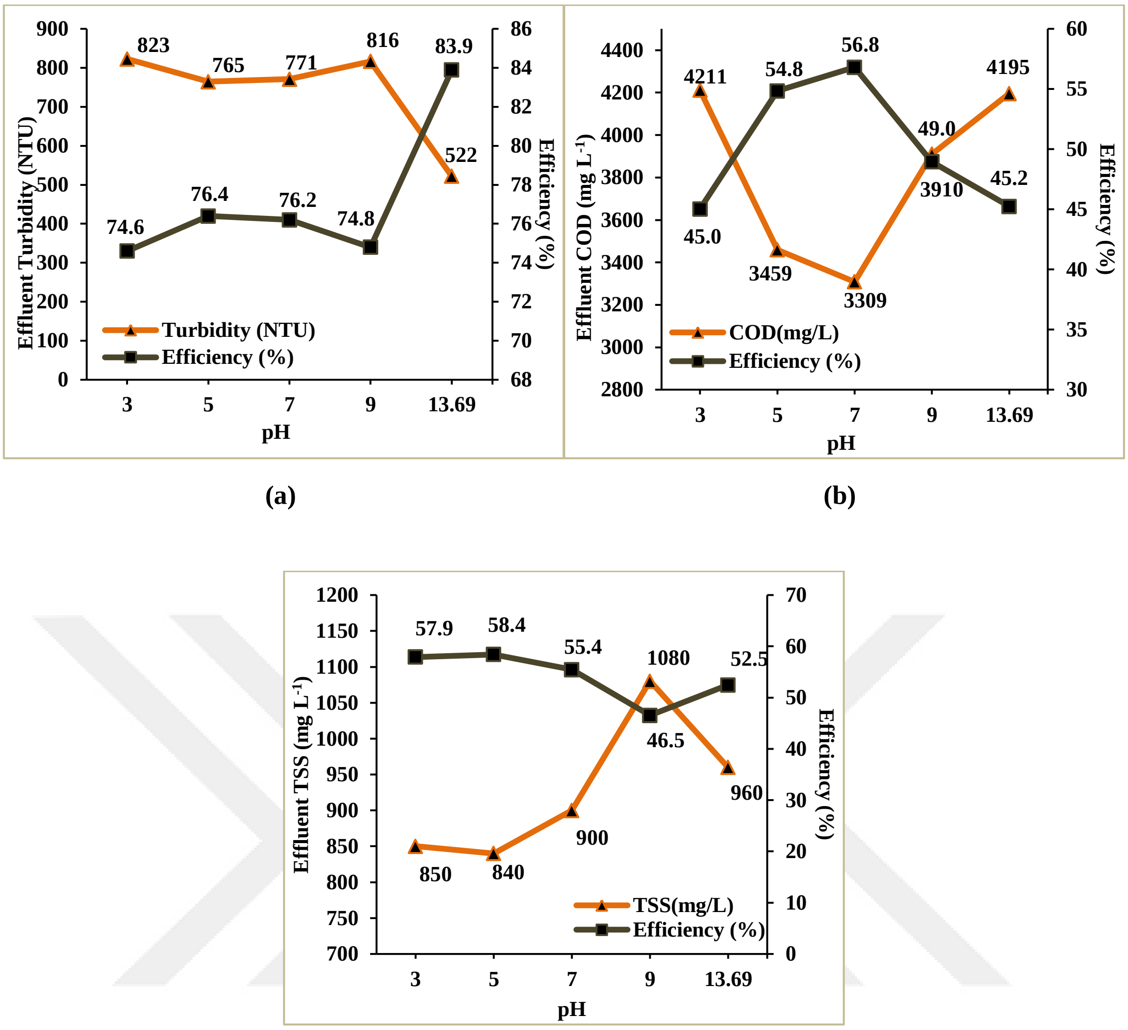


Figure 4.30. PP washing raw wastewater and effluent obtained from pH optimization with FSPET1 flocculant



(a) (b)

(c)

Figure 4.29. Change of FSPET2 flocculant performance with initial pH in the treatment of PS washing wastewater for (a) Turbidity, (b) COD and (c) (Initial Turbidity = 3240 NTU, Initial COD = 7661 mg L^{-1}, Initial TSS = 2020 mg L^{-1})

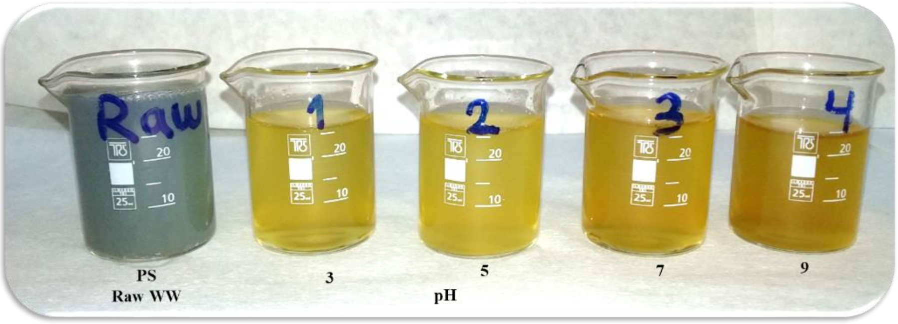
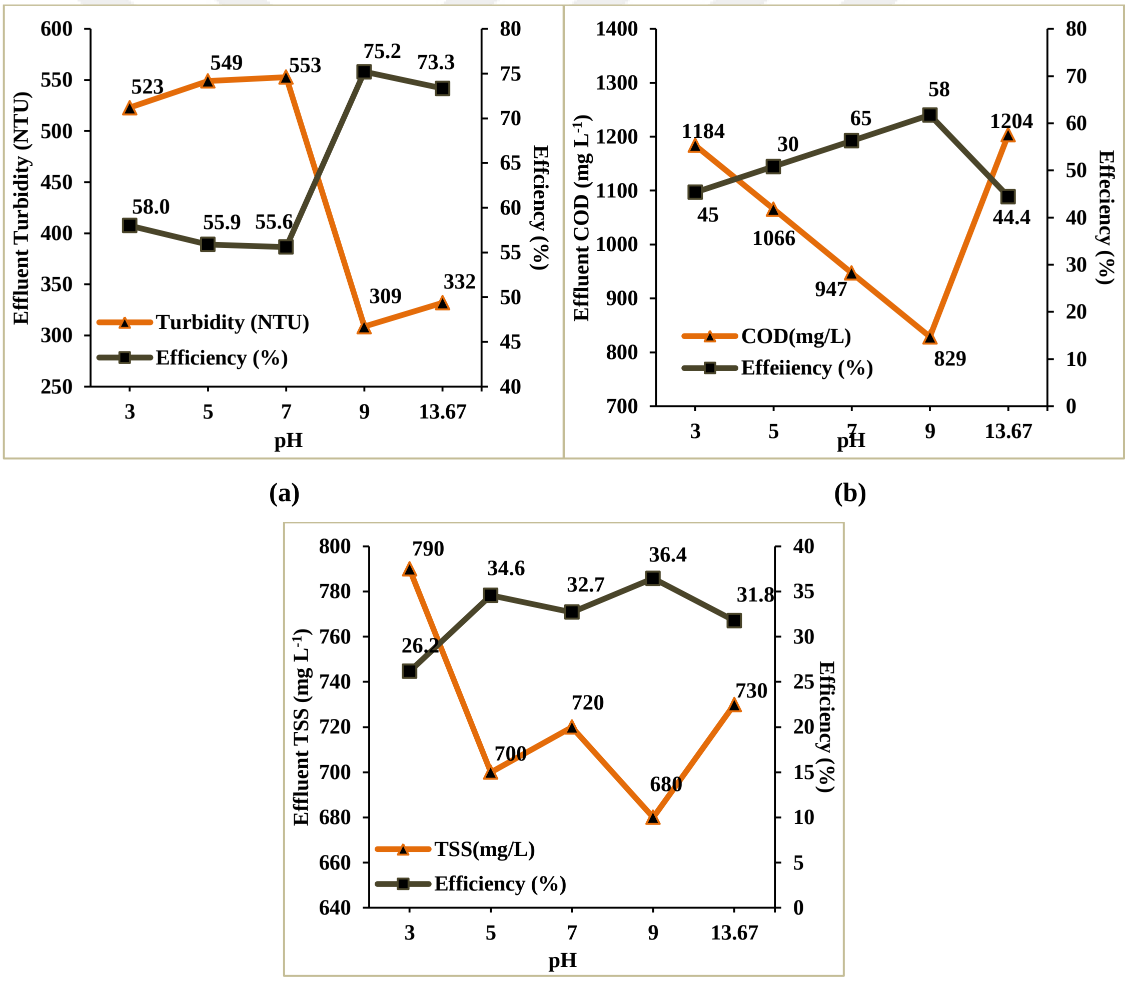


Figure 4.30. PS washing raw wastewater and effluent obtained from pH optimization with FSPET2 flocculant

4.4.2.4. Effect of pH in Mixed Plastic WPWW Treatment

As PP washing wastewater, the FSPET1 flocculant was used for pH optimization in Mixed plastic washing wastewater. But the dose of 10 mg L^{-1} for this wastewater was tested as the most efficient dose. As a result of the experiments, a decrease in turbidity was observed when the pH value decreased from 7 to 3 (Figure 4.31a). This is due to the dissolution of flocs at low pH. However, as shown in Figure 4.32 compared to the effluents of other wastewater, in Mixed plastic washing wastewater treatment, when pH is 3, the treated water appears more clear. COD removal decreased at low pH and the highest efficiency was seen at pH 9 (Figure 4.31b). TSS removal has the highest value at pH 9 (Figure 4.31c). Thus, pH9 was selected as optimal pH for Mixed plastic WPWW.



(a) (b)

(c)

Figure 4.31. Change of FSPET1 flocculant performance with initial pH in the treatment of Mixed plastic washing wastewater for (a) Turbidity, (b) COD and (c) TS (Initial Turbidity = 1245 NTU, Initial COD = 2167 mg L^{-1}, Initial TSS = 1070 mg L^{-1})

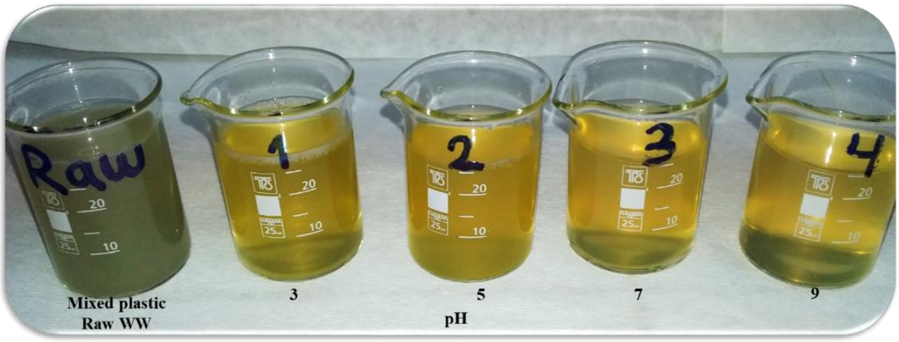


Figure 4.32. Mixed plastic washing raw wastewater and effluent obtained from pH optimization with FSPET1 flocculant

In Table 4.5, all optimum doses and pHs obtained from dose and pH optimization at six different WPWWs are compared. The highest turbidity removal was obtained at initial pH with a dose of 50 mg L^{-1} FSPET2 flocculant in HDPE WPWW and the highest COD and TSS removals were achieved in PS and PET WPWWs.

PS and HDPE WPWWs treatment performances were high at the original pH, whereas LDPE and PP wastewater had the best treatment at pH 7, PET and mixed plastic wastewater had high treatment at pH 9.

Table 4.5. The most effective dose and pH suggested for each wastewater

WPWW	Flocculant		pH	Removal Efficiency %		
	Name	Dose (mg L^{-1} / mL L^{-1})		Turbidity	COD	TSS
HDPE	FSPET2	50	13	86.0	53	40
PS	FSPET2	10	13	83.9	45	52
PP	FSPET1	30	7	73.7	34	37
Mixed plastic	FSPET1	10	9	73.0	44	31
LDPE	ASPET2	40	7	77.4	15	0
PET	ASPET2	30	9	76.8	79	14

4.5. Treatment Sludge Properties

In general, the amount and the characteristics of the sludge produced during the coagulation/flocculation process are highly dependent on the specific coagulant/flocculant used and on the operating conditions (Amuda and Alade, 2006). The wet sludge volume settled after coagulation/flocculation process was used to quantify the treatment sludges generated in this study.

The treatment sludge properties of the treatment processes with eight synthesized flocculants in six WPWW are presented in Table 4.6. The treatment sludge properties of the synthesized substances obtained at the original pH of wastewaters and conventional flocculant PEL are presented in these tables. Treatment sludge data of the two synthesis flocculants selected in Table 4.4 are color marked in Table 4.6, as they have higher performance than others for each WPWW. The minimum, maximum and average values of the sludge suspended solids are 4350 mg L^{-1}, 13490 mg L^{-1} and 8360 mg L^{-1} respectively. Sludge solids percents were between 0.44 and 1.34, which is an average of 0,83% Solid. The sludge densities were at the average value of 1.007 g cm^{-3} between 0.974 and 1.088. The SCR has a range of 1.36E+13 to 7.22E+13 m kg^{-1} with the average value 3.37E+13 mkg^{-1}.

Table 4.6. Properties of treatment sludges obtained by synthesized flocculants (1000 mg L^{-1} $FeCl_3$ as a coagulant and at the original pH of the wastewater)

Treatment Sludge	Flocculant	Sludge Volume, mL L^{-1}	TSS, mg L^{-1}	Density, g cm^{-3}	Solid, %	SCR, m kg^{-1}
HDPE Treatment Sludge	FSPS1	206	6520	1.088	0.60	6.66E+13
	FSPS2	208	6660	0.980	0.68	2.04E+13
	FSPS3	300	6820	1.005	0.68	2.47E+13
	FSPET1	204	7270	1.003	0.72	2.31E+13
	FSPET2	164	8680	1.0201	0.85	1.25E+13
	FSPET3	200	9290	1.005	0.92	2.53E+13
	ASPET1	208	7730	0.999	0.77	1.80E+13
	ASPET2	202	8440	0.999	0.85	1.77E+13
	PEL	170	10010	1.024	0.98	3.89E+13
LDPE Treatment Sludge	FSPS1	206	4510	1.010	0.45	2.86E+13
	FSPS2	200	4390	1.001	0.44	4.05E+13
	FSPS3	200	4350	0.974	0.45	3.41E+13
	FSPET1	150	5140	0.987	0.52	2.29E+13
	FSPET2	150	5180	0.999	0.52	1.57E+13
	FSPET3	154	4750	0.977	0.49	2.61E+13
	ASPET1	154	4700	0.991	0.47	5.49E+13
	ASPET2	152	4970	1.009	0.50	3.16E+13
	PEL	130	5860	0.998	0.59	4.64E+13

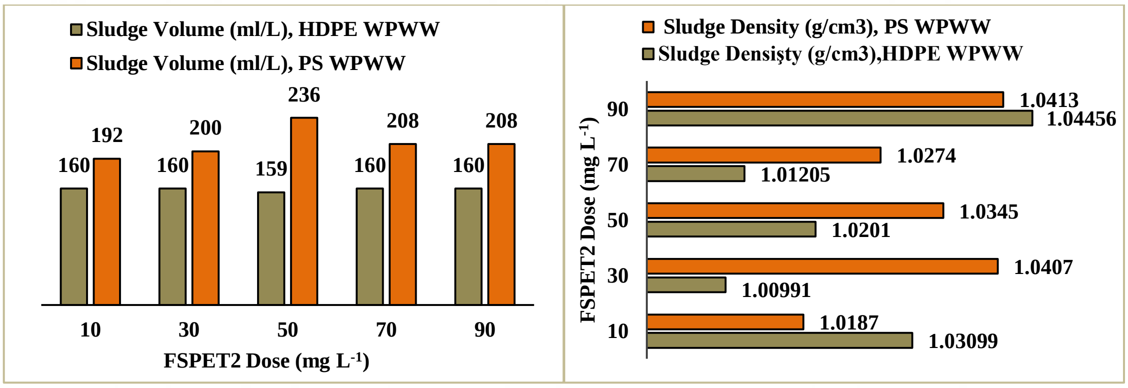
Table 4.6. (Continued)

Treatment Sludge	Flocculant	Sludge Volume, mL L^{-1}	TSS, mg L^{-1}	Density, g cm^{-3}	Solid, %	SCR, m kg^{-1}
PET Treatment Sludge	FSPS1	170	8610	0.980	0.88	2.21E+13
	FSPS2	195	8290	0.983	0.84	2.89E+13
	FSPS3	190	7710	1.022	0.75	1.89E+13
	FSPET1	210	7670	1.023	0.75	2.70E+13
	FSPET2	175	9180	1.020	0.90	1.92E+13
	FSPET3	180	8300	1.020	0.81	2.18E+13
	ASPET1	175	8230	1.020	0.81	2.67E+13
	ASPET2	268	7900	1.0290	0.78	2.04E+13
	PEL	155	5160	1.009	0.51	4.77E+13
PP Treatment Sludge	FSPS1	205	8690	1.014	0.86	2.91E+13
	FSPS2	210	8900	1.012	0.88	2.89E+13
	FSPS3	205	9110	1.015	0.90	1.76E+13
	FSPET1	136	9640	1.0263	0.95	2.09E+13
	FSPET2	225	8470	1.014	0.84	3.12E+13
	FSPET3	190	9270	1.014	0.91	2.10E+13
	ASPET1	215	8180	1.012	0.81	2.25E+13
	ASPET2	175	10330	1.017	1.02	2.12E+13
	PEL	185	9210	1.000	0,92	2.55E+13
PS Treatment Sludge	FSPS1	215	11110	1.016	1.09	6.87E+13
	FSPS2	175	12910	1.028	1.26	3.61E+13
	FSPS3	195	11440	1.006	1.14	5.70E+13
	FSPET1	175	12910	1.000	1.29	5.36E+13
	FSPET2	236	13490	1.034	1.34	5.56E+13
	FSPET3	170	12930	1.022	1.26	4.69E+13
	ASPET1	205	11640	1.006	1.16	6.50E+13
	ASPET2	210	11850	1.010	1.17	5.00E+13
	PEL	190	12500	1.005	1.24	7.22E+13
Mixed plastic Treatment Sludge	FSPS1	185	7870	1.006	0.78	4.56E+13
	FSPS2	200	7240	0.990	0.73	2.72E+13
	FSPS3	165	7960	0.994	0.80	2.69E+13
	FSPET1	160	8630	1.0205	0.85	3.02E+13
	FSPET2	200	7740	0.998	0.78	2.67E+13
	FSPET3	155	9070	1.020	0.89	3.76E+13
	ASPET1	185	8740	1.009	0.87	3.07E+13
	ASPET2	180	7150	1.013	0.71	4.21E+13
	PEL	170	8890	1.002	0.89	4.61E+13

Compared to the literature values, it is seen that all SCR values are at the recommended levels for well-dewatered coagulation sludges (Casey, 2006). The treatment sludge properties obtained with each of the synthesis materials in the same WPWW are similar but differ from the sludges obtained with PEL (Table 4.6). Although the treatability of PS washing wastewater is not very different, the sludge suspended solids and percent solid in the treatment sludge is significantly higher than the others. This low sludge volume situation shows that the sludge is easy to settle.

4.5.1. Treatment Sludges of HDPE and PS WPWW

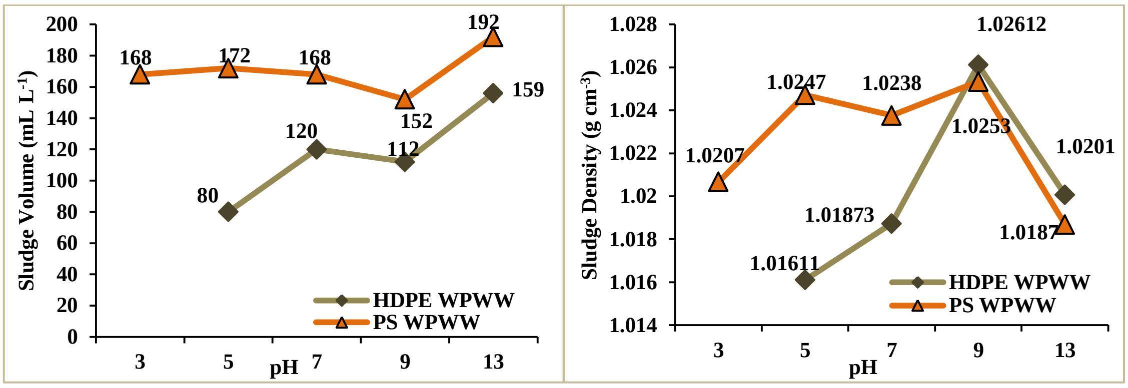
Sludge analyses were performed as described in the material-method section. The volume (mL L^{-1}) of the settled sludges are shown as functions of flocculant dose (mg L^{-1}) in Figure 4.37. The sludge volume and density values obtained from the dose and pH optimization studies of HDPE and PS washing wastewater are given in Figure 4.37 and Figure 4.38. The change of flocculant dose has no effect on the volume of sludge formed in the treatment of HDPE washing wastewater. As shown in Figure 4.37a, when flocculant dose increased up to 50 mg L^{-1} in the coagulation/flocculation process of PS WPWW the sludge volume increased significantly and then stabilized.



(a) (b)

Figure 4.37. Change of treatment sludge volumes (a) and densities (b) with FSPET2 dosage in the treatment of HDPE and PS washing wastewater

The volume and density of the sludges obtained as a result of pH optimization tests in HDPE and PS WPWW with selected doses of FSPET2 are given in Figure 4.38. The sludge of the sample treated at pH 9 for HDPE and PS WPWWs in the previous sections has the lowest volumes and highest densities (Figure 4.38). The sludge of the sample treated with 50 mg L^{-1} FSPET2 which was selected as the optimum dose for HDPE WPWW in the previous sections has the lowest volume (Figure 4.37a). In addition, the 10 mg L^{-1} dose of the same flocculant provided the lowest sludge volume in PS WPWW. However sludge densities were considered, the highest sludge density was provided 90 mg L^{-1} FSPE2 dose in both wash wastewaters (Figure 4.37b). When Figures 4.36 and 4.37 are compared, low volume and high-density sludges were provided at pH9 in both wastewaters.

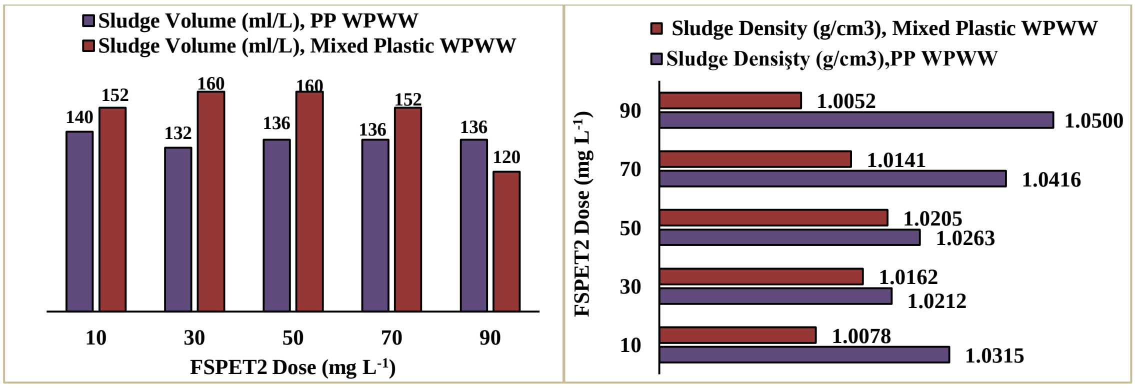


(a) (b)

Figure 4.38. Change of treatment sludge volumes (a) and densities (b) with pH in the treatment of HDPE and PS washing wastewater

4.5.2. Treatment Sludges of PP and Mixed Plastic WPWW

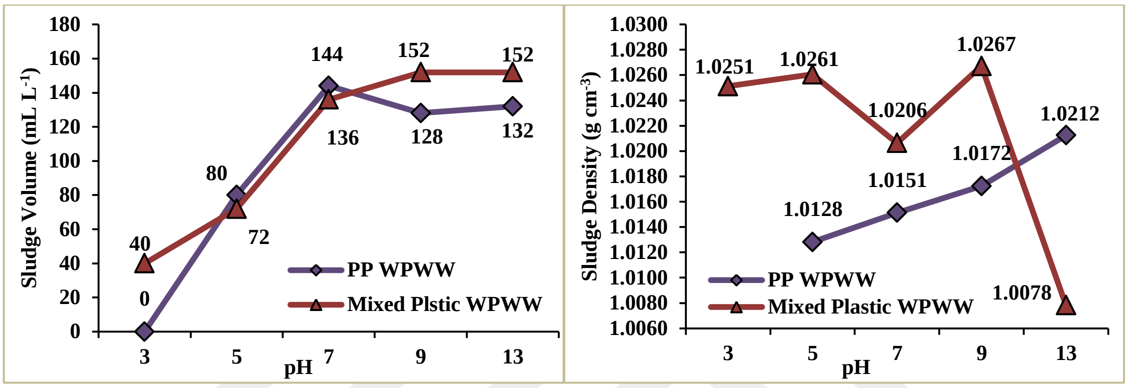
The sludge volume and density values obtained from the dose and pH optimization studies of PP and Mixed plastic washing wastewater are given in Figure 4.39 and 4.40. The lowest sludge volume for PP WPWW was at 30 mg L^{-1} (selected optimum dose) FSPET1 dose as 132 mL L^{-1}, and in Mixed plastic WPWW at 90 mg L^{-1} dose as 120 mL L^{-1} sludge was obtained (Figure 4.39a). The highest sludge density was observed in PP and Mixed plastic WPWWs at 90 and 50 mg L^{-1} doses respectively as 1.050 and 1.0205 g cm^{-3} (Figure 4.39b).



(a) (b)

Figure 4.39. Change of treatment sludge volumes (a) and densities (b) with FSPET1 dosage in the treatment of PP and Mixed plastic washing wastewater

The sludge of the sample treated at pH 13 for PP WPWW in the previous sections has a low volume (132 mL L^{-1}) and highest density (1.0212 g cm^{-3}) (Figure 4.40). When examined in Figure 4.40a, it is seen that the sludge of the sample treated with 10 mg L^{-1} FSPET1 which was selected as the optimum dose for Mixed plastic WPWW in pH 9 has the highest density with 152 mL L^{-1} volume. The results obtained from the Mixed plastic WPWW pH optimization test, low pHs show low sludge volume and high density. In fact, since there is not much treatment at these pHs, the amount of sludge appears to be low. Thus, different doses of FSPET2 do not have much effect on sludge volume and density, but as the pH gets lower, the treatment efficiency declines and decreases the sludge volume and density.



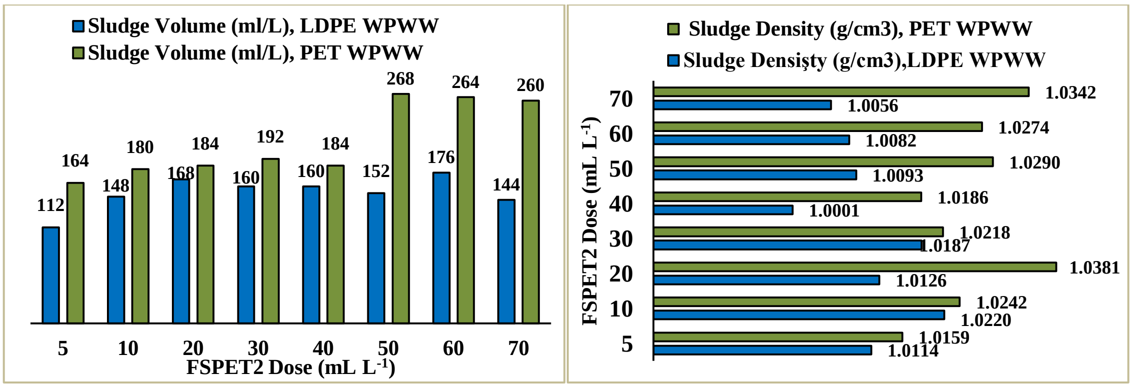
(a) (b)

Figure 4.40. Change of treatment sludge volumes (a) and densities (b) with pH in the treatment of PP and Mixed plastic washing wastewater

4.5.3. Treatment Sludges of LDPE and PET WPWW

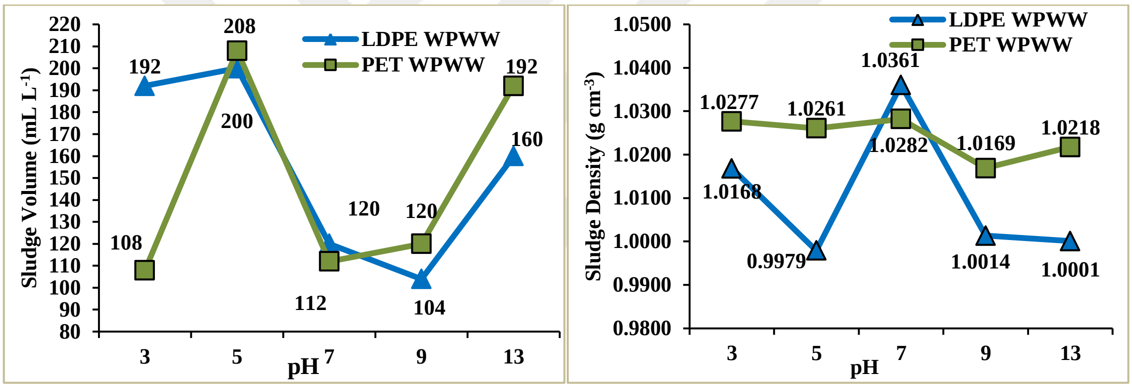
In LDPE and PET WPWWs, ASPET2 flocculant was selected as the most effective flocculant. Optimum doses were obtained as 40 and 30 mLL^{-1} for LDPE and PET WPWWs, respectively. The sludge volume and density values obtained from the dose and pH optimization studies of LDPE and PET washing wastewater are given in Figure 4.41 and 4.42. The average sludge volume and densities for LDPE WPWW were calculated as 153 mL L^{-1} and 1.011 g cm^{3}, and for PET WPWW as 212 mL L^{-1} and 1.0261 g cm^{-3} respectively. Sludges of optimum doses also have close volume and density of this average (Figure 4.41).

When the results of the analysis sludges formed under optimized pH conditions of both wastewaters were examined, they provided the highest quality treatment sludge at pH of 7-9 (Figure 4.42). The highest sludge densities were obtained at pH 7 as 1.0361 and 1.0282 g cm3 for LDPE and PET WPWW, respectively (Figure 4.42b). As a result, treatment sludges of the selected optimal pHs (i.e. 7 for LDPE and 9 for PET WPWW) of both washing wastewaters had a volume and density very close to the best sludge.



(a) (b)

Figure 4.41. Change of treatment sludge volumes (a) and densities (b) with ASPET2 dosage in the treatment of LDPE and PET washing wastewater



(a) (b)

Figure 4.42. Change of treatment sludge volumes (a) and densities (b) with pH in the treatment of LDPE and PET washing wastewater

4.5.5. Properties of the Highest Quality Treatment Sludge

In the previous sections, the most successful dose and pH for six WPWWs were selected. The properties of the sludges obtained with these selected doses are further compared in Tables 4.7 and 4.8. Among the synthesized flocculants, three of them were found more efficient in the treatment of WPWWs. FSPET2 produced very similar sludges in both HDPE and PS WPWW (Table 4.7). In HDPE WPWW treatment, properties of FSPET2 sludge was almost identical with PEL sludge, even denser and has a lower SCR (Table 4.6). In PP and Mixed WPWW, the treatment performance of FSPET1 is high at pH 7-9, whereas the produced sludges have lower quality as compared to treatment sludges obtained at original pH (Table 4.6). In addition, ASPET2 flocculant was produced a higher quality sludge at pH of 7 and 9 than initial pH in LDPE and PET WPWW. The sludges from the treatment of all wastewaters have medium solids content, compared to active and pre-settled sludges (Metcalf and Eddy, 1979). Moreover, the sludges from all coagulation/flocculation treated wastewaters have better filterability in comparison to municipal sludges (Verma et al., 2010).

Table 4.7. Sludge properties of treatments under optimized dosage and pH conditions for each wastewater

WPWW	Flocculant		pH	Sludge Volume (mL L^{-1})	TSS (mg L^{-1})	Sludge Density (g cm^{-3})	Dry Solids Content (DS) %	Specific Cake Resistance (m kg^{-1})
	Name	Dose (mg L^{-1} / mL L^{-1})						
HDPE	**FSPET2**	50	13	164	8680	1.02007	0.85	2.25E+13
PS	**FSPET2**	10	13	192	8200	1.01869	0.80	2.61E+13
PP	**FSPET1**	30	7	144	6000	1.01513	0.59	7.87E+13
Mixed plastic	**FSPET1**	10	9	152	6880	1.00782	0.68	2.97E+13
LDPE	**ASPET2**	40	7	120	7950	1.03607	0.77	2.03E+13
PET	**ASPET2**	30	9	120	7990	1.01691	0.79	2.38E+13

Every 1 liter of treated water approximately 120-200 mL of sludge is formed. Between 1/8-1/5 sludge is recovered as the treated water. This volume of sludge can be easily dewatered by looking at the SCR values. In this case recovery will increase. Sludge solids content are in the range of 0.6-0.8, these values are in the range of other chemical treatment sludges (0.2-2.0) (Reynolds and Richards, 2005). Densities range from 1.01 to 1.04 g cm^{-3}. Generally, in treatment processes the concentration of sludges with high solids content is expected to be greater than water, here, they have all higher than 1 g cm^{-3} sludge density. Sludge solids concentrations are in the range of 6000-8700 mg L^{-1}. Even in the final sedimentation tanks where the 3rd type of sedimentation is observed, the bottom sludge solid concentration is 8000 mg L^{-1} and above (Reynolds and Richards, 2005), the presence of similar values in the 2nd type (i.e. system with more dilute solids) is an indication of good sedimentation. In the light of these findings, it can be said that good quality, easily dewaterable treatment sludge will be obtained when treatment is performed under the proposed treatment conditions.

The basic disposal methods for sludge are land application (including composting), landfill, incineration, ocean dumping and lagoons of sludge. Disposal of sludge on land is an age-old practice throughout the world to avoid the higher cost of incineration. However, it leads to an increase in pollution load in the soil with numerous environmental consequences. The variable nature and concentrations of trace elements are largely dependent on the type and amount of urban and industrial discharges. The highest amount of Ca, Fe, Mg, Na and P in the sludge can be said to be the substances with the highest recovery potential from these treatment sludges. Other cations and especially heavy metals were not present at very high levels in the sludge. The elements of primary concern are Cd, Zn, Cu, Pb, Ni which, when applied to the soil in excessive amount, may decrease plant yields or degrade the quality of food or fiber products. Sludge should, therefore, be analyzed for nutrients and trace elements before applying on land and/or before utilizing it for other purposes. When examined for heavy metal concentrations (Table 4.8) they do not exceed the values given in the regulation, so they can be considered not to harmful for soil.

Table 4.8. Determination of some trace elements (or inorganics) in six selected sludges

Parameter (mg kg^{-1})	**HDPE WPWW Treatment Sludge**	**LDPE WPWW Treatment Sludge**	**PET WPWW Treatment Sludge**	**PP WPWW Treatment Sludge**	**PS WPWW Treatment Sludge**	**Mixed Plastic WPWW Treatment Sludge**	**Turkey* Sewage Sludge Limits**
Ca	64034	24638	31953	6589	41180	94220	
Cr	30.9	120	47.5	38.9	20.6	48.2	1000
Cu	37.8	295	75.9	91.7	168	121	1000
Fe	62385	135416	90524	76557	56352	76263	
K	503	503	384	339	649	545	
Mg	4454	1018	1224	417	4647	6550	
Mn	290	60.1	1858	133	186	314	
Mo	0	0	0	16	0	0	
Na	60967	10345	17224	42522	74004	55798	
Ni	48.2	60	43.7	55	28.7	57.3	300
P	1100	19851	2835	3917	936	3727	
Pb	863	4806	503	1509	662	2082	750
Zn	145	1263	1370	172	301	323	2500

* Maximum heavy metal contents allowed to be used in the soil from domestic and urban sewage sludge, according to regulations (Official Gazette, 2010)

5. CONCLUSIONS

Synthesis of polymers from waste plastic:

- In the study, flocculants were synthesized by classical PS sulfonation method and modified methods from the literature. Using the same modification approaches, sulfonated PET, another aromatic structured plastic, was synthesized with flocculant. Three of the totally 8 synthesized materials were obtained by PS sulfonation (FSPS1, FSPS2, and FSPS3) and three by PET sulfonation (FSPET1, FSPET2, and FSPET3). The last two of them were obtained by using waste PET material but with the method of synthesizing the adsorbent by sulfonation (ASPET1, ASPET2).

- Some PS sulfonation methods in the literature allow the synthesis of insoluble substances. Synthesis methods of these substances, which are reported to be used as adsorbents, have been applied here with some minor modifications or have been combined with each other. In fact, when the method for obtaining adsorbent from PS by sulfonation was carried out using PET, it dissolved in acid, and the two materials (ASPET1, ASPET2) obtained by this method were considered as flocculants in the study.

Characterization and treatability of WPWWs with Polymeric synthesis flocculants:

- The extent to which plastic washing wastewater obtained by caustic washing can be treated when subjected to coagulation/flocculation processes has been demonstrated. These experiments were first studied with flocculant synthesized by classical literature methods and then the affectivities of other syntheses under the same conditions were compared.

- The FeCl3 was preferred as the coagulant to be used together with the synthesized flocculant and previously determined 1000 mg L^{-1} dose was kept constant in all treatment trials.

- First, coagulation/flocculation was performed by using synthesis materials and conventional cationic flocculant PEL for comparison. Secondly, the turbidity removal performances were primarily based on the characteristics of this physicochemical treatment method and the best condition selection was made accordingly. Finally, the values of other parameters and sludge properties are presented in the optimized condition.

- FSPS1 and one of its modifications, FSPS2, obtained by the use of foam PS in the sulfonation process of PS in the catalyzed medium, are more successful than others only in the treatment of PET and PP washing wastewater. In addition, two more successful syntheses selected for 6 types of wastewater are those derived from PET-applied sulfonation, which is similar to conventional FSPS and even has higher yields in some wastewaters. There are syntheses that show the same or even higher performance as the conventional flocculant PEL. For example, in PP wastewater treatment 69% turbidity was removed with PEL while the yield was 80% with FSPET1.

- FSPET3 whose final precipitation phase is carried out with NaOH in the synthesis process, is no more successful than any other treatment experiment. Synthesis materials FSPS2, FSPET1, and FSPET2 are successful in treatment if in the flocculant obtaining process Na_2CO_3 and $CaCO_3$ are used for precipitation after reaction completion. There is no significant difference in yield between the carbonate ion used in precipitation in Na or Ca form, but it is more advantageous as it provides synthesis when $CaCO_3$ is added in much lower amounts. Furthermore, when the commercial prices are compared, the two are priced close to each other, even $CaCO_3$ is cheaper.

- Syntheses precipitated with $Ca(OH)_2$ provide successful purification in both liquid and filtered, dried solid form. In fact, the efficiency of plastic washing wastewater where the liquid form is efficient is higher (82% in LDPE and PET wastewaters, 75-77% in others). When used in liquid form, it shows that during the production of this material, dewatering-drying process is eliminated and production wastewater is prevented.

- The WPWWs of all plastic types studied were treated with flocculants synthesized in this study at different levels. Moreover, synthesized flocculants have higher performance under the same conditions as their conventional counterparts, PEL.

- For each type of WPWW two synthesized flocculants were selected as more effective synthesized flocculants in the treatment. Among these two successful synthesized flocculant, the most effective one for each wastewater was selected according to turbidity removal. FSPET2 flocculant for HDPE and PS wastewaters, ASPET2 flocculant for LDPE and PET washing wastewaters and FSPET1 for PP and Mixed plastic wastewater were selected as the most successful flocculants. Dosage optimization was performed for selected flocculants.

- 50 mg L^{-1} dose of FSPET2 and pH 13.94 (initial pH) achieved the highest yield of turbidity and COD removal with 86% and 53% respectively in HDPE WPWW. TSS removal, yields are close to each other for all doses. In total, 50 mg L^{-1} dose was selected as the optimum dose for treating HDPE wastewater in coagulation/ flocculation process. The change of flocculant dose has no effect on the volume of sludge formed in the treatment of HDPE WPWW with FSPET2 flocculant. Low volume and high-density sludges were provided at pH9 with selected flocculant.

- Based on turbidity removal efficiency (77.4%), 40 mL L^{-1} dose of ASPET2 was chosen as the optimum dose for LDPE WPWW. According to turbidity and COD removal efficiencies, pH range 5-9 can be used for LDPE wastewater treatment, but a pH of 7 can be selected as optimum pH. The highest quality treatment sludge was provided at pH of 7-9.

- As a result, 30 mL L^{-1} dose of ASPET2 flocculant was determined as the optimum dose with 76.8% turbidity, 29% COD and 14% TSS removal efficiency in PET washing wastewater. The optimum pH was selected as 9 for this wastewater with 85% turbidity and 55% TSS removal efficiency. Sludges of optimum doses also have close volume and density and the highest quality treatment sludge was provided at pH of 7-9.

- The optimum dose of FSPET1 flocculant was selected as 30 mg L^{-1} with 73.7% turbidity, 33.9% COD and 37.3% TSS removal efficiency for PP WPWW. According to turbidity and COD removal, PP WPWW coagulation/flocculation process can be performed very efficiently between 7-9 pH. The optimal pH as the presenter of this study was chosen as 7. In PP and Mixed plastic WPWWs different doses of FSPET1 do not have much effect on sludge volume and density, but as the pH gets lower, the treatment efficiency declines and decreases the sludge volume and density.

- The removal efficiencies of turbidity, COD and TSS parameters are very close to each other at all concentrations of FSPET2 in PS WPWW. Thus, 10 mg L^{-1} was chosen as the optimum dose for PS WPWW. In PS WPWW turbidity and TSS removal are reduced when the pH is increased from 5 to 9, but the highest pH (initial pH) yields the highest efficiency. On the contrary, at higher pH value, COD removal efficiency decreased. Thus, optimum pH was initial pH for the coagulation/flocculation process at 10 mg L^{-1} of FSPET2 dosage.

- The highest COD removal (44.4%) was achieved at dose of 10 mg L^{-1} in Mixed plastic WPWW. The removal efficiency of the TSS parameter is almost similar (31.8-35.5%) in all doses except for 70 mg L^{-1}. Therefore, 10 mg L^{-1} was chosen as the optimum dose, both in terms of efficiency and economics. pH 9 was selected as optimal pH for Mixed plastic WPWW with 75.2% turbidity and 58% COD removal efficiency. In this WPWW like PP WPWW, different doses of FSPET1 do not have much effect on sludge volume and density, but as the pH gets lower, the treatment efficiency declines and decreases the sludge volume and density.

All optimum doses and pHs obtained from dose and pH optimization at six different WPWWs are compared. The highest turbidity removal was obtained at initial pH with a dose of 50 mg L^{-1} FSPET2 flocculant in HDPE WPWW and the highest COD and TSS removals were achieved in PS and PET WPWWs. PS and HDPE WPWWs treatment performances were high at the original pH, whereas LDPE and PP wastewater had the best treatment at pH 7, PET and mixed plastic wastewater had high treatment at pH 9. In the same type of plastic wastewater, the sludge properties obtained by each of the syntheses were similar but sludges obtained by PEL were different. The sludges of this treatment are easily settleable. The sludges from the treatment of all wastewaters have medium solids content, compared to active and pre-settled sludges. The sludges from all coagulation/flocculation treated wastewaters have better filterability in comparison to municipal sludges. The highest amount of Ca, Fe, Mg, Na and P in the sludge can be said to be the substances with the highest recovery potential from these treatment sludges. Other cations and especially heavy metals were not present at very high levels in the sludge and they can be considered not to harmful for soil.

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APPENDICES

Appendendix A

Table A1. Parameters in the treatment of WPWWs with two selected flocculants

Parameters	**HDPE WPWW**			**LDPE WPWW**			**PET WPWW**		
	Raw Wastewater	**FSPET2**	**ASPET1**	**Raw Wastewater**	**ASPET2**	**ASPET1**	**Raw Wastewater**	**FSPS2**	**ASPET2**
pH	13.94	13.08	13.12	13.76	13.1	13.09	13.87	13.2	13.16
Turbidity (NTU)	1664	232	231	560	102	139	883	199	158
TSS (mg/L)	2110	1760	1560	720	1080	1120	1090	1650	1780
COD (mg/L)	2202	1705	1604	768	802	602	3021	902	2306
B (mg/L)	0.243	0.335867	0.4676	0.466	0.66652	0.788429	0.139	0.179243	0.484187
Ca (mg/L)	3.950	3.83126	3.19362	1.688	2.19133	0.957393	8.020	3.10908	1.46252
Cd (mg/L)	0	0.001464	0.001001	0	0	0.000236	0	0.000932	0.000771
Co (mg/L)	0	0.002782	0.002016	0	0.000514	0.000047	0	0.001258	0.001702
Cr (mg/L)	2.008	0.017931	0.031144	0.653	0.04698	0.03051	0.160	0.012205	0.021092
Cu (mg/L)	0.133	0.082818	0.081549	0.079	0.078877	0.073638	0.089	0.083621	0.094216
Fe (mg/L)	5.599	3.02375	3.23019	0.659	0.925322	0.585173	1.109	0.891774	1.17427
K (mg/L)	34.850	33.2095	39.5379	73.163	55.6304	56.2264	27.484	25.4207	35.4097
Mg (mg/L)	0.203	0.083561	0.014331	0.077	0.137749	0.012973	0.042	0.01574	0.010875
Mn (mg/L)	0	0.012243	0.018954	0	0.009779	0.007717	0	0.21694	0.226748
Mo (mg/L)	0.554	0.009739	0.016635	0.178	0.041748	0.04026	0.035	0.005114	0.007926
Na (mg/L)	91.901	101.377	101.391	77.164	98.1371	95.6954	92.380	101.975	101.779
Ni (mg/L)	0.130	0.020547	0.035071	0.044	0.013124	0.005141	0.010	0.003754	0.005832
P (mg/L)	3.664	2.11449	4.02966	15.554	12.5027	13.427	2.842	2.2365	4.88087
Pb (mg/L)	0.044	0	0.13987	0.785	0.044219	0	0.189	0	0.05783
S (mg/L)	435.864	47.219	14.8542	38.298	194.123	43.1872	10.358	119.213	118.238
Se (mg/L)	0	0.02329	0	0	0	0.045593	0	0.035493	0.031826
Zn (mg/L)	0.822	0.650535	0.738175	0.322	0.47478	0.456988	0.377	0.692226	0.72984

Table A1 (Continued)

	PP WPWW			PS WPWW			Mixed plastic WPWW		
Parameters	**Raw Wastewater**	**FSPS1**	**FSPET1**	**Raw Wastewater**	**FSPET2**	**FSPET1**	**Raw Wastewater**	**FSPET1**	**ASPET1**
pH	13.75	13.21	13.24	13.69	13.23	13.22	13.67	13.13	13.11
Turbidity (NTU)	989	221	203	3323	637	650	1955	617	1091
TSS (mg/L)	1090	1660	1610	1550	1710	1880	1080	1650	1630
COD (mg/L)	2304	401	802	4864	2958	2507	2918	1103	1705
B (mg/L)	0.157	0.20949	0.226206	0.088	0.186969	0.255688	0.084	0.135534	0.266019
Ca (mg/L)	9.388	2.1836	2.39397	9.530	4.42572	4.01332	11.018	3.53357	2.39081
Cd (mg/L)	0	0.000113	0.000877	0	0.00063	0.000772	0	0.000417	0.00018
Co (mg/L)	0	0.001628	0	0	0	0	0	0.009507	0
Cr (mg/L)	0.156	0.015291	0.010323	0.120	0.03376	0.024958	0.090	0.018503	0.02208
Cu (mg/L)	0.050	0.05765	0.054823	0.011	0.03214	0.029134	0.052	0.037743	0.047717
Fe (mg/L)	1.537	1.15977	1.30556	14.061	8.44981	10.7735	4.833	4.49984	3.22065
K (mg/L)	25.563	25.4687	28.0392	92.371	65.6777	73.3642	66.346	56.3385	52.3846
Mg (mg/L)	0.044	0.007084	0.000974	0.134	0.054968	0.049049	0.057	0.020913	0.007016
Mn (mg/L)	0	0.051886	0.021156	0	0.027637	0.029693	0	0.03657	0.037753
Mo (mg/L)	0.033	0.008224	0.013681	0.027	0.008647	0.006523	0.043	0.020172	0.022213
Na (mg/L)	92.429	102.234	101.542	92.548	102.451	102.345	93.109	101.608	86.8758
Ni (mg/L)	0.013	0.00716	0.008848	0.062	0.024725	0.030897	0.049	0.030239	0.019816
P (mg/L)	2.333	2.09601	1.96178	16.351	12.6425	15.4448	11.994	11.4671	10.5808
Pb (mg/L)	0.074	0.052006	0.061363	0.000	0	0.059628	0.196	0.036273	0.018063
S (mg/L)	17.922	40.0826	16.8014	14.164	11.9413	11.9994	10.318	16.3619	11.9737
Se (mg/L)	0	0.01459	0.006179	0	0.002409	0.052845	0	0.001974	0.010497
Zn (mg/L)	0.361	0.790532	0.821662	1.232	1.35941	1.50591	0.486	0.856122	0.854493

Appendendix B

Results from dose optimization of six WPWW with selected effective flocculants.

Table B1. Analysis results obtained in determining the optimum dose of FSPET2 for HDPE WPWW (Initial Turbidity = 1597 NTU, Initial COD = 2310 mg L^{-1}, Initial TSS = 1560 mg L^{-1})

Flocculant Dose, mg L^{-1}	**Turbidity, NTU**	**COD, mg L^{-1}**	**TSS, mg L^{-1}**
10	254.7	1581	960
30	256.7	1216	900
50	232.0	1094	940
70	228.7	1216	910
90	234.7	1338	870

Table B2. Analysis results obtained in determining the optimum dose of ASPET2 for LDPE WPWW (Initial Turbidity = 645 NTU, Initial COD = 1354 mg L^{-1}, Initial TSS = 650 mg L^{-1})

Flocculant Dose, mg L^{-1}	**Turbidity, NTU**	**COD, mg L^{-1}**	**TSS, mg L^{-1}**
5	166.7	752	800
10	164.0	852	780
20	151.3	953	770
30	148.7	1053	800
40	146.0	1153	690
50	173.3	1203	770
60	182.0	1354	820
70	192.7	1454	840

Table B3. Analysis results obtained in determining the optimum dose of ASPET2 for PET WPWW (Initial Turbidity = 654 NTU, Initial COD = 2457 mg L^{-1}, Initial TSS = 1100 mg L^{-1})

Flocculant Dose, mg L^{-1}	**Turbidity, NTU**	**COD, mg L^{-1}**	**TSS, mg L^{-1}**
5	181.3	1905	920
10	164.7	1855	910
20	168.7	1755	880
30	151.3	1755	950
40	181.3	2055	860
50	158.7	2156	940
60	158.0	2356	1090
70	170.0	2356	1050

Table B4. Analysis results obtained in determining the optimum dose of FSPET1 for PP WPWW (Initial Turbidity = 763 NTU, Initial COD = 2030 mg L^{-1}, Initial TSS = 1340 mg L^{-1})

Flocculant Dose, mg L^{-1}	**Turbidity, NTU**	**COD, mg L^{-1}**	**TSS, mg L^{-1}**
10	202.0	1892	1040
30	200.7	1342	840
50	216.0	1410	880
70	217.3	1598	910
90	221.3	1479	860

Table B5. Analysis results obtained in determining the optimum dose of FSPET2 for PS WPWW (Initial Turbidity = 3240 NTU, Initial COD = 7661 mg L^{-1}, Initial TSS = 2020 mg L^{-1})

Flocculant Dose, mg L^{-1}	Turbidity, NTU	COD, mg L^{-1}	TSS, mg L^{-1}
10	522	4195	960
30	549	4195	840
50	549	4104	900
70	527	4195	830
90	540	4104	800

Table B6. Analysis results obtained in determining the optimum dose of FSPET1 for Mixed plastic WPWW (Initial Turbidity = 1245 NTU, Initial COD = 2167 mg L^{-1}, Initial TSS = 1070 mg L^{-1})

Flocculant Dose, mg L^{-1}	Turbidity, NTU	COD, mg L^{-1}	TSS, mg L^{-1}
10	332	1204	730
30	323	1892	710
50	347	1754	710
70	357	1892	820
90	421	1479	690

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English

YAYINLAR

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