T.R.
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TREATMENT OF PRE-TREATED REAL TEXTILE INDUSTRY WASTEWATER BY HYBRID PROCESS IN THE PRESENCE OF WALNUT SHELL AND CORNCOB BASED MATERIALS

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Sırma BENER tarafından yüksek lisans tezi olarak sunulan "Önceden İşlem Görmüş Gerçek Tekstil Endüstrisi Atık Suyunun Ceviz Kabuğu ve Mısır Koçanı Esaslı Malzemelerin Varlığında Hibrit Yöntemi ile Arıtımı-Treatment of Pre-treated Real Textile Industry Wastewater by Hybrid Process in the Presence of Walnut Shell and Corncob Based Materials" başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 05/07/2019 tarihinde yapılan tez savunma sınavında aday oybirliği/~~oyçokluğu~~ ile başarılı bulunmuştur.

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ÖZET

ÖNCEDEN İŞLEM GÖRMÜŞ GERÇEK TEKSTİL ENDÜSTRİSİ ATIK SUYUNUN CEVİZ KABUĞU VE MISIR KOÇANI ESASLI MALZEMELERİN VARLIĞINDA HİBRİT YÖNTEMİ İLE ARITIMI

BENER, Sırma

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Bu çalışmada yerinde ön arıtıma tabi tutulmuş gerçek tekstil endüstrisi atıksuyunun sulama suyu olarak yeniden kullanılabilmesi için çevre dostu, sürdürülebilir ve yenilikçi bir arıtım süreci test edilmiştir. Bu amaç doğrultusunda, birden fazla yöntem sırasıyla elektrokoagülasyon, adsorpsiyon, foto-Fenton benzeri ileri oksidasyon yöntemi ve mikrobiyal yakıt hücresi ardışık bir şekilde incelenmiştir. Elektrokoagülasyon yönteminde, alüminyum ve demir olmak üzere, iki farklı elektrot malzemesi test edilmiştir. Al elektrotların daha yüksek toplam organik karbon giderimi sağladığı tespit edilmiştir. Adsorpsiyon yönteminde aktif karbon yapımında tarımsal atık olan mısır koçanı ve ceviz kabuğu kullanılmıştır. Çalışmanın üçüncü basamağı olan Foto-Fenton benzeri ileri oksidasyon yönteminde en iyi sonuçlar mısır koçanı destek malzemeli $BiNiO_3$ katalizörü ile elde edilmiştir. Hibrit prosesin son adımı olan mikrobiyal yakıt hücresi ile yapılan deneylerin sonuçları incelendiğinde, bu son basamağın çok fazla etkili olmadığı sonucuna varılmıştır. Hibrit proses sonunda %87 oranında Toplam Organik Karbon, %49 Kimyasal Oksijen İhtiyacı, %96 bulanıklılık, yaklaşık %90 civarında renk ve %95-97 civarında askıda katı madde giderimi sağlanmıştır. Sulama suyu standartları kimyasal oksijen ihtiyacı ve tuzluluk hariç sağlanmıştır. Katalizör ve adsorbent yapımında tarımsal atıklar yenilikçi, çevre dostu ve ekonomik malzemeler olarak teşvik edilmiştir.

Anahtar Sözcükler: Tekstil atıksuyu arıtımı, hibrit proses, mısır koçanı, ceviz kabuğu.

ABSTRACT

TREATMENT OF PRE-TREATED REAL TEXTILE INDUSTRY WASTEWATER BY HYBRID PROCESS IN THE PRESENCE OF WALNUT SHELL AND CORNCOB BASED MATERIALS

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In this study, an eco-friendly, sustainable and innovative treatment methodology was investigated for the treatment of pre-treated wastewater of textile industry. In this purpose, more than one methods were tested as a hybrid process. This study includes electrocoagulation, adsorption, photo-Fenton-like advanced oxidation method and microbial fuel cell methods, respectively. Two different electrode materials, including aluminum and iron, were tested for electrocoagulation method and Al electrode was found to provide higher total organic carbon removal. In addition, the method has resulted in turbidity, color and suspension removal. In the adsorption method, corncob and walnut shell were used as agricultural wastes for preparation of the actvated carbon. The $BiNiO_3$ catalyst with corn cob support material was effective for the photo-Fenton like oxidation method. Microbial fuel cell, which is the last step of the process, is found not be very effective. At the end of the hybrid process, 87% total organic carbon, 49% chemical oxygen demand, 96% turbidity, approximately 90% color and 95-97% suspended solids removal were achieved. The hybrid sytem was effective to achieve the irrigation water standards except for salinity and chemical oxygen demand. Agricultural wastes used in catalysts and adsorbents was promoted to be innovative, environmentally friendly and economical.

Keywords: Treatment of textile wastewater, hybrid process, corncob, walnut shell.

PREFACE

In this study, the reusability of real pretreated textile wastewater as irrigation water was investigated. The main objective is to determine an innovative, environmental, economic and sustainable treatment system for textile wastewater reuse.

The thesis is a part of the project which is in the frame of the joint transnational research call of ERANETMED funded by the European Commission’s 7th Framework Programme. The research project (acronym: SETPROpER) on waste water treatment technology and re-use in agriculture accounting for public health, land management and environment has been financially supported by Scientific and Technological Research Council of Turkey (Project Number: 315M537-ERANETMED –SETPROpER Project).

I would like to acknowledge SUN Textile for providing the wastewater.

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1. INTRODUCTION

Fresh water and groundwater becomes an increasingly limited resource because of the increasing of water pollution, and hence industries drawn attention to reusability technologies (Ribeiro et al., 2017). Reusability of wastewater is important point for the water supply for the future. The treated water can be used in many applications such as irrigation, industry and urban (Akhoundi and Nazif, 2018).

Textile macufacturing is a major industry. It is based on a process that uses many dyes and various chemicals, and during this process water consumption is a very high and due to these different chemicals, its wastewater has various kinds of pollutans by comparison with other industries. Also, some reports indicate that it contributes to 20% of the fresh water pollution (Haddad et al., 2018). Dyes, surfactants, solvents and other organic compounds are the most commonly used chemicals found in textile wastewaters. As a result of the presence of these chemicals, textile wastewater has high chemical oxygen demand (COD) value, total organic carbon (TOC) value, and also low biodegradability (GilPavas et al., 2017; Bisschops and Spanjers, 2003; Al-Kdası et al., 2004) and hence the treatment of the textile wastewater is not easy. Although different treatment methods can be applied for the removal of textile wastewater, each method may not be suitable treatment depending on the quality of the wastewater. Finding the appropriate method is an important approach for the efficiency of the treatment. The selected methods should be economically feasible and their impact on the environment should also be considered.

Electrocoagulation is an environmentally friendly process since the electrodes are used as the coagulants, so no other chemicals are required and also it is an inexpensive method which is very effective for the treatment of various types of pollutants, organics, dyes, and heavy metals (Khandegar and Saroha, 2013; Naje et al., 2015). Electrocoagulation is based on the formation of metal hydroxide flocs in the wastewater by dissolition of the electrode materials as anode. Electrocoagulation combines the coagulation, flocculation, and electrochemistry processes at the same time without using any chemicals. In electrocoagulation process, when the repulsive forces are neutralized, the collodial particles will destabilize and form larger particles. Neutralizing the repulsive forces is the main idea for the removal of pollutants in the wastewater and hence the particles keep suspended in water (Moussa et al., 2017).

Adsorption process attracts attention due to its high removal efficiencies and it is very effective method for the treatment of wastewater. The efficiency of the treatment is mainly related to the type of adsorbent. Clay, biomaterials, activated carbon, zeolites, and some solid wastes can be used as adsorbents for the removal of the organics in the wastewater (Wang and Peng, 2010). Especially, the activated carbon is the most preferred adsorbent due to the porous structure, pore volume, and high adsorption capacity. Although activated carbon is very effective, because of the high cost of it there are some limitations for the applications. In recent years, agricultural wastes were examined for the production of activated carbon such as fruit wastes, coconut shell, sawdust, corncob, rice husk, orange peel, tea/coffee residues, oil palm shell, sawdust, and nuts (Ghasemi et al., 2014; Bhatnagar et al., 2015; Ali et al., 2016; Crini et al., 2018).

Advanced oxidation methods include many different processes such as Fenton/Fenton-like oxidation, photo-Fenton oxidation, catalytic wet air oxidation, and ozonation. In Fenton reactions, the iron catalyst is used to decompose the peroxide and convert it into highly reactive hydroxyl radicals. High removal performance, moderate operating conditions such as low temperature and low pressure, and non toxic properties are the main advantages of this process. Due to the these advantages of process, Fenton process is applied for many industrial wastewater treatment such as olive-oil mill wastewater, pharmaceutical wastewater, textile wastewater, cosmetic wastewater, etc. (Cheng et al., 2016; Wang et al., 2016). In recent years, the mechanism of Fenton process has been widely used in many wastewater treatment research such as; a) Homogenous Fenton and Fenton-like system using different kinds of Fe(II) and/or Fe(III) salts, b) Heterogenous Fenton and Fenton-Like system using different kinds of catalysts, and c) Introduction an UV irradiation. Generally, heterogeneous process is preferred because of the high removal efficiencs and applicability at wider pH range (Pouran et al., 2014).

Recently, the use of perovskite-type metal oxides has become increasingly widespread in different subjects. In particular, its popularity as a heterogeneous catalyst is gradually increasing due to their chemical structure, usage of perovskite type catalysts is important in heterogeneous fenton-like process with their good stability and narrow band gap properties (Lin et al., 2017; Lam et al., 2017).

The use of microbial fuel cells (MFCs) for the treatment of wastewater is considered to be an environmentally friendly, novel, and sustainable technology. In this method, electricity production can be obtained while wastewater is treated (Gude, 2016). In the microbial fuel cell, electricity is generated by the microorganisms used in the anode compartment (Rahimnejad et al., 2015). There are some methods that electrons and their energy can be converted into forms that people can use with the help of the microorganisms (methanogenesis to CH_4, biohydrogen to H_2, MFCs). MFCs have more advantages because of the their ability to directly produce electric energy from organic subtances in wastewater (Lee et al., 2008; Li et al., 2014).

Reuse of wastewater can be considered in four different categories. These are agricultural irrigation, urban, industrial cooling water, and finally combinations of these options. In Turkey, the potential of reusability of wastewater is too high but reclamation of wastewater is not so much. Although agriculture has an important role for economy, a detailed study for the use of wastewater for irrigation has not been considered (Maryam and Büyükgüngör, 2017). Countries can be divided three categories according to the their water volume per capita year. Poor; if this value is less than 1000m^3/capita-year, insufficienct; if less than 2000m^3/capita-year and rich; 8000-10000m^3/capita-year. Today, the water per capita year is 1500m^3 and according to the studies it will decrease to 1120-1000m^3 in 2030, Turkey. Water scarcity constitutes a danger for future not only for Turkey, but for all countries of the world (Arslan-Alaton et al., 2011).

The main objective of this study is to develop an eco-friendly, sustainable and innovative treatment methodology for the treatment of the pre-treated wastewater of textile industry. For this purpose a hybrid process is applied to textile pre-treated wastewater including electrocoagulation, adsorption, and photo-Fenton like oxidation methods. The study mainly focused on the removal of total organic carbon. In addition, chemical oxygen demand, color, turbidity, total dissolved solid, and conductivity were analyzed. The other important point is to obtain high removal efficiencies by reducing the cost of hybrid process by using low-cost materials and minimize the use of chemicals and develop an eco-friendly catalyst. Because of this reason, corncob and walnutshell were used for preparation of activated carbon and catalyst supports. The results of the experiments were compared to the requirements for irrigation reuse.

This study is a part of a project which is in the frame of the joint transnational research call of ERANETMED funded by the European Commission's 7th Framework Programme. It is an innovative research project (acronym: SETPROpER) on waste water treatment technology and re-use in agriculture accounting for public health, land management and environment. This study has been financially supported by Scientific and Technological Research Council of Turkey (Project Number: 315M537-ERANETMED –SETPROpER Project). In the frame of the Project, The Life Cycle Assessment (LCA) was performed to evaluate the project in terms of economic, social, and environmental aspects.

2. THEORETICAL BACKGROUND

2.1 Industrial Wastewater

The environmental pollution is gradually increasing as a result of the increasing human population and industrialization. Industrial wastewater is one of the major environmental pollutants. Most of these waters are charged into the rivers with their toxic chemicals without a sufficient treatment (Lakherwal, 2014). The characteristic properties of industrial wastewater are different for each sector. Textile industry, food industry, paper plants, chemical and fertilizer plants, petrochemical industries are the major industries which generate large amount of wastewater (Sonune and Ghate, 2004).

With the increase of industrialization, industrial processes cause serious health problems for humans. Each year, nearly 300 million ton heavy metals, chemical toxic wastes, and dyes and other wastes are released to waters (Xiao et al., 2015). It is reported that approximately 40% of the population in the world has a water shortage and more than 25% of the population has health problems (Pera-Titus et al., 2004). Because of these reasons the requirement of fresh water (for irrigation, urban, etc.) is increasing day by day. Nearly 7.1 billion m^3 / year of water is reused in the world and about half of the reused water is used for irrigation and 20% is used for industrial purposes. Wastewater treatment and reuse have many advantages both economically and environmentally. Wastewater treatment greatly reduces the pollution of water resources and provides more options for irrigation water (Vergine et al., 2017).

2.2 Textile Wastewater

The textile industry has a complex process and large amount of chemical substances are used during the production process. Dyes, surfactants, solvents and other organic compounds can be given as examples of these chemicals. As a result of these chemicals used, textile wastewater is high in chemical oxygen demand (COD) and total organic carbon (TOC) values and also low biological degradation (GilPavas et al., 2017). Textile processing has different steps and generally in each step wastewater is generated (Bisschops and Spanjers, 2003). The main pollution caused by textile wastewater comes from the painting and finishing steps. The chemicals used in these operations are generally complex organic compounds and cause serious problems in terms of environment and human health (Al-Kdası et al., 2004; Djehaf et al, 2017). The list of the some pollutants which are generated at each level of textile processing is given in Figure 2.1 (Holkar et al., 2016).

Desizing	• enzyme , starch, waxes
Scouring	• NaOH, surfactants, soaps ,fats ,oils
Bleaching	• H_2O_2 sodium silicate, organic stabilizer, alkaline pH
Dyeing	• colour, metals, salts, surfactant, alkaline/acidic
Printing	• colour, metals, urea, formaldehyde, solvents
Finishing	• softner, solvents, resins, waxes

Figure 2.1. Pollutants for each level of textile wet processing

An important environmental problem for the textile sector is that there is a lot of water consumption. Approximately 100-200 liters of water is consumed per kg of textile products (Lotito et al., 2014).

During the production of textile products, because of many different chemicals and dyes used, wastewater treatment is not easy and due to these different chemicals the characteristic of textile wastewater is very wide. General properties of textile wastewater are given in Table 2.1 (Vajnhandl and Valh, 2014; Kehinde and Aziz, 2014; Bisschops and Spanjers, 2003). Because of all of these reasons, it is certainly necessary to treat these wastewaters before discharging to the environment.

Table 2.1. Characteristic properties of textile wastewater

Parameters	Values
Temperature (°C)	21-62
pH	2-13
Conductivity (mS/cm)	0.1-120
Total organic carbon (mg/l)	250-5800
Chemical oxygen demand (mg/l)	110-60000
Biological oxygen demand (mg/l)	200-60000
Total suspended solid (mg/l)	18-9500
Total Dissolved Solids (mg/L)	55-19000
Total Kjeldahl Nitrogen (mg/L)	70-80
Turbidity (NTU)	0-200
Sulphide mg/L)	0.2-900
Oil and grease (mg/l)	5-5500

2.2.1 Treatment of textile wastewater

The textile wastewater includes many organic substances, dyes, and additives. These substances cause many serious health and environmental problems. Many treatment processes are tested including chemical, physical, biochemical, and also hybrid treatment (Babaei et al., 2017, Holkar et al., 2016). Physical, chemical, and biological methods are accepted as conventional methods. For physical treatment; sedimentation, screening, aeration, filtration, flotation and degasification; for chemical treatment; neutralization, coagulation, adsorption and for biological treatment; activated sludge trickling filtration, aerobic and anaerobic digestion, septic tanks can be given as example processes. Table 2.2 summarizes the methods which can be used generally for the treatment of textile industry wastewater (Kehinde and Aziz, 2014; Holkar et al., 2016; Chandran, 2016).

Table 2.2. Treatment methods for textile wastewater

Conventional methods	
Pyhsical methods	Membrane filtration
	Adsorption*
	Ion exchange
	Sedimentation
	Screening
	Aeration
Chemical/Electrochemical methods	Coagulation/flocculation
	Electrocoagulation
	Neutralization
	Chlorination
Biological methods	Aerobic, Anaerobic, Biofilmbased, Fungal Metabolic activities.
Oxidation Methods	Advanced Oxidation (UV (Photochemical), H_2O_2, Ozonation based Processes)

* Adsorption can be pyhsical or chemical method due to the forces between adsorbent and adsorbate.

2.3 Electrocoagulation

Electrocoagulation (EC) method is an effective method for destabilizing small colloidal particles. Simple equipment is enough for this process and there is no volume limitation. The electrodes are used as the coagulants, so no other extra chemicals are required. It is an environmentally friendly process with low cost (Khandegar and Saroha, 2013). In the electrocoagulation process, usually aluminum or iron electrodes are used as coagulant because the adsorption capacities of the metal hydroxides such as $Al(OH)_3$, $Fe(OH)_2$ and $Fe(OH)_3$ are very high (Kabdaşlı et al., 2012).

The EC process can be summarized in three steps (Mollah et al., 2001; Ozyonar and Karagözoglu, 2012);

I. **Dissolution;** Electrolytic reactions at electrode surfaces,

II. **Coagulation;** Formation of coagulants in aqueous phase,

III. **Flocculation;** Adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation.

EC is based on the formation of metal hydroxide flocs in the wastewater by dissolving anodes with the applied current (Ozyonar and Karagozoğlu, 2012). Electrocoagulation stabilizes suspended solids and colloidal materials. Therefore, when the particles are properly contacted with the electrodes in electrical applications, the particles are neutralized and the different particles combine to form large flocs (Mollah et al., 2001).

The most important chemical reaction is the dissolution of anode material for the electrocoagulation. The metallic anode dissociated into metallic ions and releases electrons (Reaction 1). At the same time, simultaneously hydrogen gas and hydroxyl ion (OH^-) are degraded at the cathode (Reaction 2) (An et al., 2017).

$$M \rightarrow M^{+} + ne- \qquad (1)$$

$$nH_2O + ne^- \rightarrow (n/2)\ H_{2\ (g)} + nOH^-_{\ (aq)} \qquad (2)$$

Finally, the metallic ions formed in the anode combines with the hydroxide generated at the cathode generated metallic hydroxide which are good adsorbents (Reaction 3).

$$M^{+n} + OH^- \rightarrow M(OH)_2 / M(OH)_3 / M(OH)_n \qquad (3)$$

In the following Figure 2.2, electrocoagulation mechanism is shown with all reactions;

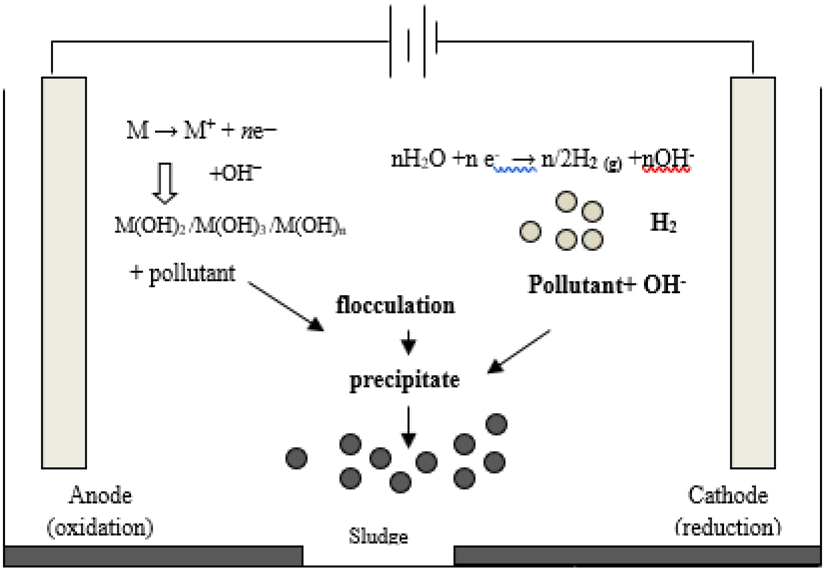


Figure 2.2. Electrocoagulation mechanism (Nidheesh et al., 2017)

Electrode type is an important parameter for the processes. The most widely used electrode materials in electrocoagulation process are aluminum and iron (Siringi et al., 2012; Zhang et al., 2016; Tezcan et al., 2014). Different reactions occur for different type of electrode and properties of the metal hydroxides which formed during reactions are important for the efficiency of electrocoagulation process.

Reactions for Al Electrode;

The electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as Al^{3+} and $Al(OH)^{2+}$ at low pH, which at appropriate pH values are transformed initially into $Al(OH)_3$ and finally polymerized to $Al_n(OH)_{3n}$ (Reactions 4, 5, and 6) (Mollah et al., 2001):

- Anode:

$$Al \rightarrow Al^{+3}\,(aq) + 3e^- \qquad (4)$$

- Cathode:

$$3H_2O + 3e \rightarrow 3/2\ H_2 + 3OH^- \qquad (5)$$

- Overall:

Al^{+3} (aq) + $3H_2O \rightarrow Al(OH)_3 + 3H^+$ (aq) [sweep floc $Al(OH)_3$] can be polymerized and adsorb pollutants rapidly.

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \qquad (6)$$

However, depending on the pH of the aqueous medium other ionic species, such as $Al(OH)^{2+,}$ $Al_2(OH)_2\ ^{4+}$ and $Al(OH)^{4\ -}$ may also be present in the prosess (Siringi et al., 2012).

Reactions for Fe Electrode;

Iron upon oxidation in an electrolytic system produces iron hydroxide, Fe $(OH)_n$, where n = 2 or 3. Two mechanisms have been proposed for the production of Fe(OH)n (Ni'am et al., 2007). All of the reactions for both mechanisms are summarized in Table 2.3.

Table 2.3. Reaction for iron electrode

Mechanism 1:	**Mechanism 2:**
Anode	
$4Fe \rightarrow 4Fe^{+2}(aq) + 8e-$ $4Fe^{+2}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 8\ H^+(aq)$	$Fe(s) \rightarrow Fe^{+2}(aq) + 2e-$ $Fe^{+2}(aq)+OH^-(aq) \rightarrow Fe(OH)_2(s)+8H^+(aq)$
Cathode	
$8\ H^+(aq) + 8e^- \rightarrow 4\ H_2(g)$	$2H_2O(l) + 2e^- \rightarrow H_2(g)+2OH^-(aq)$
Overall	
$4Fe^{+2}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s)$	$Fe(s)+2H_2O(l) \rightarrow Fe(OH)_2(s)+ H_2(g)$

There are many parameters affecting the elcetrocoagulation process. Current density, pH, electrode materials and the electrode connection modes. Optimization of current density is the important parameter for the treatment efficiency. Also cost of treatment is directly related with the current density. Cost of system can increase if excessive current density is applied or sludge formation increases in parallel with current density. The effects of pH of electrocoagulation is related to the solubility of metal hydroxides. Generally aluminium and iron electrodes prefer for the electrocoagulation method and for Al electrode generally acidic medium pH <6, while iron electrode neutral and alkaline medium, between 6 <pH <9 is more suitable for the treatment efficiency (Zodi et al., 2009; Chen, 2004; Kobya et al., 2003).

2.4 Adsorption

The basis of the adsorption process is the separation of contaminants from water by accumulating on a solid surface. Adsorption process is generally uses to remove substances from fluid phase. There are two important terms in the adsorption process, adsorbate and adsorbent. Adsorbent can be expressed as the solid material that provides the surface for adsorption and adsorbate is the species that will be adsorbed (Worch, 2012). The main advantages of adsorption process are, easy design, non-toxicity, non-harmful sludge formation when compared the some other treatment methods (Aljeboree et al., 2017).

Adsorption can be divided in two part, physical (physisorption) and chemical adsorption(chemisorption). These groups are determined by the depending on forces between adsorbent and adsorbate. Adsorption occurs due to the weak van der Waals forces, it is called physical adsorption. If the force of attraction existing chemical bonding between adsorbent and adsorbate molecule this type of adsorption known as chemisorption (Bhatnagar and Sillanpää, 2010).

There are many adsorbent types in the adsorption process, mainly activated carbons, zeolites, clay minerals, industrial solid waste, and biomaterials (Burakov et al., 2018). Beause of high adsorption capacity and large surface area activated carbon is generally used as adsorbent. Although the most preferred adsorbent is activated carbon, because of the high cost materials used in preparation of activated carbon causes limitations in the use of it (bituminous coal, lignite and petroleum coke) (Utomo and Salim, 2007; Saygılı and Güzel, 2016; Kamaruddin et al., 2013).

Because of these reasons the production of active carbon using environmental-friendly and low cost materials such as agricultural wastes become more popular. Rice husk, orange peels, coffe husk, sawdust, hazelnut husk corncob waste, etc., are mostly used as low-cost adsorbents (Rafatullah et al.,2010; Worch, 2012 ; Abas et al., 2013; Alqaragully, 2014).

Activated carbons are prepared by physical or chemical activation. Pyhsical activation is occured by using a reactant gas, such as steam and CO_2 at high temperature. In chemical activation, KOH, NaOH, K_2CO_3, $ZnCl_2$, $FeCl_3$, H_3PO_4, and H_2SO_4 are used generally as activating agent at low temperature. Chemical activation is generally preferred because the activated carbon which chemically activated has higher carbon yield. Since the chemical substances reduce the production of other volatile substances and tar formation is prevented (Yang and Qiu, 2010; Huang et al., 2015).

There are many parameters that affect the adsorption efficiency. The nature of the adsorbents, contact time, adsorbent dosage, pH, speed of stirring, temperature are the main factors affecting the treatment efficiency (Janyasuthiwong et al., 2015; Fu et al., 2015; Saleh et al., 2017).

Adsorption isotherms show the relationship between equilibrium concentration of adsorbate and the adsorbed amount of adsorbent surface. This relationship is expressed by various empirical isotherm equations (Nanta et al., 2018). Different models are developed for the adsorption isotherms like Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, etc. (Nanta et al., 2018; Vuono et al., 2017).

The Langmuir isotherm is the model which shows the equilibrium between the amount of solute adsorbed per unit mass of adsorbent and the solute remaining in the solution at low surface coverage (Nanta et al., 2018). There are some accepted assumptions in the Langmuir model (Belhachemi and Addoun, 2011). These are;

- Adsorbent surface is uniform
- No interaction between molecules adsorbed on adjacent site,

- Each site can hold at most one molecule (monolayer coverage)
- Adsorbed molecule and desorbed molecule exist in equilibrium

The nonlinear model for langmuir isotherm is given in Equation 1;

$$q_e = \frac{q_L * b * C_e}{1 + b * C_e} \qquad (1)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), b is Langmuir equilibrium constant (L/mg) and q_L is maximum monolayer adsorption (mg/ g). This equation can be linearized as Equation 2;

$$\frac{1}{q_e} = \frac{1}{b * C_e * q_L} + \frac{1}{q_L} \qquad (2)$$

If the adsorption model is Langmuir isotherm the plot of $1/q_e$ versus $1/C_e$ should be straight line whose slope and intercept are used to determine values of Langmuir constants q_L and b (Nanta et al., 2018).

Freundlich isotherm is suitable for both monolayer and multilayer adsorption. The model assumes that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. The Freuncdlich equation is expressed in Equation 3;

$$q_e = K_f * C_e^{\frac{1}{n_f}} \qquad (3)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), K_F is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g), and $1/n_F$ is the heterogeneity factor (Belhachemi and Addoun, 2011). The linearization form of this equation is given Equation 4;

$$lnq_e = lnK_f + \frac{1}{n_f} * lnC_e \qquad (4)$$

The Temkin isotherm describes the the effect of indirect interactions between adsorbent and adsorbate on adsorption. The Temkin theory assumes that adsorption temperature is considered to decrease with the coverage area. The heat of adsorption of the molecules in decrease linearly with coverage. The Temkin equation is expressed in Equation 5;

$$q_e = \frac{R*T}{B} ln(K_T C_e) \qquad (5)$$

where, R is the gas constant (8.314 J/molK), K_T is the Temkin isotherm equilibrium binding constant (L/mg) and B (J mol-1) is the Temkin constant and T is the temperature (K) (Dada et al., 2012). The linearization form of this equation is given Equation 6;

$$q_e = \frac{R*T}{B} * lnK_T + \frac{R*T}{B} * lnC_e \qquad (6)$$

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well. The nonlinear equation of the Temkin isotherm is expressed in Equation 7;

$$q_e = q_s e^{-K_{ad}{}^{\varepsilon^2}} \qquad (7)$$

$$\varepsilon = RT * \ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

Where R, T and q_e is represent the gas constant (8.314 J/mol K), temperature (K) and adsorbate equilibrium concentration (mg/L), respectively and where q_s adsorption capacity (mg/g) and K_{ad} (mol^2/kJ^2) is the Dubinin–Radushkevich isotherm constant and ε is the Polanyi potential (Vijayaraghavan et al., 2006). The linearization form of this equation is given in Equation 9;

$$\ln q_e = \ln q_s - K_{ad}\epsilon^2 \qquad (9)$$

2.5 Advanced Oxidation Processes

Advanced oxidation processes are useful methods for the treatment of wastewaters containing organic substances. Although these methods involve different reactions, the main purpose is to ensure that the organic compounds are oxidized to inorganic ions and carbon dioxide by the production of reactive hydroxyl radicals. Examples of such processes include ozonation, cavitation, fenton reactions, and photocatalytic oxidation (Deng and Zhao, 2015; Blanco et al., 2014; Wang and Xu, 2012). The resulting hydroxyl radicals have a high oxidation potential, except for fluorine, when compared to other oxidizers like sulfate radicals, chlorine, permanganate, persulfate anion, hydrogen peroxide. The basic properties of the hydroxyl radicals formed are short-lived, easy to produce and not selective (Boczkaj and Fernandes, 2017). When it reacts with the organic compounds main reaction is as follow;

$$\text{organic species} + \bullet HO \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} + \text{inorganic species}$$

AOPs involve many effective oxidative agents to treat water such as ultraviolet (UV) radiation, ozone (O_3), hydrogen peroxide (H_2O_2), and oxygen (O_2).. Common AOPs are the Fenton process, ozonation, catalytic wet peroxide oxidation, heterogeneous photocatalysis, catalytic wet air oxidation, electrochemical oxidation or even the combination of some of them (Ribeiro et al., 2015).

2.5.1 Fenton - photo Fenton/like oxidation

Fenton systems are the most commonly used method in advanced oxidation methods. In addition to classical Fenton, there are three Fenton based processes which Photo-Fenton and photo-Fenton like, and electro-Fenton systems (Ribeiro et al., 2015).

The classical Fenton reaction includes the activation of hydrogen peroxide (H_2O_2) by ferrous (Fe^{2+}) ions to generate hydroxyl radicals (•HO) over a complex reaction sequence (Bokare and Choi, 2014).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet HO + OH^{-} \quad (7)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet HO_2 + H^{+} \quad (8)$$

$$\bullet HO + H_2O_2 \rightarrow \bullet HO_2 + H_2O \quad (9)$$

$$\bullet HO + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (10)$$

$$Fe^{3+} + \bullet HO_2 \rightarrow Fe^{2+} + O_2H^{+} \quad (11)$$

$$Fe^{2+} + \bullet HO_2 + H+ \rightarrow Fe^{3+} + H_2O_2 \quad (12)$$

$$2 \bullet HO_2 \rightarrow H_2O_2 + O_2 \quad (13)$$

•HO is generated from reaction 1 through electron transfer. However, the produced •HO can be scavenged by both of Fenton reagents as shown in reaction 2 and 3. So that the molar ratio of iron ion to hydrogen peroxide should be determined correctly to decrease of undesirable scavenged (Deng and Zhao, 2015). Also, hydroxyl radicals can react with hydrogen peroxide to produce other radicals like Eq. 3 (Malik and Saha, 2003).

When compared the photo-Fenton and Fenton like oxidation, photo- Fenton process is the same as the Fenton process, it takes place in presence of UV light or visible light. (Sreeja and Sosamony, 2016). For Fenton-like oxidation, regarding Fe other transition metals can be used to produces hydroxyl radicals from hydrogen peroxide (Krishnan et al., 2017).

When the reaction occurs in the presence of light, more hydroxyl radicals consists when compared the Fenton process. These more hydroxyl radicals cause of the increasing the rate of the degradation of organic compounds due to the photoreduction of Fe(III) to Fe(II) ions (Primo et al., 2008; Perez et al., 2002). The reactions of Photo-Fenton process are given in reactions 14 and 15 (Bakare and Choi, 2014; Pouran et al., 2015);

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + \bullet HO + H^{+} \quad (14)$$

$$H_2O_2 + hv \rightarrow 2 \bullet HO \quad (15)$$

Fenton like process can be investigated in two groups in terms of the physical situation of the catalyst; homogeneous and heterogeneous processes. The main advantages of heterogeneous Fenton process are oxidizing a many type of organic pollutants at different pH with rapidly and non-selectively when compared the homogeneous processes (Phan et al., 2018; Herney-Ramirez et al., 2010).

2.5.2 Perovskite-type catalyst

In heterogeneous system perovskite-type oxides catalyts (ABO_3) are important heterogeneous catalysts in industrial reactions. Perovskite-type oxides with the general elemental composition of ABO_3, where A is a rare earth metal and B a transition metal (Rusevova et al., 2014). Perovskite-type oxides have a cubical crystal structure. A-type atoms are located on the corners of cubical structure, smaller cations B sitting in the body center, and oxygen atoms in the face center. (Pradhan and Roy, 2013; Labhasetwar et al., 2015). The Structure of Perovskite is given in Figure 2.3. Due to the its structure, perovskites type catalyts are very effective for the removal of organic pollutants by narrow band gap and good stability.

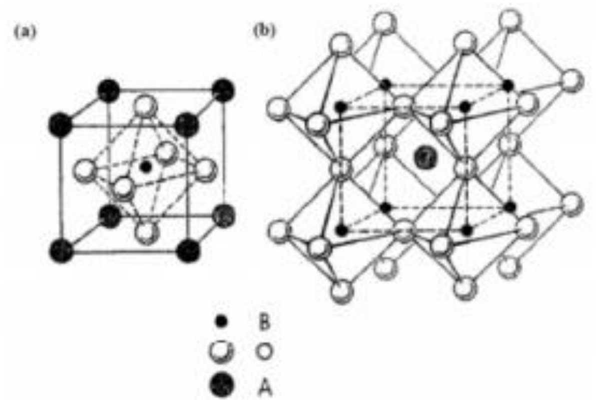


Figure 2.3. Structure of perovskite (Pradkonwarhan and Roy, 2013)

2.6 Microbial Fuel Cell

Microbial fuel cells (MFCs) are systems which use bacteria as the catalysts to oxidize organic and inorganic matter and generate current (Logan et al., 2006). MFC system includes two chamber, anode and cathode. In anode, the organic compounds are oxidized by bacteria to carbondioxide and at the same time electrons and protons can be generated. The electrons generated by oxidation is transffered to the cathode with external circuit (Solanki et al., 2013; He et al., 2017).

MFCs are similar to any fuel cell with properties of two electrodes connected through an electrical wire. The difference is that the MFCs use organic substrate as a fuel on the anode side to generate electricity (Oliveira et al., 2013). Various substrates can be used for electricity production in MFCs systems such as acetate, glucose, ethanol, cellulose and chitin as particule substrates. In the most studies of the literature, acetate is used as substrate because of the carbon source to induce electroactive bacteria (Pant et al., 2010). When acetate is used as substrate the following reactions occurs (Darus, 2011);

Anode: $2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O$ (16)

Cathode : $8H_2O + 8e^- \rightarrow 8OH^- + 4H_2$ (17)

Overall: $CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + H^+ + 4H_2$ (18)

The general schematic diagram of two chamber microbial fuell cell system is given in Figure 2.4.

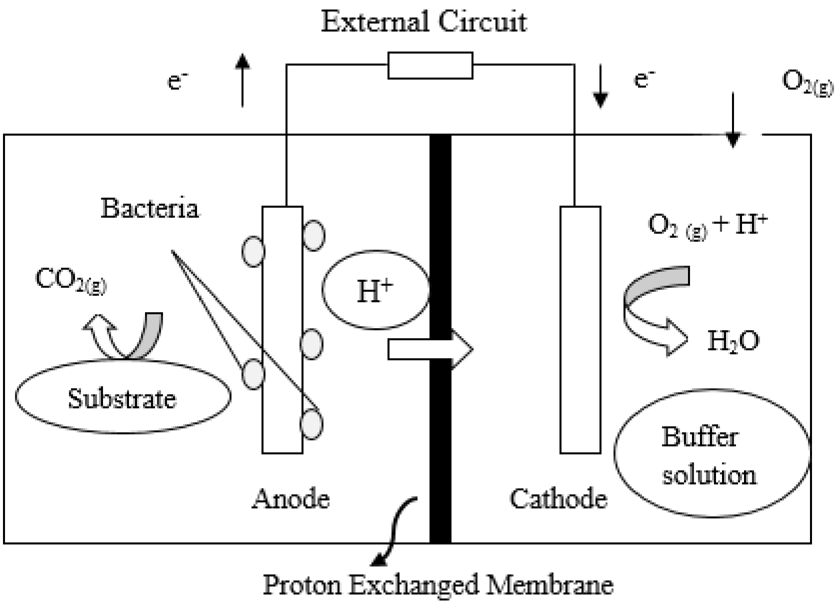


Figure 2.4. Two chamber microbial fuel cell

2.7 Irrigation Water Quality in Turkey

Agricultural sector has an important role in the economy of Turkey. The water usage for agricultural purposes is quite high. According to the researches, 42000 m^3 of water was spent in 2000 for irrigation purposes and as a semi-arid country, careful management is required to use a limited number of water resources in the agricultural area (Maryam and Büyükgüngör, 2017; Kiziloğlu et al., 2008). Only a few of the 597 water treatment plants are used for irrigation water ın Turkey. There are a few cities that have a treatment plants for reuse of irrigation as Aksaray, Balıkesir, Bilecik, Edirne, İzmir, Kırklareli and Konya (Maryam and Büyükgüngör).

Turkey confirmed its irrigation water quality standards in 1991 with five different classifications. Other updated version of laws for reuse of wastewater as irrigation water published on March 20, 2010 in Annex 7, Technical Notification Procedures No. 27527 (Maryam and Büyükgüngör, 2017).

The comparison of the discarged values of textile wastewater which has been in this study and irrigation water standards acording to the first and second class are given in Table 2.4.

Table 2.4. Comparison of wastewater and irrigation water standards

Water parameter	**Sun Textile Treated Discharge**	**Usual range in irrigation water (based on class 1st and 2nd)**
COD mg/L	280-290	25-50
TOC mg/L	240-30	5-8
Turbidity (NTU)	15-35	1
Conductivity(ms/cm)	8.8-9.5	0.7-3
pH	7.5—8.5	6.5-8.5
Total Suspended Solid mg/L	34	20-30
Oil.mg/L	<10	0.02-0.3
Sulfur.mg/L	<1	0.002
Sulphide. mg/L	0.031	
Total Cr.mg/L	0.028	trace-0.02
Zinc. Zn.mg/L	0.09	0.2-0.5
Free Chloride. mg/L	0.1	0.01
Ammonium-Nitrogen.NH4-N.mg/L	0.54	0.2-1
Phenol. mg/L	0.355	0.002-0.001

3. LITERATURE SURVEY

In this study, electrocoagulation, adsorption, and photo-Fenton methods were applied in series. Walnut shells and corn cob wastes were examined as raw materials for preparation of adsorbents and support materials of catalysts. For these purposes, the literature survey was investigated and categorized for each treatment method. As a result of the literature survey, it is found that there are several studies which included the same methods used in this study. However, this study is distinguished from the literature due to the studying of real wastewater treatment and the focus on organic carbon removal with hybrid process. There are a few studies about the hybrid process for real wastewater treatment with these methods. The details of the literature survey are given below.

3.1 Electrocoagulation

There are many studies in the literature for the treatment of wastewater by electrocoagulation method. The studies are generally focused on the type of electrode used. Aluminum and iron are the most widely used electrodes because of low cost and easily accessible. Some studies with aluminum and iron electrodes are summarized:

3.1.1 Treatment by electrocoagulation with Al electrode

In 2010, Tchamango et al., investigated the treatment of dairy effluents by electrocoagulation. Chemical oxygen demand (COD) removal efficiency was found as 61% and removal efficiencies of phosphorus, nitrogen contents, and turbidity were 89, 81 and 100%, respectively. Also, chemical coagulation and electrocoagulation was compared and according to the results electrocoagulation was more effective because of the less reagent and lower aluminium amount when compared the anode dissolution and quantitiy of aluminium salt used (Tchamango et al., 2010).

In 2015, Kobya and Demirbaş studied on the treatment of can manufacturing wastewater by electrocoagulation process using Al electrodes. In this study, different parameteres were tested like current density, operating time and electrode connection modes to see the effect on removal efficiencies of aluminium, zirconium and phosphate, chemical oxygen demand (COD) and total organic carbon (TOC). The results showed that the 20A/m^2, 40 min and MP-P electrode connection mode were most suitable condition with removal effciciency 99.41% for Al, 99.38% for Zr and 99.80% for phosphate, 72% for COD, and 37% for TOC in the wastewater. The amount of sludge operating cost was found as 1.674 kg/m^3 and 0.366 € /m^3 (Kobya and Demirbaş, 2015).

In 2016, Aswathy et al., investigated the ‘‘Removal of organics from bilge water by batch electrocoagulation process’’. In this study, Al electrodes were used for the treatment of synthetic bilge water. Various different parameters were investigated on the treatment which were solution pH, voltage value, spacing of electrode and electrode effective area. The results showed that at a pH of 7, applied voltage of 10 V, spacing of 1 cm and effective electrode area of 45 cm^2, a maximum soluble COD removal efficiency of 85% was obtained after an electrolysis time of 120 min (Aswathy et al., 2016).

3.1.2 Treatment by electrocoagulation with Fe electrode

In 2008, Kongjao et al., examined the removal of organic and inorganic pollutants in tannery wastewater using iron electrode in electrocoagulation. The initial pH, current density and flow rate were investigated as parameters. The optimum condition was found by applying the mono-polar parallel configuration at the current density of 22.4 Am^{-2}, flow rate of wastewater of 3.67 L/min and 20 min electrolysis time. The chromium removal efficiency was more than 95% at optimum conditions and also, total dissolved solid and total kjeldahl nitrogen were completely removed (Kongjao et al., 2008).

In 2012, Al-Shannag et al., investigated the removal of total suspended solid and chemical oxygen demand of the wastewater using electrocoagulation or chemical coagulation. Fe electrode was used for electrocoagulation and current density, initial pH and time were tested as parameters. The removal efficiency was found more than 80% for total suspended solid and chemical oxygen demand by electrocoagulation method (Al-Shannag et al., 2012).

In 2017, Vidal et al., examined the treatment of textile dyes using electrocoagulation method with Fe electrodes. In this study four different current densities were examined (0.5, 2.5, 5 and 10 mA/ cm^{-2}) and the experimental results showed that the TOC removal was increased when current density increased. The maximum removal of dye was at an initial pH of 8.5 and current density of 5.0 mA/ cm-2 with 76% for COD and 74% for TOC and 83% for turbidity (Vidal et al., 2017).

3.1.3 Treatment by electrocoagulation with comparison of Al and Fe electrode

In 2007, Bayramoğlu et al., published their study called ‘’Treatment of The Textile Wastewater By Electrocoagulation Economical Evaluation”. In this study, the method of electrocoagulation was investigated. In the study, the effect of the electrodes arrangement and economic analysis were examined. Both aluminum and iron electrodes were used which were compared in parallel and serial connection modes. It was observed that the most suitable configuration was monopol-parallel mode for two different electrodes. 30Am^{-2} current density and 15-minute for reaction time and the optimum pH value for the Fe electrode was 7 while for Al this value was 5 (Bayramoğlu et al., 2007).

In 2010, Zodi et al., published their study called ‘’Treatment of the textile wastewaters by electrocoagulation: Effect of operating parameters on the sludge settling characteristics’’. Electrode material, current density, pH and time were investigated in this study. High COD removals were achieved at low current density with the two electrode materials, 85-92% with Al electrode and 85-94% with Fe electrode (Zodi et al., 2010).

In 2016, Kobya et al., studied on ‘‘Operating parameters and costs assessments of a real dyehouse wastewater effluent treated by a continuous electrocoagulation process’’. In this study, continuous process was applied for the treatment of real dyehouse wastewater and the removal efficiencies of COD, TOC and turbidity were obtained as 85%, 76% and 95% for Fe electrode and 77%, 72% and 95% for Al electrode at current density of 65 A/m^2, inlet flow rate of 0.010 L/ min, operating time of 80 min (hydraulic retention time of 350 min), and current density of 65 A/m^2 (the optimum operating conditions). Operating costs for Fe and Al electrodes at the optimum operating conditions were calculated as 1.562 $\$/m^3$ or 7.282 \$/kg COD for Fe electrode and 1.851 $\$/m^3$ or 14.257 \$/kg COD for Al electrode (Kobya et al., 2016).

In 2017, Zazouli et al., studied on the treatment of pulp and paper industry wastewater. Aluminum and iron electrodes were tested in this study and initial pH and voltage values were examined as parametric study. The optimum conditions were selected as 60 mV for initial voltage and 7 for inital pH, the higher removal efficiencies were found with Fe electrodes. 92% COD and 100% color removal was achieved at the optimum conditions (Zazouli et al., 2017).

In 2018, Omwene and Kobya studied the treatment of domestic wastewater phosphate by electrocoagulation. In this study aluminium and iron electrodes performances were compared and some parameters like inital pH, current density, time, and initial phosphorus concentration were investigated. Higher removal efficiency was found with Al electrode with the less time. Also, when compared the operating cost, energy and electrode consumption, Al electrode was found more effective with the values 1.032 $\$/m^3$, 1.143 kWh/m^3 and 0.218 kg/m^3, respectively (Omwene and Kobya, 2018).

In 2018, Tanatti et al., examined the treatment of biodisel wastewater with using iron and aluminium electrodes. The removal of the chemical oxygen demand (COD) and the total organic carbon content (TOC) were investigated in this study. Current density, initial pH and time were examined as parameters. The results showed very similar removal efficiencies for both electrodes. COD removal effciencies were found as 91.74 and 90.94% for iron and aluminum electrode, respectively and 91.79 and 91.98% removal efficiencies were obtained for TOC for the iron and aluminum electrodes (Tanatti et al., 2018).

Some of the studies are summarized in Table 3.1.

Table 3.1. Summary of literature survey for electrocoagulation

Type of wastewater	Anode-cathode material	Properties of wastewater COD, BOD, TSS Turbidity				Optimum operating conditions			Removal efficiency (%)				References
		COD (mg/l)	BOD (mg/l)	TSS (mg/l)	Turbidity (NTU)	pH	C.D (A/m^2)	Time (min)	COD	BOD	TSS	Turbidity	
Tannery wastewater containing organic and inorganic pollutants	Fe	4100-6700	630-975	600-955	*	7-9	22.4	20	95	96	96	*	Kongjao S. et al., 2008
Textile wastewater	Al	1260	*	*	1310	7	80	70	66	*	*	89.6	Zodi S., et al., 2010
Pulp and paper mill wastewater	Fe	2950	*	3446	*	7.5	60	30	82	*	78	*	Al-Shannag M. et al., 2012
Textile Wastewater	Al-Fe	2031	*	102	671	5-7	30	15	65	*	*	83	Bayramoğlu et al., 2007
Bilge Wastewater	Al	21,120	*	4590	2870	7	6500	120	89.94	*	*	*	Aswathy et al., 2016
Real Dyehouse Wastewater	Al-Fe	1940–2060	*	210–250	1850–2600	5.5	85	80	77-85	*	93-95	95	Kobya et al., 2016

C.D: current density, *:not available

Table 3.1 Cont'd

Type of wastewater	Anode-cathode material	Properties of wastewater COD, TOC		Optimum operating conditions			Removal efficiency (%)		References
		COD (mg/l)	TOC (mg/l)	pH	C.D (A/m^2)	Time (min)	COD	TOC	
Manufacturing wastewater	Al	850	300	3	20	40	72	37	Kobya and Demirbaş, 2015
Tannery wastewater	Al-mild steel	2413	1000	*	70	20	68	55.1	Feng et al., 2007
Textile wastewater	Fe	*	95	8.5	50	60	74	75	Vıdal et al., 2017
Biodiesel wastewater	Al-Fe	305,500–403,540	54,000-110,000	6	3.226	-	91.74 -90.94	91.79 -91.98	Tanattı et al., 2018

C.D: current density, *: not available

3.2 Adsorption

In the literature, activated carbon is the most useful and preferred adsorbent type due to the its high adsorption capacity and large surface area. Because the raw materials of activated carbon have a high cost , many researchers are interested in the alternative materials such as agricultural wastes, (Amirza et al., 2017; Ali et al., 2012; Kadirvelu et al., 2003; Mohan et al., 2008; Asubiojo and Ajelabi, 2009). The studies about the adsorption with low-cost adsorbents are given details below.

3.2.1 Treatment by adsorption with low-cost adsorbents

In 2008 Mohan et al., studied the wastewater treatment by adsorption using activated carbon which was produced by agricultural wastes. In this study coconut shell, coconut shell fibers and rice husk were used as agricultural wastes and the removal efficiency of COD and heavy metals were compared. When the temperature was increased, the removal efficiency of chloride and fluoride increased unlike COD removal efficiency with the rice husk based activated carbon. The COD removal was found 47–72% by coconut shell fiber carbon, 50–74% by coconut shell carbon and 45–73% by rice husk carbon. The kinetics of COD removal was found to be suitable for first order rate law (Mohan et al., 2008).

In 2009, Ahmad and Hameed, published their study ‘’Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon’’. In this study, different parameters were investigated like the effect of activated adsorption dosage (m), solution pH and contact time. Color and COD removal were found 91.84% and 75.21% at the optimum conditions; pH 3, m = 0.30 g/100 mL solution and time = 10 h (Ahmad and Hameed, 2009).

In 2013, Abdurrahman et al., studied on the removal of dyes using orange peels adsorbent. In this study, effect of adsorption dosage, pH and contact time have been investigated. It was found that 60-70% of dyes were removed at pH=7 with a retention time of 120 minutes with the 1.5g/25mL optimum adsorbent dosage. Also, the equilibrium adsorption fit Langmuir adsorption isotherm model (Abdurrahman et al., 2013).

In 2017, Nayl et al., published their study ‘‘Adsorption studies on the removal of COD and BOD from treated sewage using activated carbon prepared from date palm waste’’. In the study chemical oxygen demand and (COD) and biological oxygen demand (BOD) removal efficiencies were investigated at the different conditions. Adsorbent dosage, pH, contact time, agitation rate, and temperature were tested as the parameteres. The optimum conditions were found 0.1 g/100 ml adsorbent dosage, 150 min, pH 6.0, agitation rate of 400 rpm and temperature 25 °C. Final results showed that COD and BOD removal percentage was 95.4 and 92.8% at the determined optimum conditions (Nayl et al., 2017).

In 2006, Khan and Wahab investigated the adsorption of copper using corncob based adsorbent. It was examined that copper removal efficiency decreased by 53%, 27% and 19% in the presence of Pb(II), Ca(II) and Zn(II), respectively. Regeneration study indicated that the sulfuric acid treated corncobs could be regenerated by acidified hydrogen peroxide solution and as much as 90% copper could be recovered (Khan and Wahab, 2006).

In 2009, Asubiojo and Ajelabi studied on the heavy metal treatment using natural adsorbents. In this study five different materials were used for adsorbent preparation; paddy husk, corn cob, wheat bran, peanut skin, and human hair. Different parameters were investigated such as column height, adsorbent loading, particle size of the adsorbents. The adsorption capacities of natural adsorbents were compared. The maximum adsorption capacities were found 87.6–92.2% for corncob (Asubiojo and Ajelab, 2009).

In 2015, Garg et al., studied on the removal of Cr (VI) and COD by corncob based activated carbon. The surface area of corncob based activated carbon was found 399.006 m^2 /g. Adsorbent dosage, pH, temperature, and contact time were examined as parametric study and the maximum removal efficiency of chromium ions and COD were found to be 95.27% and 82.28%, respectively at the optimum conditions (pH of 3, and 15 g/l of adsorbent dosage) (Garg et al., 2015).

In 2017, Tharaneedhar et al., studied on the removal of methylene blue by adsorption. In this study, the corncob activated carbon was used for the removal of cationic dye (methylene blue, MB). Initial MB dye concentration, contact time, solution pH, adsorbent dosage and temperature were studied as the parameteres. When the contact time was increased from 10 to 90 min, the removal of dye increased. The removal of dye decreased with increasing initial dye concentration from 25 to 150 mg L^{-1}. Also, when temperature was increased from 30 to 60 °C, removal efficieny decreased. The maximum monolayer adsorption capacity was found 82.71 mg g^{-1} (Tharaneedhar et al, 2017).

In 2018, Mahdavi et al., studied on the adsorption with activated carbon from walnut shell agricultural waste for treatment of landfill leachate. BET surface area was found as 1,851.1 m^2 /g. The optimum operating conditions were found pH =4, adsorbent dosage =15 g/L, temperature = 30°C. According to the results, the maximum adsorption capacity was found as 123.1 mg/g with the 84.7% COD removal efficiency at the optimum conditions (Mahdavi et al., 2018).

Some of these studies are summarized in Table 3.2

Table 3.2. Literature survey for adsorption with low-cost adsorbent

Type of Wastewater	Type of Adsorbent	Properties of wastewater COD, BOD, TSS			Optimum Conditions				Removal Efficiency (%)		References
		BOD (mg/l)	COD (mg/l)	TSS (mg/l)	pH	Adsorbent dosage (g/L)	Temp. (K)	Speed (rpm)	BOD	COD	
Industrial wastewater	Coconut shell, Coconut shell fibers and rice husk based Activated Carbon	260	553	260	6	20	313	*	*	47-74	Mohan et al.,2008
Textile wastewater	Bamboo-based activated carbon	<50	200-260	<50	3	3	303	120	*	75	Ahmad and Hameed, 2009
Landfill leachate	Walnut shell based activated carbon	170	2180	*	4	15	303	*	*	84.7	Mahdavi et al., 2018
Sewage wastewater	Palm waste based activated carbon	14	38	24	6	1	298	400	92.8	84.7	Nayl et al., 2016
Electroplating Wastewater	Corncob Based activated carbon	*	1443	89	3	15	*	*	*	82.28	Garg et al., 2015

*: not available

3.3 Treatment by Photo-Fenton Like Oxidation

In 2005, Hsueh et al., studied about Fenton and Fenton-like system for degradation of azo dyes. In this study, three different azo dyes were investigated. The optimum pH value was selected as 2.5-3. Also the effects of H_2O_2 and Fe^{2+} and Fe^{3+} concentrations were examined and optimum conditions were found. H_2O_2 concentration was changed between 20-200 mg/L and removal efficiency of organic compounds increased with increasing H_2O_2 concentration. For Fe^{3+} concentration, after 1h 13%, 95%, 96% and 97% removals were obtained with 0.1, 1, 5 and 10 mg/L Fe^{3+} concentrations, respectively. The optimum Fe^{3+} concentration was selected as 1 mg/l (Hsueh et al., 2005).

In 2009, Arslan-Alaton et al., examined the treatment of wastewater which containing synthetic azo dyes, Acid Blue 193 and Reactive Black 39. Photo-Fenton like oxidation was tested on treatment of real Reactive Black 39. In this study Fe^{3+} and H_2O_2 concentrations, initial chemical oxygen demand (COD) and reaction time were investigated as parameters. Treatment efficiency was evaluated by the removal of chemical oxygen demand, total organic carbon, and color. Optimum conditions were found Fe^{3+} = 1.5 mM; H_2O_2 = 35 mM for CODs ≤ 200 mg/L and a reaction time of 45 min for Acid Blue 193 with 98% color, 78% COD and 59% TOC removal efficiencies. Lower removal efficiency was found for Reactive Black 39 when compared the removal efficiency of Acid Blue 193 because of its high chloride content (Arslan -Alaton et al., 2009).

In 2012, Hasan et al., studied on the treatment petroluem rafinery wastewater by Photo-Fenton like oxidation. In this study, removal of TOC and COD were investigated. Reaction time, ratio of H_2O_2 to catalyst amount and ratio of H_2O_2 to organic amount were tested and TOC and COD removal was found 70% and 98.1% under the optimum conditions with 30 min reaction time. The ratio of H_2O_2 to catalyst amount and ratio of H_2O_2 to organic amount were selected 12 and 5, respectively (Hasan et al., 2012).

In 2014, Blanco et al., published their study ‘Photo-Fenton and sequencing batch reactor coupled to photo-Fenton processes for textile wastewater reclamation:

Feasibility of reuse in dyeing processes'. In this study, the optimum conditions were found concentration of Fe (II) was 216 mg/ L; concentration of H_2O_2 was 4950 mg/L; pH = 2.7 and T = 35 ^{0}C for the single photo-Fenton method with the removal of COD and TOC 79% and 75%. This removal efficiencies were increased by coupled biological-photo-Fenton processes. Sequencing batch reactor was used for biological treatment with an hydraulic retention time of 1 day and 75% of TOC removal was obtained after 25 cycles. The optimum conditions were found for coupled photo-Fenton method concentration of Fe (II) = 66.5 mg/ L and concentration of H_2O_2 = 1518 mg /L with the 97% and 95% removal of COD and TOC, respectively (Blanco et al., 2014).

In 2016, Sreeja and Sosamony examined the treatment of textile wastewater by homogenous and heterogenous photo-Fenton process. Some parameters tested for this study were: pH, catalyst loading, hydrogen peroxide concentration and UV power. It was seen that the removal efficiency increased with the increasing UV power and hydrogen peroxide concentration and the optimum conditions for both homogenous and heterogenous photo-Fenton process, pH 3, hydrogen peroxide concentration 150 mM, catalyst loading 10 mg/l and 16W UV power. The removal efficiencies were found for COD and colour are 47% and 82% for homogeneous process and 62% and 85% for heterogeneous process, respectively (Sreeja and Sosamony, 2016).

In 2017, Ebrahiem et al., investigated the removal of organic pollutants for the cosmetic wastewater using Photo-Fenton oxidation method. In this study some parameters were examined like pH, hydrogen peroxide concentration, ferrous sulfate dosage, initial dye concentration, and time. Experimental results showed that the optimum conditions for treatment; pH 3, the dosage of 1 ml of H_2O_2 per liter and 0.75 g/ of Fe(II) and Fe(III) per liter and reaction time 40 min with the more than 95% removal of COD (Ebrahiem et al., 2017).

Some of these studies are summarized in Table 3.3.

Table 3.3. Literature survey for photo-Fenton like oxidation

Type of Wastewater	Type of Catalyst	Optimum Conditions				Removal Efficiency (%)			References
		pH	Catalyst loading (mg/l)	$[H_2O_2]$ (mM)	Time	TOC	COD	Color	
Synthetic wastewater	Fe^{3+}	2.5	1	3	480	38-28	*	*	Hsueh et al.,2005
Azo Dyes (Orange II)	Carbon aerogel/Fe Activated carbon/Fe	3	200	6	*	55-94	*	*	Ramirez et al., 2007
Azo Dyes (Acid Blue 193, Reactive Black 39)	Fe^{3+}	2.8	82.5	35	45	59	78	98	Arslan-Alaton et al., 2009
Petroluem rafinery wastewater	Fe^{3+}	3	H_2O_2/catalyst :12 H_2O_2/organic :5		30	70	98	*	Hasan et al., 2012
Textile wastewater	Fe^{2+} / Fe^{3+}	2.7	66.5	45	*	75-95	79-97	*	Balanco et al., 2014
Textile wastewater	iron oxide	3	10	150	*	*	47-62	82-85	Sreeja and Sosamony, 2016

*: not available

3.4 Treatment by Microbial Fuel Cells

In the literature, there are few studies for wastewater treatment by microbial fuel cells (MFC) and some of them are given in below;

In 2004, Liu et al., were studied on the production of electricity during wastewater treatment using MFC and results showed that MFC by reactor electrical power could be generated (maximum of 26 mWm-2) at the same time removal of COD was found 80 % (465 ohm (Ω)), 33 hours hydraulic retention time) (Liu et al., 2004).

In 2011, Kalathil et al., published their study called ‘’Granular activated carbon based microbial fuel cell for simultaneous decolorization of real dye wastewater and electricity generation’’. Decolorization and removal of COD were investigated and the results showed that after 48h, 73% color and 71% COD removal were found at anode. Experiments were tested at 30 ^{0}C and using external resistance of 800 ohm (Ω) (Kalathil et al., 2011).

In 2012, Kalathil et al., examined the decolorization of real dye wastewater by microbial fuel cell. The granular activated carbon based single chamber microbial fuel cell produced a high power density with high removals of color, toxicity and COD. 71% and 56% COD removals were found for closed and open circuit systems, respectively. Also, the system (granular active carbon based single chamber microbial fuel cell) produced a power density of 8W/m^3 and the discharged effluent was almost non-toxic (Kalathil et al., 2012).

In 2014, Ren et al., investigated the two stage microbial fuel cell for the treatment of the domestic wastewater. The system included microbial fuel cells and an anaerobic fluidized bed membrane bioreactor. The system was examined during 50 days at room temperature. COD removal was found 67% after 24h hydraulic retention time for MFC and the COD removal was found 92.5% and total suspended solid removal almost completed for combined system. The total electrical energy required for the operation was 0.0186 kWh/m^3 for combined system and it was 0.0197 kWh/m^3 by MFCs (Ren et al., 2014).

In 2017, Logrono et al., studied on microbial fuel cell for treatment of textile wastewater dyes. The removal of Zn, Cr metal ions and COD were investigated and the results showed that the air exposed single-chamber microbial fuel cell system was suitable for using in the removal of textile wastewater. Removal efficiences were found as 98%, 54-80%, and 92-98% for Zn, Cr, and COD, respectively (Logrono et al., 2017).

Some of these studies are summarized in Table 3.4.

Table 3.4. Literature survey for microbial fuel cell

Type of Wastewater	Type of MFC	Operating Conditions	Removal Efficiency (%) and Power Densities	References
Real Textile dye wastewater	Granular activated carbon based single chamber microbial fuel cell	• HRT 48h • Electrode distance : 2 cm • Number of electrodes : 4 • Closed circuit	• $8 W/m^3$ power density • 71-56% COD • Discharged effluent was almost non-toxic.	Kalathil et al., 2012
Domestic wastewater	Air-cathode microbial fuel cells and an anaerobic fluidized bed membrane bioreactor	• HRT: 24 h • 500 Ω	• 67% for MFCS and 92.5% COD for MFC-AFBMBR • Nearly 100% TSS • Electrical energy $0.0186 kWh/m^3$ by combined system $0.0197 kWh/m^3$ by MFCs	Ren et al., 2014
Real dye wastewater	Granular activated carbon based microbial fuel cell	• pH: 7.6 • HRT: 48 h • Open circuit • 800 Ω	• 73% color • 71% COD • $1.7 W/m^3$ power density	Kalathil et al., 2011
Textile wastewater	Single chamber microbial fuel cell with a cathodic microalgal biofilm	• Room temperature • Open circuit	• $123.2 mWm^{-3}$ power density • COD 92-98% COD color, 84-93% color ,98% Zn, 54-80% Cr	Logrono et al., 2017

3.5 Hybrid Process for Wastewater Treatment

In the literature, there are a few studies on hybrid processes applied for the treatment of wastewater. In recent years the studies on hybrid process treatment subject have been intensified. The details of the studies about the hybrid process treatment are given below.

In 2014, Mannenti et al., investigated the hybrid process for treatment of textile wastewater which includes electrocoagulation, solar photo-Fenton and biological oxidation processes. With the electrocoagulation method 36% COD removal was achieved. When the photo-Fenton process was applied after the electrocoagulation process, it was seen that COD removal increased and 70% biodegradabilitiy was achieved. Finally, by applying a biological process COD value was reduced to 139 mg O_2 L^{-1} which was below the maximum limit put by their country (Mannenti et al., 2014).

In 2017, Gilpavas et al., studied on the treatment of textile wastewater by the hybrid prcocess including coagulation-flocculation and Fenton or Photo-Fenton processes. In this study firstly, coagulation-floculation method was applied and 98% of turbidity, 48% of COD removal were achieved. The BOD_5/COD ratio was increased slightly from 0.136 to 0.212. When coagulation-flocculation was combined with Fenton process, COD removal was achieved 74% and BOD_5/COD ratio increased from 0.212 to 0.68. 87% COD removal was obtained when cogulation/flocculation and photo-Fenton methods were applied sequentially (Gilpavas et al., 2017).

In 2018, Myllymäki et al., investigated the removal of total organic carbon by electrocaogulation combined adsorption. In this study, both Al and Fe electrode were tested for electrocoagulation. Adsorption experiments were tested with 10 g/L adsorbent dosage and 24hours. According to the results, the total organic carbon removal was found 95% by using first adsorption and the electrocoagulation. Also, it was seen that the removal of TOC was the same for both Al and Fe electrodes (94.4% for Al, 94.5% for Fe) (Myllymäki et al., 2018).

In 2018, Flores et al., studied on the treatment of olive oil mill wastewater. In this study single electrocoagulation and electrocaogulation/ electrochemical Fenton process were applied sequentially. The results showed that 97.1% removal of TOC efficiency was achieved with sequential Electrocoagulation/photoelectro-Fenton method which was higher than single electrofenton or photo-electro Fenton (Flores et al., 2018).

4. FOREWORD TO THE STUDY

The conclusions extracted from the literature survey assisted and guided in developing the structure and the experimental plan of the study and the main reasons for selection of wastewater, hybrid process, and types of adsorbents/catalysts are listed below with details.

4.1 Choice of Textile Wastewater

Water scarcity has become an important problem for today and also for the future. Therefore, the treatment and reusability of the wastewaters for effluent of industries have become increasingly important point for our future and because of the large water consumptions, the treatment of textile industry wastewater has a critical point.

The textile industry is one of the major industries that has an important economic role in many countries as in Turkey. Turkey is the 5th in textile export with 11 billion \$ and 9th in textile import with 6 billion \$ in the world. At the same time, it is the 7th with 15 billion \$ in clothing export (Gunduz et al., 2018). The main critical point of the textile industry is the consumption of large amount of water. Approximately 200 L of water is consumed for 1 kg of textile product. In Turkey, textile is the second industry for water consumption when compared the all other industries (Güyer et al., 2016). According to Turkish Statistical Institute, 15% of industrial water consumption is due to the textile industry (191.5 million m^3) (Alkaya and Demirer, 2014).

Due to the process of textile industry, many dyes and chemicals are used in the production process causing a lot of water consumption. Each year 280,000 tons of dyes are discharged to the fresh water with 8000 dyes and 6900 auxiliary chemicals and salts (Asghar et al., 2015). In Europe, 108 million tons of wastewater is produced each year and 36 million tons of chemicals come from the textile wastewater (Vajnhandl and Valh, 2014).

Treated textile industry wastewater has been chosen to test the hybrid treatment system due to the great environmental concern of its.

4.2 Choice of Hybrid Process

In the literature, many treatment methods for textile wastewater were investigated and good results were obtained. However, instead of using a single method, it was found useful to apply different methods in combination by searching the appropriate conditions (making it more economical, using less chemicals). The textile industry has a complex process. Different chemicals and dyes are used for each step of the process. In addition, the variety of chemicals used can vary depending on the fabric produced and each factory can use different chemicals. Therefore, it may be not possible to obtain an efficient removal with a single treatment method and achieve the standards values for reuse. In the treatment of wastewater, if the purpose is reusability of wastewater, there should be a detailed treatment process and it should be targeted to get the best results by testing more than one method. For these reasons, in this study, electrocoagulation, adsorption, photo-Fenton like oxidation, and microbial fuel cell methods were investigated alone or sequentially to achieve the higher removal efficiencies.

4.3 Choice of Adsorbent

Activated carbon is one of most preferred and effective adsorbent types due to the its high surface area (500-2000 m^2/g) and high porous structure. Also, it has high adsorption capacity and high porous structure. Lignin, coal, petroleum residues are generally used for the preparation of commercial activated carbon which are expensive and non-renewable materials. Low cost and efficiency are the main advantages when compared the commercial activated carbon produced non-renewable coal contents and activated carbon produced from agricultural wastes. Due to these reasons preparation of activated carbon from corncob and walnut shells (easy to find in Turkey) were preferred in order to improve low cost adsorbents derived from agricultural wastes and generating new usage areas for the recovery of the wastes.

4.4 Choice of Catalyst

Carbon-supported perovskite type catalysts were used for photo-Fenton like oxidation experiments. Perovskite-type mixed oxides (ABO_3) is a useful and effective heterogeneous catalyst with the special structure. The large atoms at the positions led to increasing the stabilitiy and activity. The chemical structure of these types of catalyst contribute decomposition of many organic pollutants (Shang et al., 2018). Bi-contained oxide catalyst is preferred in this study because its narrow band gap and good stability is very effective to removal of organic pollutant. Also, literature survey showed that the activated carbon is extensively used as catalyst supports materials for removal of pollutant (Zhai et al., 2018; Konwar et al., 2014; Liu et al., 2010). Due to these studies the low-cost activated carbon was decided as supported materials for Bi-contained perovskite catalysts in this study.

5. EXPERIMENTAL STUDY

5.1 Textile Wastewater

All experiments were tested with pre-treated real textile wastewater which was supplied from SUN Textile factory in Turkey, İZMİR. Certain amount of the real textile wastewater were provided from the factory in regular periods. As the pre-treatment process the textile wastewater was subjected to physical, biological and chemical treatment methods at the factory. Physical treatment including coarse grind, fine grind, and microsieve. Aeration and sedimentation processes were applied in biological treatment and coagulation was applied in chemical treatment process.

Since different batches were obtained from different dying processes, the initial characteristic properties of the textile wastewater were varying. The wastewater for each batch were analyzed and the maximum and minimum values of properties for textile wastewater are shown in the following Table 5.1. These values meet the discharge standards in Turkey but not acceptable for irrigation water qualification criteria.

Table 5.1. Characteristics of the wastewater used

<table>
<tr><th colspan="2">Characteristics</th><th>Value</th></tr>
<tr><td colspan="2">pH</td><td>8.5-7.5</td></tr>
<tr><td colspan="2">TOC (mg/L)</td><td>230-30</td></tr>
<tr><td colspan="2">COD(mg/L)</td><td>295-106</td></tr>
<tr><td colspan="2">Turbidity (NTU)</td><td>25-17</td></tr>
<tr><td colspan="2">Conductivity (mS/cm)</td><td>7.44-9.6</td></tr>
<tr><td colspan="2">Dissolved O_2 (mg/L)</td><td>4.11</td></tr>
<tr><td rowspan="3">Color (1/m)</td><td>436 nm</td><td>29</td></tr>
<tr><td>525 nm</td><td>25</td></tr>
<tr><td>620 nm</td><td>17.7</td></tr>
</table>

5.2 Hybrid Processes

The experimental study has been carried out by four different methods which including electrocoagulation (EC), adsorption, AOP (Photo-Fenton Like Oxidation) and Microbial Fuel Cell (MFC). These methods were applied as a hybrid process as shown in Figure 5.1.

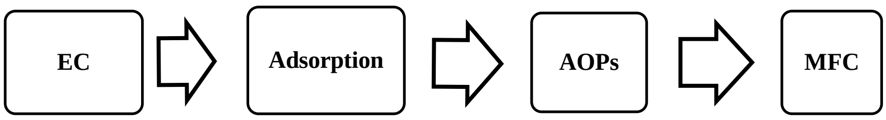


Figure 5.1. Hybrid process steps

Electrocoagulation process is the first step of the hybrid process. Electrocoagulation experiments were realized in two parts; electrode selection experiments and parametric study experiments with the selected electrode. After the optimum conditions were determined, the pre-treated wastewater by electrocoagulation was retained for the adsorption process.

For adsorption method, two different activated carbons were investigated which were prepared by corncob and walnut shell materials. Then, some important parameters such as adsorbent dosage and initial pH were examined and optimum conditions were selected.

Photo-Fenton process is the third step of hybrid process and experiments were subjected to the wastewater treated by adsorption. Finally microbial fuel cell method was tested. Details for experimental study is given in Figure 5.2 schematically.

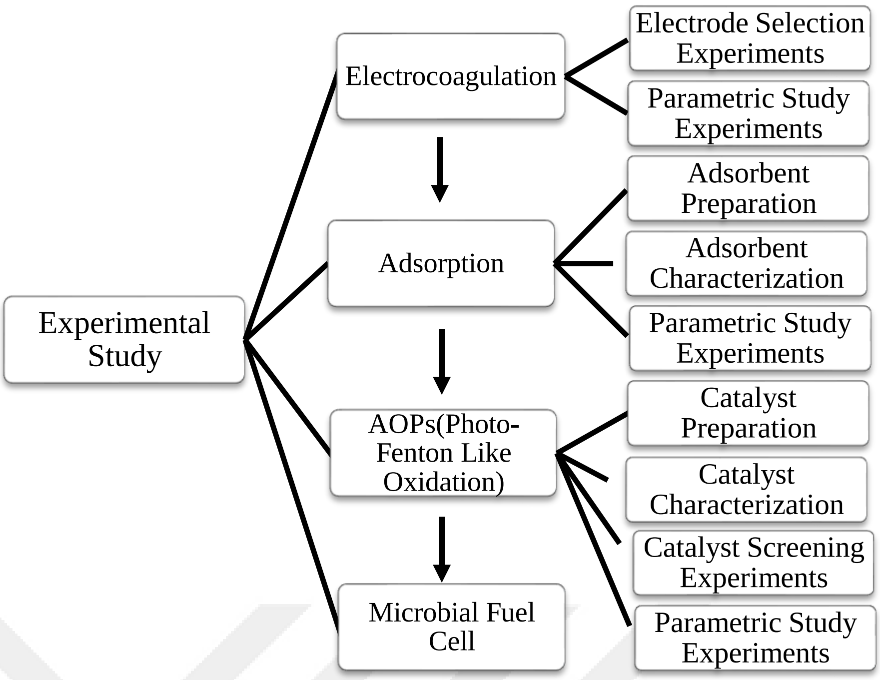


Figure 5.2. Schematic presentation of experimental study

5.3 Adsorbent Preparation

In this study, activated carbon (AC) was used as adsorbent. Two different activated carbons were examined which produced from agricultural wastes as corncob and walnut shell.

Preparation of adsorbent involved three steps; pre-treatment, carbonization-activation and neutralization (Aygun et al., 2003; Nowicki et al., 2010; Köseoglu and Akmil-Basar, 2015; Zabihi et al., 2010).

Pre-treatment:

Pre-treatment method included grinding, washing and drying (120^{o}C, 3h). Corn cobs and walnut shells were primarily ground. Then washed with distilled water 2-3 times to get rid of dust and dirt, and allowed to dry for 3 hours at 120^{o}C.

Carbonization and Activation:

Zinc chloride was selected as the chemical activating agent to develop porous carbonaceous structures during the carbonization. $ZnCl_2$ and the agricultural wastes were mixed by weight of 1:1 and heated until the water evaporated. Drying process was applied at 120°C for 3 h prior to the carbonization. The mixture was pyrolyzed at 750°C for 3 hours under Argon gas flow.

Neutralization:

Finally carbonizate obtained from the prolysis was washed with HCl to remove the inorganic impurities and then washed with deionized water to increase the pH up to the neutral value.

All preparation steps are given in Figure 5.3 and images after each steps are given in Figure 5.4.

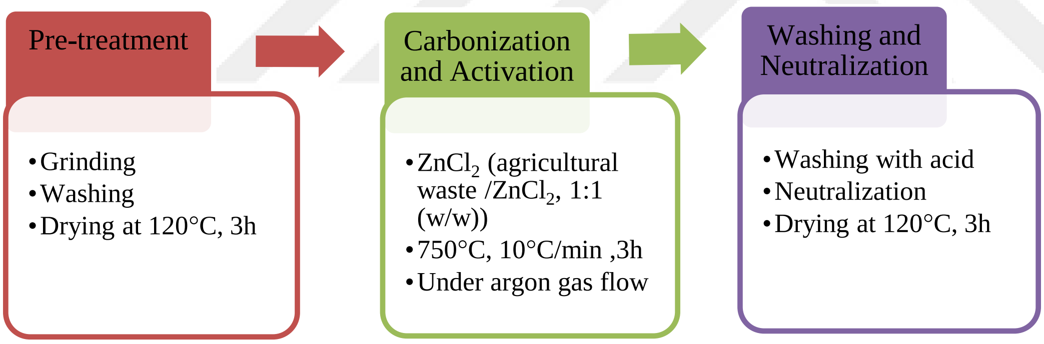


Figure 5.3. Preparation steps of adsorbent

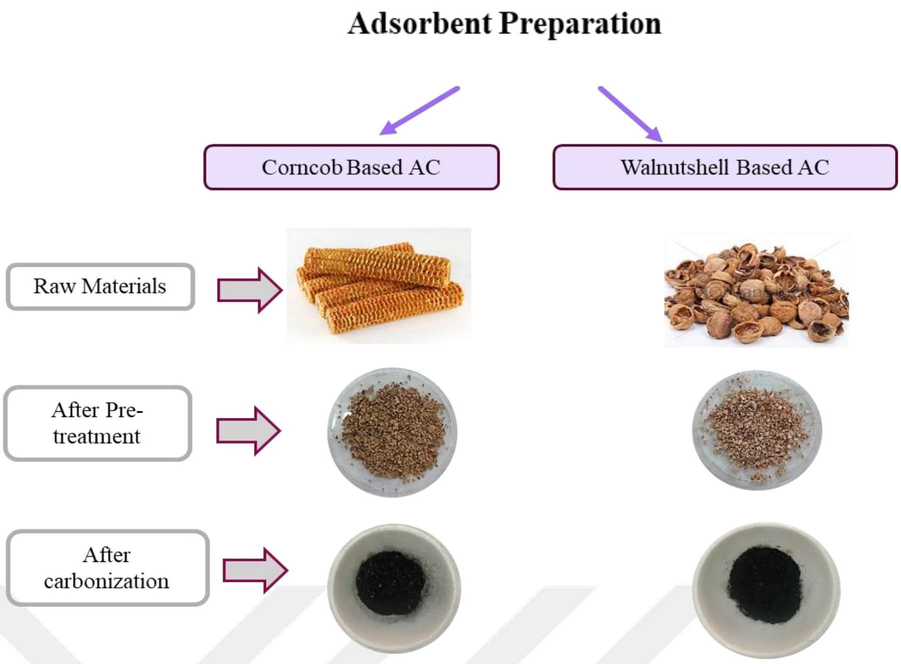


Figure 5.4. Images of after each steps for adsorbent preparation

5.4 Catalyts Preparation

The catalysts $BiFeO_3$ and $BiNiO_3$ on corncob activated carbon were prepared for using in photo Fenton-like oxidation process. The perovskite catalysts were selected to be used in the hybrid catalyst structure due to their high performance and chemical stability (Labhasetwar et al., 2015). The activated carbon catalyst was used as suppport due to the high surface area porous structure and high stability.

5.4.1 $BiBO_3$-activated carbon (B: Fe, Ni) catalyst preparation

$BiBO_3$-activated carbon (AC) catalysts were used as catalyst in photo-Fenton like oxidation process. In order to prepare catalysts, metals were impregnated on the prepared adsorbent. Catalyst preparation can be investigated mainly three step; metal impregnation, gel form formation, and calcination.

Metal impregnation:

For first step $Fe(NO_3)_3.9H_2O$ or $Ni(NO_3)_2$ $.6H_2O$ metal nitrate was used. The procedure for metal impregnation included dissolving $Bi(NO_3)_3.5H_2O$, metal nitrate and citric acid monohydrate in ethanol solution.

Gel-form formation:

After the dissolution was completed activated carbon was added and ultrasonication of the mixture for 30 was applied. Mixture was heated at 70°C under vigorous stirring until gel formation and dried at 150°C for 4 h.

Calcination:

For calcination, ABO_3/activated carbon gel form was heated at 400°C for 4h.

The procedure for $BiBO_3$-activated carbon preparation is shown schematically in Figure 5.5.

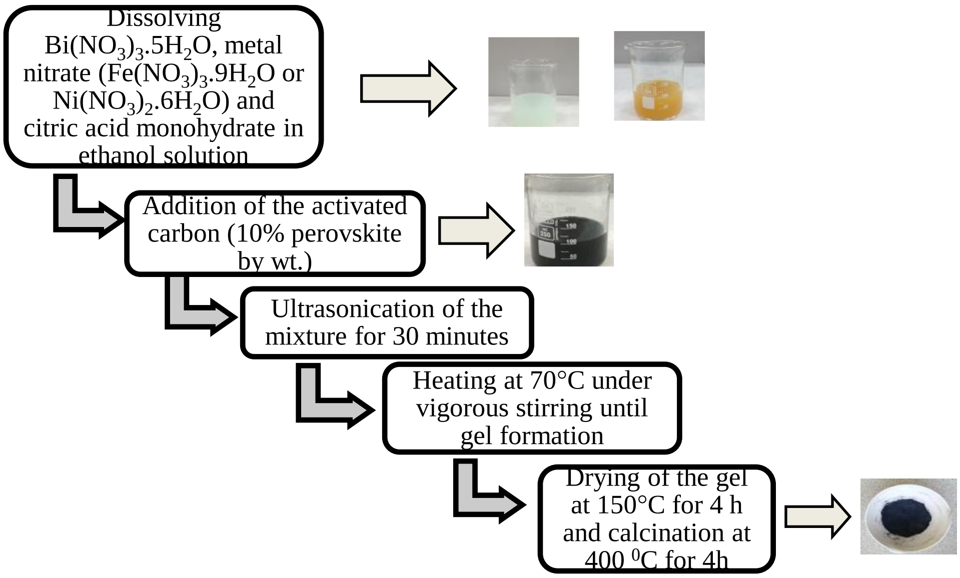


Figure 5.5. Preparation steps of catalyts

5.5 Adsorbent and Catalysts Characterization

The characterization analysis was performed for the corncob and walnut shell based activated carbon adsorbents and $BiNiO_3$/$BiFeO_3$-corncob based activated carbon catalyts. Characterization study includes examination of surface morphology by scanning electron microscope (SEM) (Quanta 400F Field Emission SEM), calculation of surface area, pore size and N_2 adsorption-desorption curves by Brunauer, Emmett and Teller (BET) (Autosorb-6B) method, and thermogravimetric analyses (TGA-FTIR).

The catalyst characterization was performed for the $BiNiO_3$ and $BiFeO_3$ with corncob activated carbon supported catalyst. SEM (Carl Zeiss 300VP*)*, BET analysis and TGA (TA Instruments SDT Q600) analyses were examined for the catalysts to investigate the surface morphology.

5.6 Experimental Setups and Procedures

Set-up and procedure for each process are explained in detail and set-up for each method are shown in the following figures.

5.6.1 Experimental set-up and procedure for electrocoagulation

The setup for electrocoagulation consists of the following components:

- DC power supply and connections (0-30 V, 0-6 A)
- Electrodes: Aluminum / Iron plates (50x50x1 mm). Electrode number was chosen 4 and placed in a monopolar array with a gap of 2 cm between them.
- Magnetic stirrer
- 800 mL beaker

The experimental setup is shown in Figure 5.6. All runs were performed at room temperature and before each run electrodes were washed to remove impurities on the surfaces of electrodes. For a typical run the following procedure is applied;

- 600 mL of the wastewater solution is charged into the beaker

- Current is set to a desired value and the experiment is started
- After 2 hours, current is turned off
- The wastewater was allowed to settle nearly 2 hours and filtered before the final sample is taken.

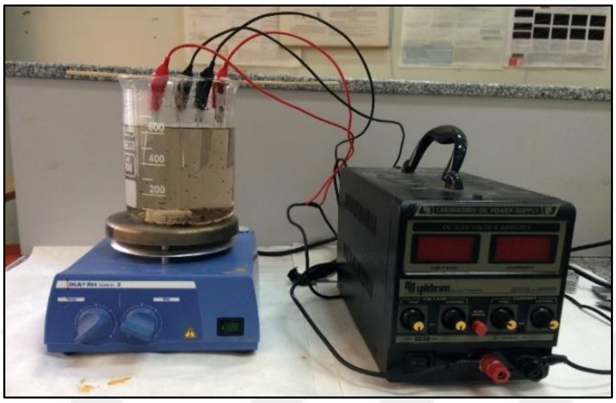


Figure 5.6. Set-up for electrocoagulation

5.6.2 Experimental set-up and procedure for adsorption

Experimental setup for adsorption process is shown in Figure 5.7. An orbital shaker (Jeiotech, SKF-2025) and erlenmeyer flask are used for the adsorption experiments.

Figure 5.7. Experimental setup for adsorption

For a typical run following procedure is applied;

- 250 mL textile wastewater is charged in to the Erlenmeyer flask
- Desired amount of adsorbent is weighed and added to wastewater
- Speed of shaker is set to 300 rpm and samples are taken hourly until the equilibrium is reached.

5.6.3 Experimental set-up and procedure for photo-Fenton like oxidation

The setup for photo-Fenton like oxidation method consists of the following components;

- Cylindrical beaker
- 100 watt halogen lamp
- Magnetic stirrer
- Temperature controller

Experiments were performed by 250 mL wastewater in a cylindrical beaker for 2 hours under visible light irradiation. A 100 watt halogen lamp was used as the visible light irradiation source. The set-up is shown in Figure 5.8.

Figure 5.8. Set-up for photo-Fenton like oxidation

For a typical run the following procedure is applied;

- 250 mL textile wastewater is charged into cylindrical beaker and the initial sample is taken
- If pH adjustment is necessary, sulfuric acid solution or sodium hydroxide solution is added to set of the wastewater initial pH value
- Required amount of hydrogen peroxide and catalyst are added
- Experiment is continued for 120 min and the final sample is taken

5.6.4 Experimental set-up and procedure for microbial fuell cell

The setup for MFC consists of the following components:

- Two-compartment glass reactor,
- A proton exchange membrane (ultrex),
- An Ag / AgCl reference electrode (gamry, 930-00015),
- 0.5 mm thick 50 × 50 mm two graphite paper electrodes (aldrich, GF87162857-10EA)
- Copper cable

The set-up is shown in Figure 5.9.

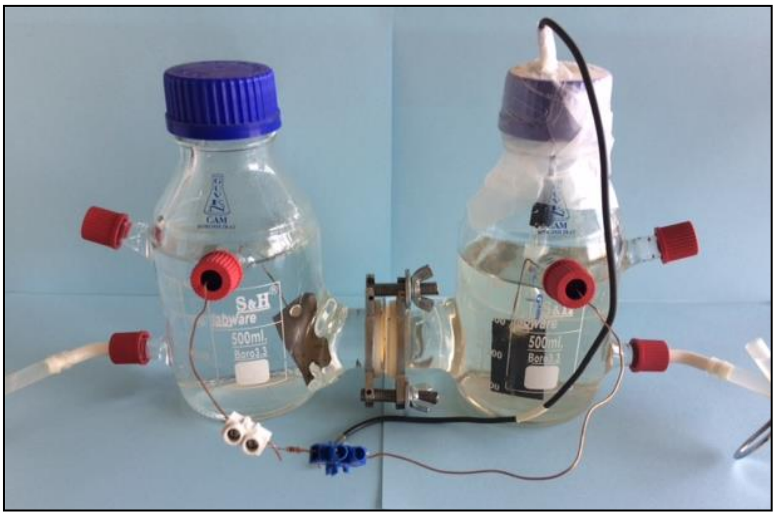


Figure 5.9. Set-up for microbial fuell cell

For a typical run the following procedure is applied;

- The total organic carbon value of the pretreated textile wastewater is measured and an equal amount of the carbon-containing acetate solution is prepared. The reaction solution is obtained by mixing the acetate solution and the pretreated textile wastewater.

- The reference electrode and the carbon paper electrode are placed in the anode chamber which is operated on anaerobic conditions with content; pretreated textile wastewater is mixed culture anaerobic microorganism and substrate as acetate.

- The buffer solution in the cathodic region is prepared in pure water with 0.31 g / L NH_4Cl, 0.13 g / L KCl, 2.69 g / L NaH_2PO_4 and 4.33 g / L Na_2HPO_4 g / L dissolution.

- The carbon paper electrode in the anode compartment is connected to the carbon paper electrode in the cathode compartment which containing the phosphate buffer solution with a copper wire.

- Mixed culture anaerobic microorganism is used for inoculation in system. The vaccine microorganism culture was obtained from the liquid that remains in the upper part of the cultured animal manure for 2 minutes at 600 rpm. Before the inoculation, adaptation studies were carried out to provide their growth on the carbon electrode surface. In the adaptation process the textile wastewater from the pre-treatment and the liquid from the upper part of the centrifuged manure were mixed in equal volumes. 2 ml of culture of microorganisms adapted for 500 ml reaction solution in the fuel cell is used.

- Finally, the anaerobic environment in the anode compartment is provided by nitrogen gas flow.

5.7 Parametric Study

For each method, important parameters were investigated to find the optimum conditions and the best treatment efficiency by also considering the effect on environment.

5.7.1 Parametric study for electrocoagulation

The electrocoagulation method the following three parameters were examined (Inan et al., 2004; Katal and Pahlavanzadeh, 2011; Kabdaşlı et al., 2012);

- Electrode type
- Current density
- Initial pH

Firstly, electrode selection experiments were performed. The most common types of electrodes used in the electrocoagulation process which are aluminum and iron were tested. The main reason for the preference of these electrodes are; having high adsorption capacities of metallic ions, easy accessibility and low cost when compared with the alternatives (Alinsafi et al., 2005; Al-Shannag et al., 2012; Ouaissa et al., 2012). Two different current densities were applied for selection of the electrode type. The results were evaluated on the basis of total organic carbon, and then other parameters were examined. The electrode selection experiments are given in Figure 5.10.

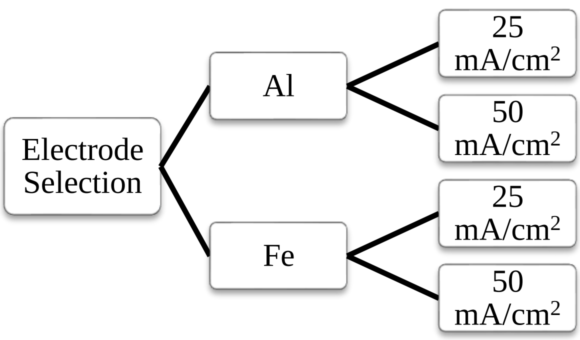


Figure 5.10. Electrode selection experiment

In the literature, electrode type, current density, and initial pH value were given as main parameters so that these three parameters were tested after selecting the electrode material. Four different current densities between 12.5-100 mA/cm^2 were tested with selected electrode. Then, pH effect was tested with three different initial pH values between 5-10. Parametric study experiments are given in detail in Figure 5.11.

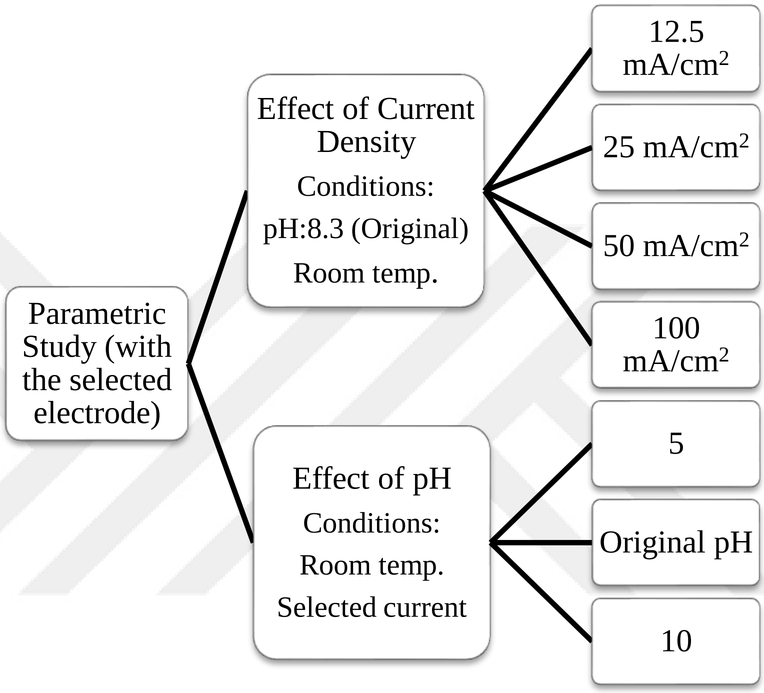


Figure 5.11. Parametric study experiments

5.7.2 Parametric study for adsorption

In the parametric study, the effect of adsorbent type, adsorbent dosage, and initial pH value were investigated to find the more suitable adsorbent with the higher removal efficiency (Tsai et al., 2001; Wu et al., 2001; Suteu et al., 2010; Yang et al., 2010; El-Sayed et al., 2014; Xie et al., 2013). Figure 5.12 summarizes the parametric study experiments for adsorption process which is the second step of hybrid process in this study.

Agricultural wastes were used to prepare the activated carbon as adsorbent. Corncob and walnut shell agricultural waste were used for preparation of two different adsorbent and results were compared. For both adsorbent, three different adsorbent dosages were tested to find optimum amount of adorbent and finally initial pH value was changed and effect of initial pH value was examined.

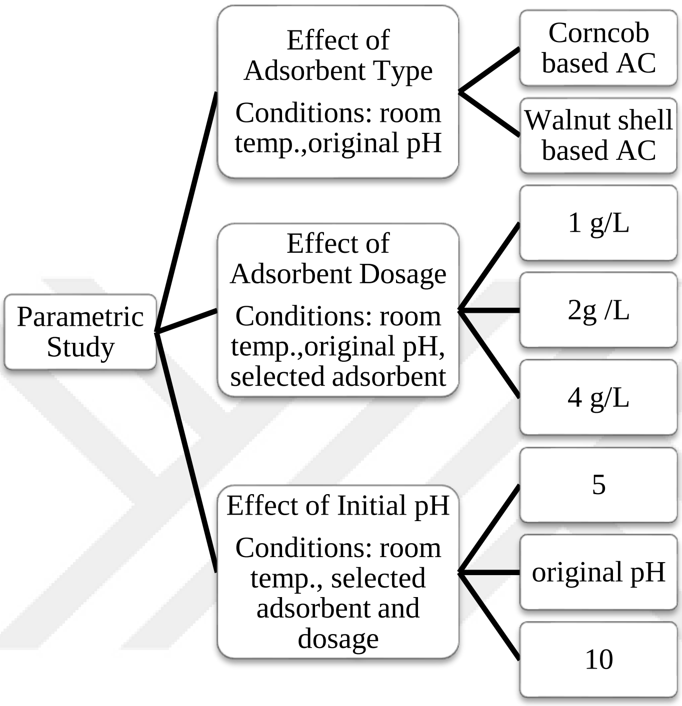


Figure 5.12. Parametric study experiments for adsorption

5.7.3 Parametric study for photo-Fenton like oxidation

Parametric study for photo-Fenton like oxidation process includes the tests on the effect of catalyst loading, initial pH, and hydrogen peroxide concentration. The following Figure 5.13 explains the details for these experiments.

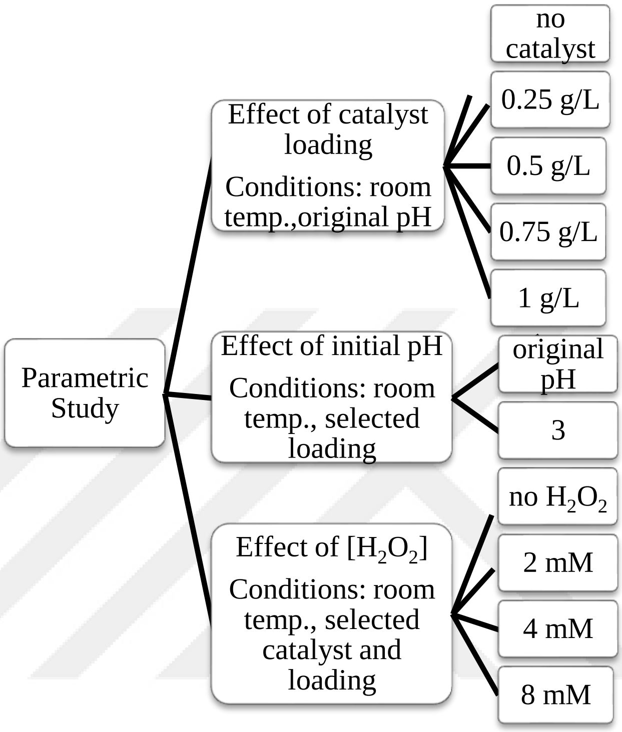


Figure 5.13. Parametric study for photo-Fenton like oxidation

5.8 Analysis

Total organic carbon, Chemical oxygen demand, turbidity, color, conductivity, pH, dissolved oxygen, and total suspended solid were analyzed. Shimadzu TOC-L TOC analyzer was employed for the analysis of TOC removal. COD cell kits, thermoreactor and VIS spectrophotometer were used for measuring of COD. The efficiency of COD and TOC are calculated using the following equation;

$$\mathrm{TOC, COD\ \ Removal,\ \%} = \left[\frac{A_o - A_t}{A_o}\right] \times 100$$

where,

A_o: the initial TOC, COD value, mg/L

A_t: the TOC, COD values measured at any time, mg/L

Turbidity was measured by WTW 550 Turbidimeter. For color measurement the absorbance values were measured at three different wavelenghts including 436 nm, 525 nm, and 620 nm indicating yellow, red, and blue colors, respectively. Color was determined by UV-VIS spectrophotometer (Thermo Genesys 10S).

Toxicity Tests;

The toxicity tests were performed by the comparison of the root lengths of the *Lepidium sativum* growing in the textile wastewater, distilled water, and treated wastewater at the end of the hybrid process to determine whether any toxic end products were generated at the end of the hybrid process. The seeds of the *Lepidium sativum* were purchased from a local market. 5 mL of textile wastewater, distilled water, and treated wastewater pipetted onto filter paper fitted into of plastic petri dishes separately. 25 seeds were dealt out uniformly on the dishes. The dishes were kept in the dark. At the end of the 96 hours, the lengths of the roots were measured for all of the mediums (Jonstrup et al., 2011, Almeida and Corso, 2014). In this study growth inhibition was calculated according to the following equation;

$$\text{Growth Inhibition} = \frac{RL_0 - RL_t}{RL_0} \; X \; 100$$

where, RL_o is average length of the roots growing in distilled water; RL_t is average length of the roots growing in treated wastewater by hybrid process.

6. RESULTS AND DISCUSSION

6.1 Adsorbent Characterization

The surface morphology of activated carbons obtained from the corncob and walnut shell based agricultural wastes were analyzed at 1000x and 2500× magnifications by Scanning Electron Microscope (Quanta 400F Field Emission). The surface area, pore volume, and pore diameter were determined by Brunauer, Emmett and Teller (BET) (Autosorb-6B). The samples were degassed at 300°C using nitrogen gas during 3 hours. The N_2 adsorption/desorption curves were carried out over a relative pressure, P/P_0. TGA-FTIR analyses were performed to understand the thermal behavior of the activated carbon between 30 and 950^{o}C at heating rate of 20°C/min and FTIR spectra were performed between 450 and 4000 cm^{-1} (Perkin Elmer Pyris STA 600 Thermogravimetric Analysis & Spectrum). All analyses were performed at Middle East Technical University, Materials Research Center and results are shown in following figures and tables.

6.1.1 SEM analysis

Scanning electron microscope results of the activated carbons obtained from walnut shells and corn cobs at 1000 and 2500 magnifications are given in Figure 6.1.

When the activated carbon surfaces are examined, it is seen that the activated carbon structure has a heterogeneous structure consisting of particles with different sizes and depths, which generally contain protrusions.

The different size cavities and gaps are occurred on the surface structure for both adsorbent. The formation of complex pore webs on the surface of adsorbents shows a sponge-like porous structure leading to large surface areas.

The pores and the cavities of the surface of the activated carbons at different sizes are formed by the evaporation of $ZnCl_2$, which is used as the activation agent in the process of active carbon preparation, during pyrolysis. In the literature, there are many studies related to preparation of activated carbon with different activation agent such as KOH, H_3PO_4, H_2SO_4, K_2S, HNO_3, H_2O_2, NaOH, and K_2CO_3.When compared the studies, $ZnCl_2$ is found to be the most preferred among them (Yahya et al., 2015; Donald et al., 2011; Yorgun et al., 2011).

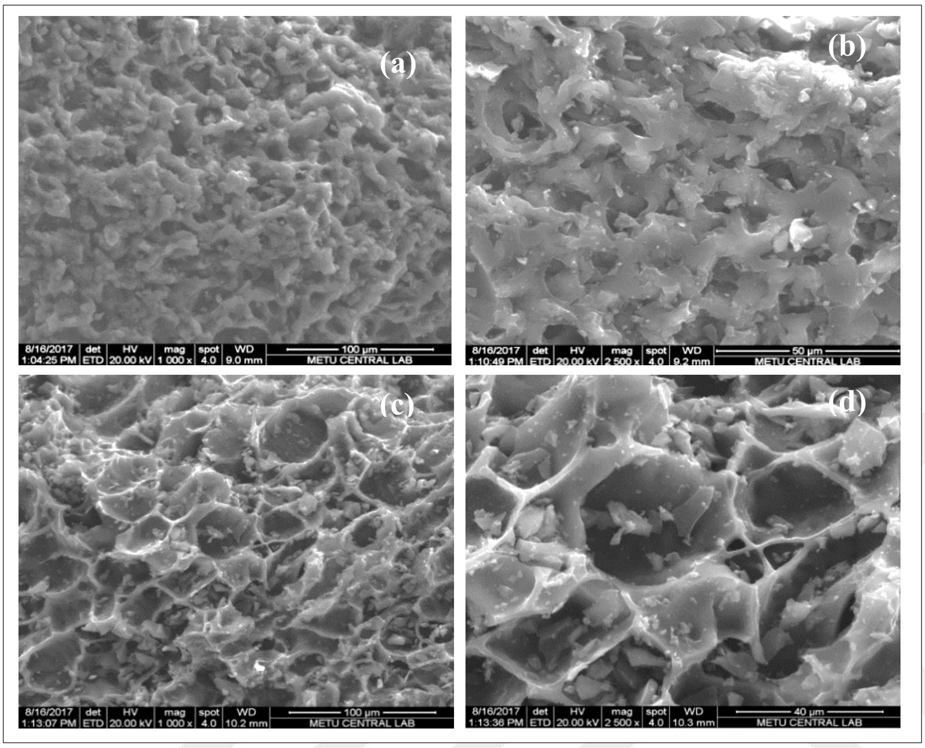


Figure 6.1. SEM analysis for walnut shell and corncob based activated carbon. (a) walnut shell based activated carbon-1000x times magnifications, (b) walnut shell based activated carbon-2500x times magnifications, (c) corncob based activated carbon-1000x times magnifications, (d) corncob based activated carbon-2500x times magnifications.

6.1.2 BET analysis

Surface area analysis was performed using nitrogen gas at 300 ° C degassing temperature and 3 hours degassing time.

Very high surface areas were found according to Brunauer -Emmett-Teller (BET) surface analysis results. The surface areas of activated carbons were obtained 1433 and 1364 m^2/g for corn cob and walnut shell adsorbents, respectively. The surface areas of both adsorbents were very close to each other but the surface area of corncob based activated carbon was higher with a small difference. The pore volume and pore diameter were found as 1.09 cm^3/g and 5.91 Å, 1.05 cm^3/g and

5.92 Å for corncob and walnut shell based AC adsorbent, respectively. The results are given in the Table 6.1.

Table 6.1. Surface area and pore size analysis results of different adsorbents

Biomass	Walnut Shell Based	Corncob Based
Activation Agent	$ZnCl_2$	$ZnCl_2$
BET Surface Area, m^2/g	1364	1433
Pore Volume, cm^3/g	1.05	1.09
Pore Diameter, Å	5.92	5.91

Other studies are reviewed in the literature and the findings are presented in Table 6.2. As seen in Table 6.2 the BET surface areas obtained by the same activation agent in the previous studies for the walnut shell was found to be close to the result of this study. For corn cobs, it was determined that the surface area obtained by the $ZnCl_2$ activation agent in the present study was higher than the surface areas obtained with the different activation agents in the previous studies, that is, $ZnCl_2$ is more successful than the activating agents previously used in the literature for corn cobs. Adsorbents may have micro (<2 nm), meso (between 2-50 nm) or macroporous (above 50 nm) structures (Liu et al., 2007) and micropores can be divided into ultramicropores (<0.7 nm) and supermicropores (between 0.7–2 nm) (Mamaní et al., 2019). When compared the pore diameter with other studies, it can be said that activated carbon prepared from corncob and walnut shell materials have ultramicropores structure. The differences in the pore diameter may be due to the type of chemical activation agent, and the ratio of the agent. The presences of micropore- structure increases the surface area of adsorbent. The usage of corncob wastes as a raw material for activated carbon is considered to be a significant development in terms of valorization of corn plant wastes having an important agricultural waste potency in our country.

Table 6.2. Comparison with the previous studies

Biomass	**Walnut Shell**	**Walnut Shell**	**Walnut Shell**	**Walnut Shell**	**Corncob**	**Corncob**	**Corncob**	**Corncob**
Activation Agent	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$	KOH	$ZnCl_2$	CO_2	KOH	H_3PO_4
BETSurface Area, m^2/g	1364	1452.1	803	1439	1433	759	466.37	600
Pore volume, cm^3/g	1.05	0.715	0.387	0.769	1.09	0.41	0.081	0.003
Pore diameter, Å	5.92	--	176	21.4	5.91	21.8	44	-
Referans	This Study	Nazari et al., 2016	Zabihi et al., 2010	Alimohammadi et al., 2016	This Study	Song et al., 2013	Tan et al., 2016	El-Sayed et al., 2014

N_2 adsorption-desorption curves are given in Figures 6.2 and 6.3. The adsorption isotherm types categorized by IUPAC classification are shown in Figure 6.4. According to the classification, corncob and walnut shell based activated carbon are compatible with Type 1 same as in the literature (Ioannidou et al.,2010). In Type 1 isotherms microporous is effective. Adsorption occurs by filling of the micropores and this type is suitable for monolayer adsorption and it can be easily explained using Langmuir Adsorption Isotherm.

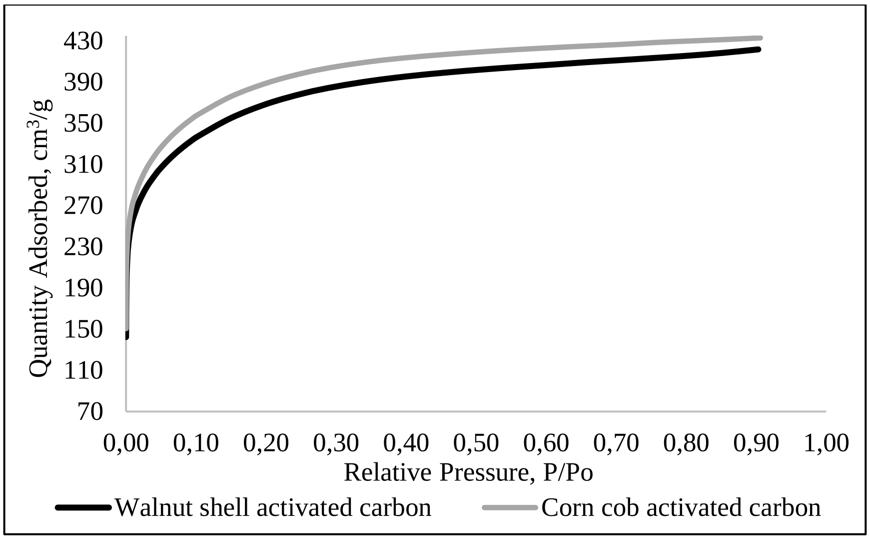


Figure 6.2. N_2 adsorption curves

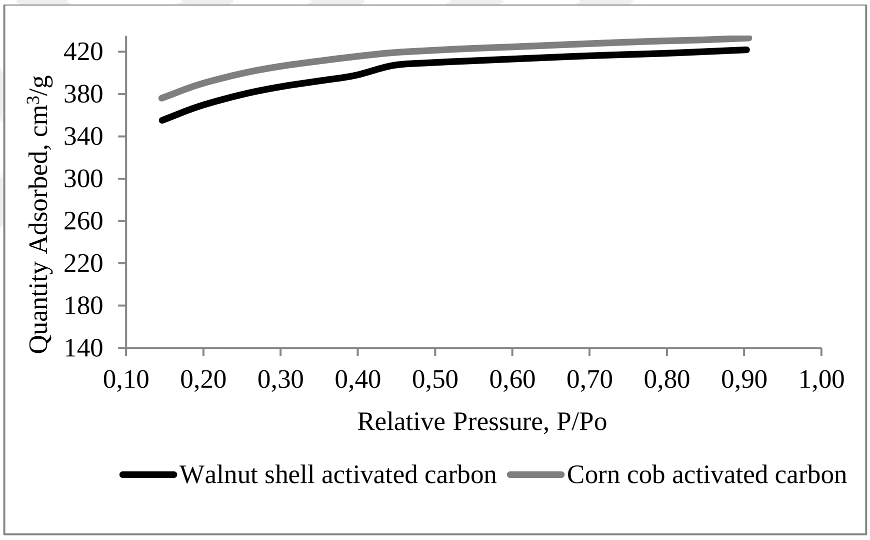


Figure 6.3. N_2 desorption curves

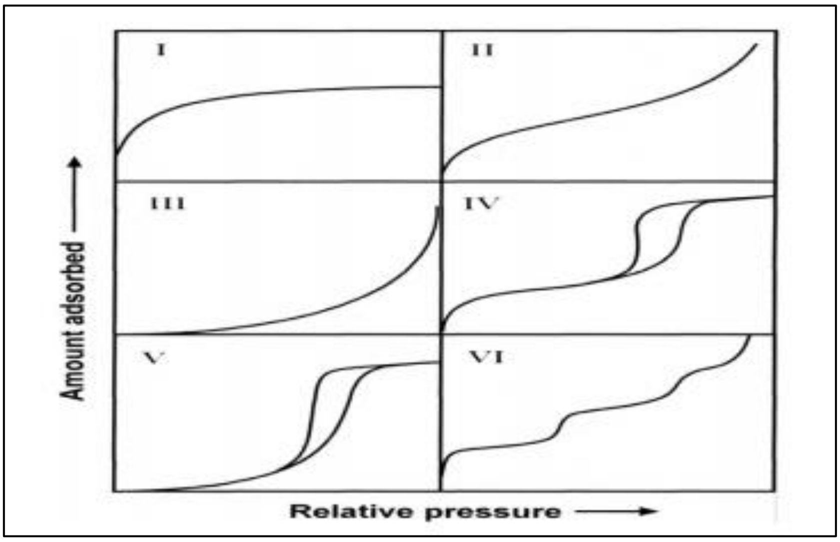


Figure 6.4. The IUPAC classification of adsorption isotherms (Alothman, 2012)

6.1.3 TGA and FTIR analyses

TGA and FTIR analyses for both adsorbents are shown in Figures 6.5 and 6.6. TGA analyses are examined between 30 and 950^{o}C at heating rate of 20°C/min. The weight losses were found 6.6% and 8.6% for walnut shell and corncob based activated carbon, respectively.

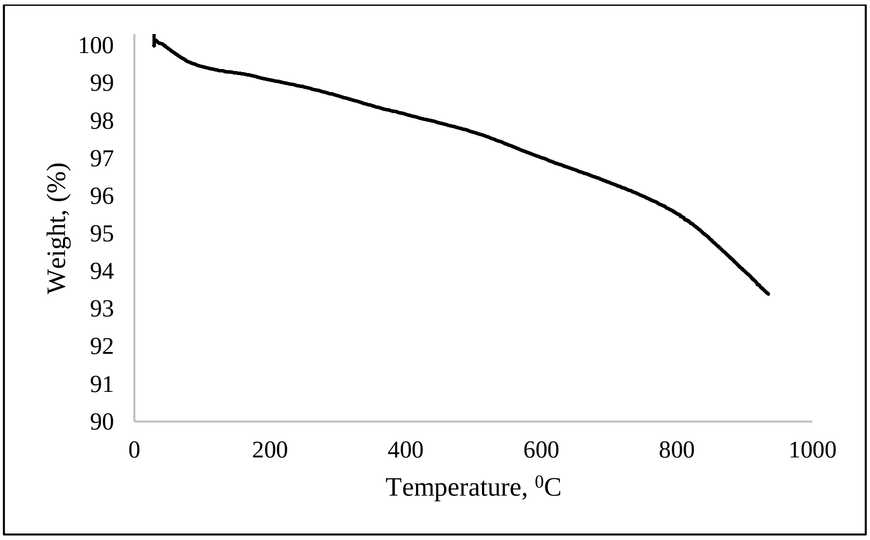


Figure 6.5. TGA analysis for walnut shell based activated carbon

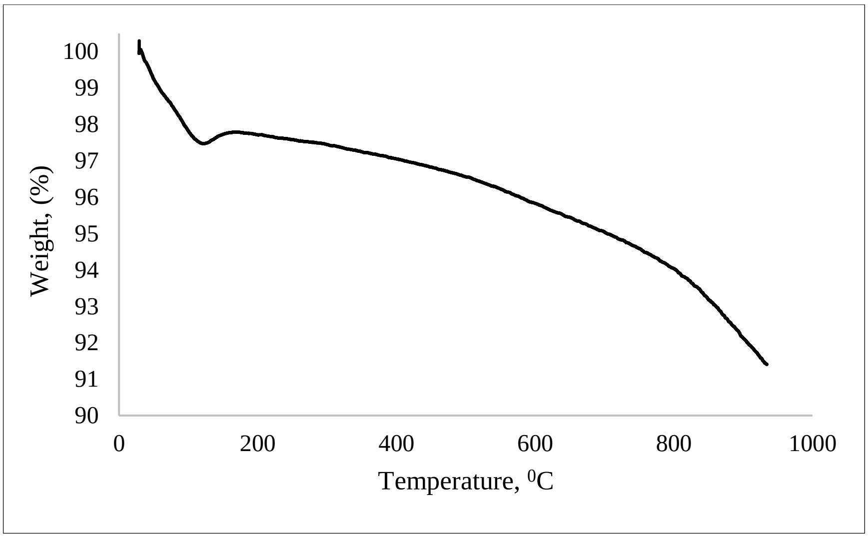


Figure 6.6. TGA analysis for corncob based activated carbon

According to these results, the loss of weight for both adsorbents are nearly same and it can be investigated in three stages. From the TGA obtained, it can be seen that between 50°C -150 °C there is a loss of nearly 1-3% of the initial mass in relation of moisture from the sample. In addition to moisture also loss is by volatile compounds. The loss between nearly 200-810^{o}C is due to elimination of the material such as cellulose, hemicellulose and a few lignin. In this stage the weight loss is found nearly totally 4-5% for both adsorbent. It can be said that beyond 800 ^{o}C 1-2% weight loss occurred. When compared the other activated carbon in the literature, it can be said that weight loss of activated carbon was very small at high temperature so that thermal stability is very high (Saka, 2012; Sun and Webley, 2010).

FTIR spectra at 900^{o}C for walnut shell based activated carbon and at 911 ^{o}C for corncob based activated carbon given in Figures 6.7 and 6.8.

FTIR results are found same for both adsorbent. From these figures the strong peaks are found between 3200-2800 cm^{-1} ,1800-1600 cm^{-1}, 1400-1200 cm^{-1}, and 800-600 cm^{-1}. The peaks which is occured between 3200-2800 cm^{-1} are assigned the presence of O-H groups. C=O functional group is occurred between 1800-1600 cm^{-1}. The peak about 1300 cm $^{-1}$ are assigned to vibration binding of C–O group and 800-600 cm–1 correspond to C–N/C–O/C–H bindings (Sun and Webley, 2010; Lıngegowda et al., 2012; Song et al., 2013).

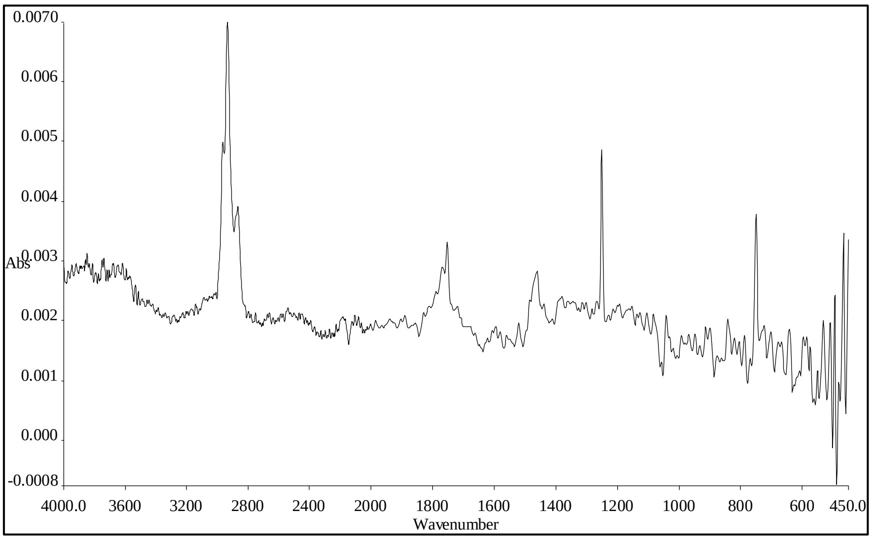


Figure 6.7. The FTIR spectra of walnut shell pyrolysis at 900ºC

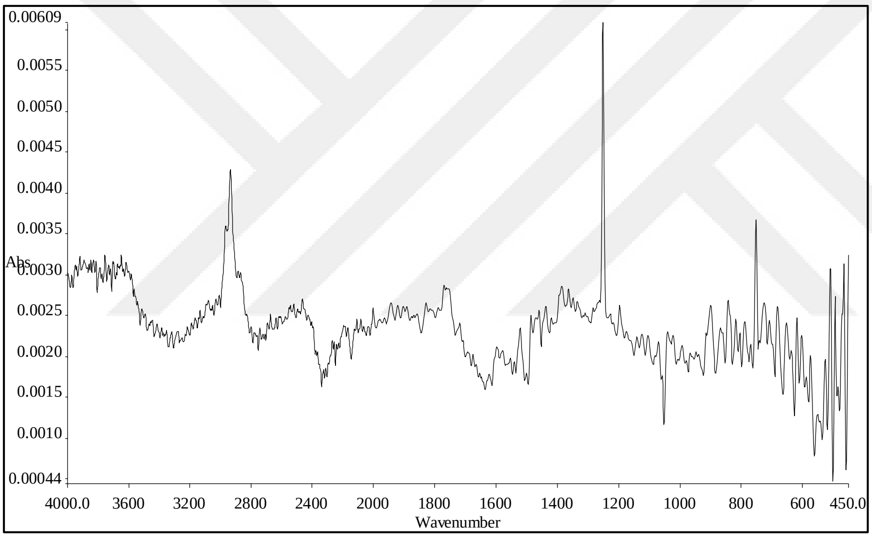


Figure 6.8. The FTIR spectra of corncob pyrolysis at 911ºC

6.1.4 Point of zero charge analysis

Point of zero indicates the pH at which the net charge on the activated carbon surface is zero. When the pH is lower than pH_{pzc}, the activated carbon surface is charged positively and when it is higher than pH_{pzc}, the surface is charged negatively.

The point of zero charge tests were performed as follows: 50 mL of 0.01 mol/L NaCl solution was placed in a titration vessel and the pH was adjusted to a value between 4 and 10 (4,5, 6, 7, 8, 9, 10) by addition of 0.1 mol/L HCl or 0.1

mol/L NaOH solutions. 0.15g carbon sample was added to the solution and after 3 hours final pH was measured. After that, final pH value plotted against the initial pH value (Rivera-Utrilla et al, 2001). The pH_{pzc} value is the point of the $pH_{initial} = pH_{final}$ intersects on the curve.

The graph of final pH value is given in Figure 6.9. According to the Figure 6.9, the point of zero charge of walnut shell and corn cob based activated carbon adsorbents was found around 7.

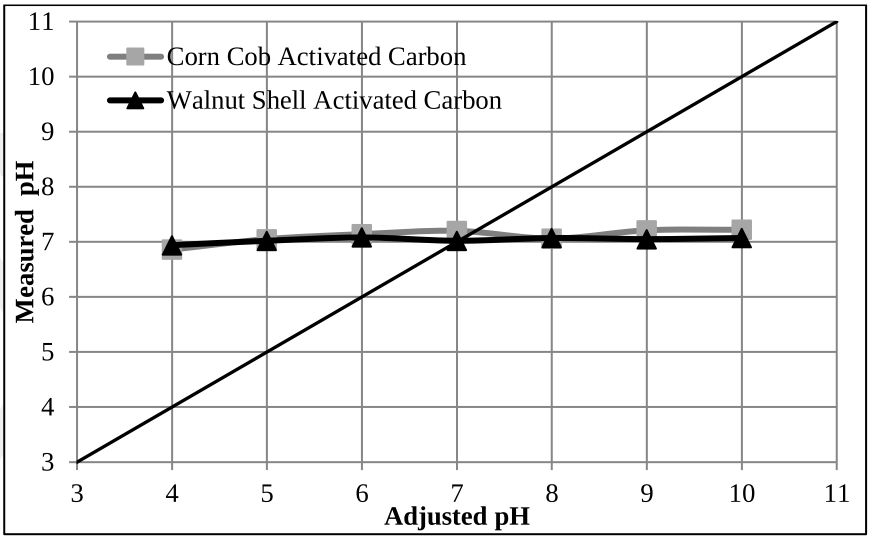


Figure 6.9. Point of zero charge analysis

6.2 Catalyst Characterization

The surface morphology of $BiFeO_3$/corncob based AC and $BiNiO_3$/corncob based AC catalysts were analyzed at 5000x and 10000x magnifications by Scanning Electron Microscope (Carl Zeiss 300VP). The surface area was determined by Brunauer, Emmett and Teller (BET). TGA analysis was performed to understand the thermal behavior of the catalyst between 25 ^{o}C and 1000^{o}C (TA Instruments SDT Q600). The SEM analysis was performed at Katip Çelebi University and the TGA analysis was performed at Ege University, Central Research Test and Analysis Laboratory Application and Research Center. The results are given in the following figures and tables.

6.2.1 SEM analysis

The results of scanning electron microscope analyses for catalysts at 5000 and 10000 magnifications are given in Figure 6.10 and 6.11.

When SEM results of catalysts are examined, it has been observed that the catalyst has a heterogeneous structure with cornered particles formation in various shapes and sizes. When compared the two catalysts, it is seen that $BiNiO_3$/ corncob AC catalyst has more porous structure.

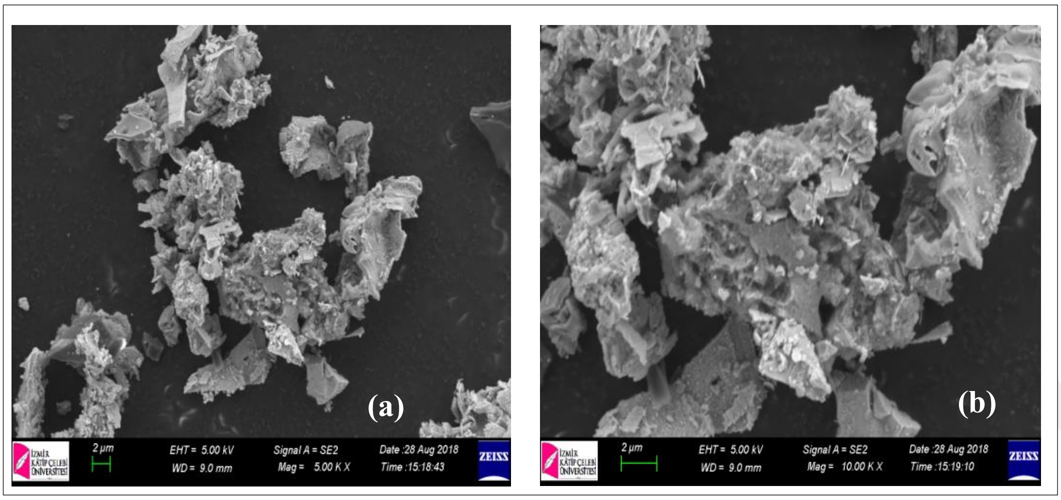


Figure 6.10. SEM analysis for $BiFeO_3$/corncob AC catalyst (a) 5000x magnification (b)10000x magnification

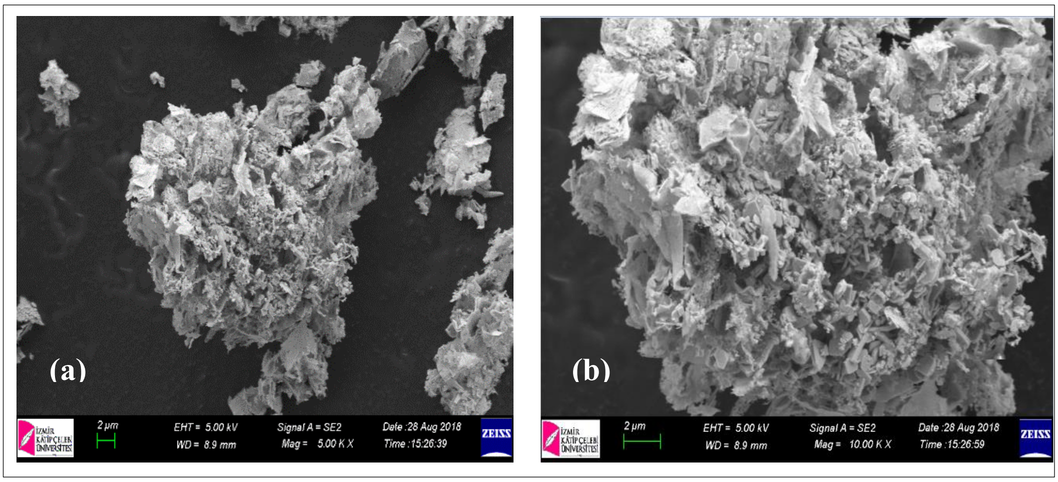


Figure 6.11. SEM analysis for $BiNiO_3$/corncob AC catalyst (a)5000x magnification (b)10000x magnification

6.2.2 BET analysis

According to the BET surface areas of catalysts, it is seen that the highest surface area is observed for the $BiNiO_3$ corncob AC supported catalyst. BET surface areas of catalysts were found 399.46 m^2/g and 845.73 m^2/g for $BiFeO_3$ and $BiNiO_3$ corncob AC supported catalysts, respectively. When compared the literature studies related to the perovskite type catalyst, using corncob activated carbon as support material caused an increase in surface area (Leanza et al., 2000; Su et al., 2014). The results are given in Table 6.3.

Table 6.3. BET Analyses of Catalysts

Catalyst	$BiNiO_3$-corncob AC	$BiFeO_3$-corncob AC
Activation agent	$ZnCl_2$	$ZnCl_2$
BET Surface Area, m^2/g	845.73	399.46
Pore Volume, cm^3/g	0.39	0.38

The surface areas of the $BiFeO_3$/corncob and $BiNiO_3$/corncob AC catalysts are low when compared to the activated carbon obtained from the corncob. This is an expected result due to the filling of the pores of the activated carbon by the metal oxides. The pore volumes for both activated carbons are low when compared to the activated carbon and very close to each other.

N_2 adsorption curves are given in Figure 6.12 for $BiFeO_3$/corncob and $BiNiO_3$/ corncob AC catalyst and desorption curves are given in Figure 6.13. According to the IUPAC classification, $BiNiO_3$ is compatible with Type 1 and $BiFeO_3$ catalyst is compatible with Type II same as in the literature. In Type 1 isotherms microporous structure is effective with a monolayer adsorption and in Type II isotherm reflects the macroporous or non-porous structure. In this type isoterms, the catalyst conforming to the Type II isotherm are suitable for both single- and multilayer adsorption, and the turning point at the end of the isotherm curve generally indicates the point where single-layer adsorption is complete and the multilayer adsorption begins.

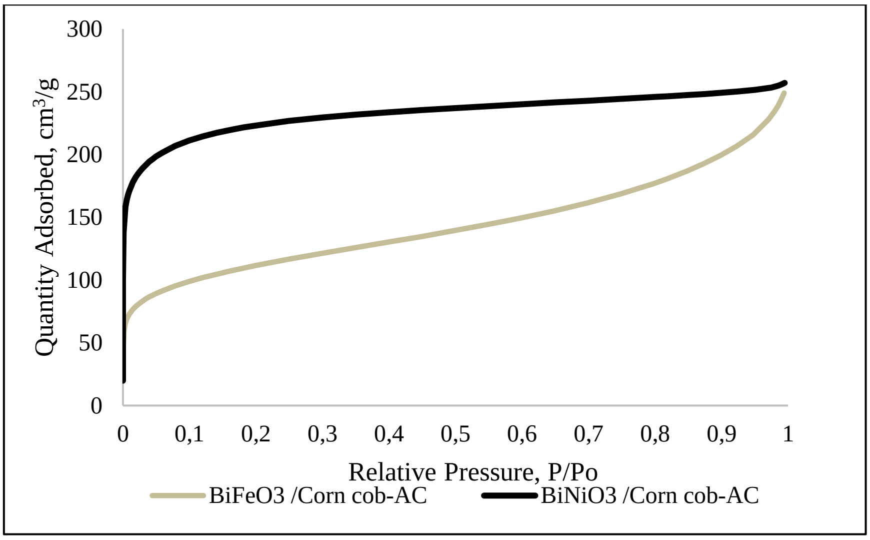


Figure 6.12. N_2 adsorption curves for $BiFeO_3$/corncob and $BiNiO_3$ /corncob AC catalyst

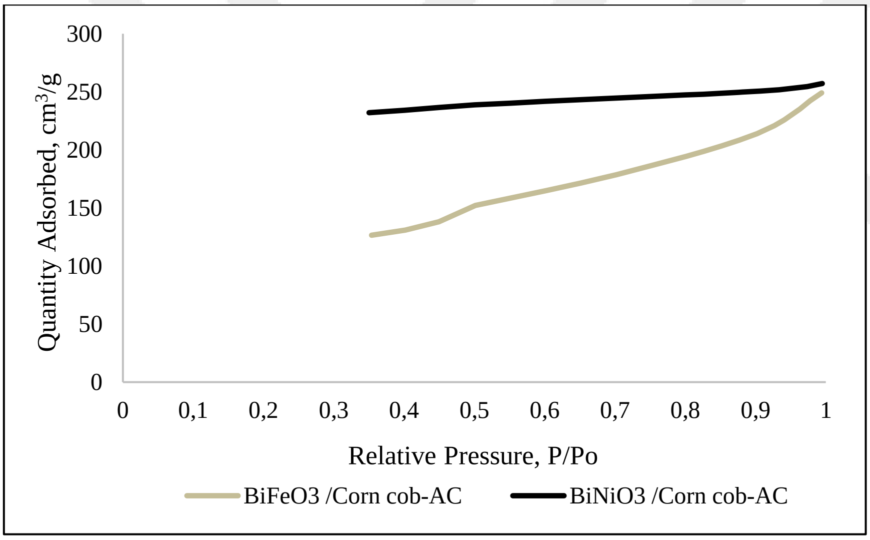


Figure 6.13. N_2 desorption curves for $BiFeO_3$ and $BiNiO_3$ corncob AC catalyst

6.2.3 TGA analysis

The TGA curves obtained for $BiFeO_3$/corncob AC and $BiNiO_3$/corncob AC catalysts are given in Figure 6.14 and 6.15, respectively. According to these figures, a mass loss of about 10% was observed in the range of 100-200 ° C for both catalysts. This loss was associated with the removal of the water in the structure. The changing of original structural was observed after about 450 ° C and the mass loss was reached 35-40% at 950 °C. Since the studied temperature in the experiments is lower than 450 ° C, it can be concluded that the thermal stability of the catalyst is high below 450°C.

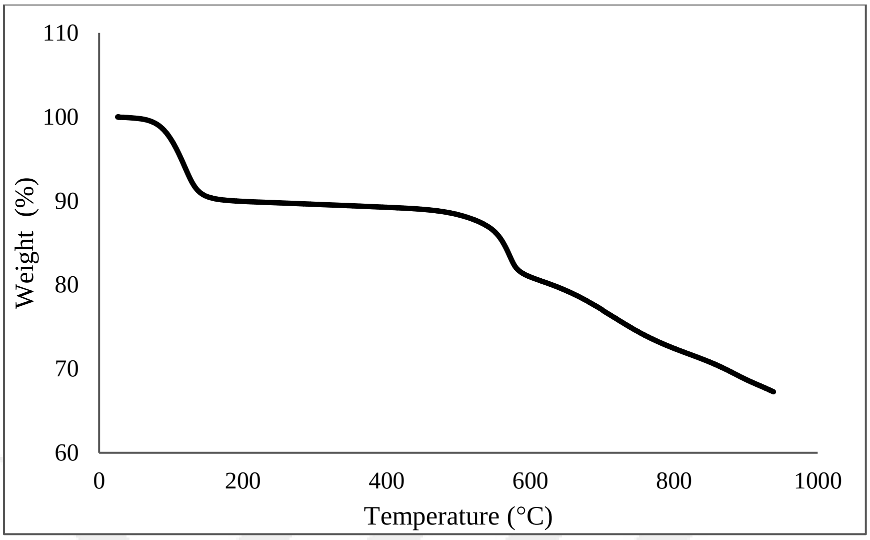


Figure 6.14. TGA analysis of $BiFeO_3$ /corncob AC catalyst

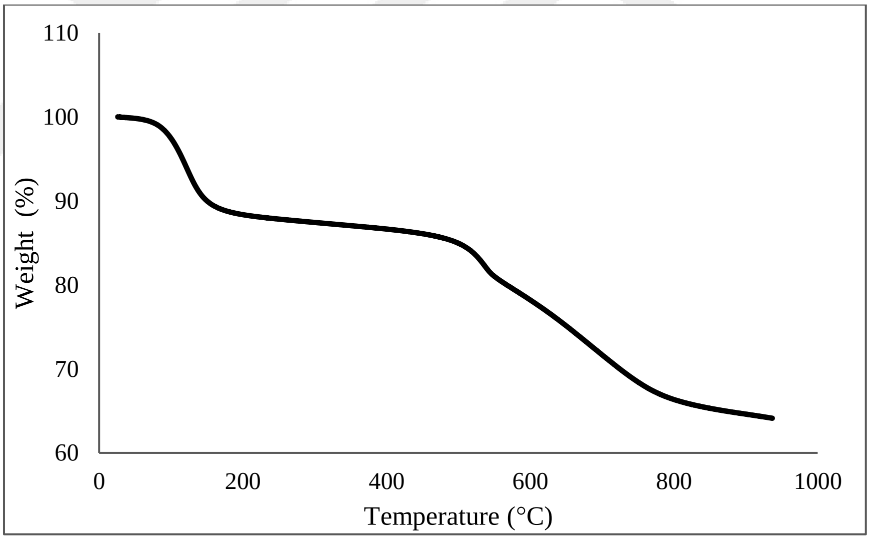


Figure 6.15. TGA analysis of $BiNiO_3$/corncob AC catalyst

6.3 Results of Electrocoagulation

6.3.1 Electrode selection

Iron and aluminum are widely used electrodes for electrocoagulation and hence the TOC removal efficiencies of the two were tested. In the literature there are many studies with various type of electrodes but it was seen that these electrodes can generate some harmful elements such as Pb^{2+} which cause another pollution in the wastewater. Al electrodes are recommended for the reasons of low cost and easy accessibility (Elazzouz et al.,2018; Garcia-Segura et al., 2017; İlhan et al., 2008 and Demirci et al., 2015).

The experiments were carried at original pH (8-8.5), at room temperature and at a voltage of 3V in the presence of the iron or aluminum electrodes to compare the performance of the electrodes. The results of TOC removal with respect to current density is shown in Figure 6.16.

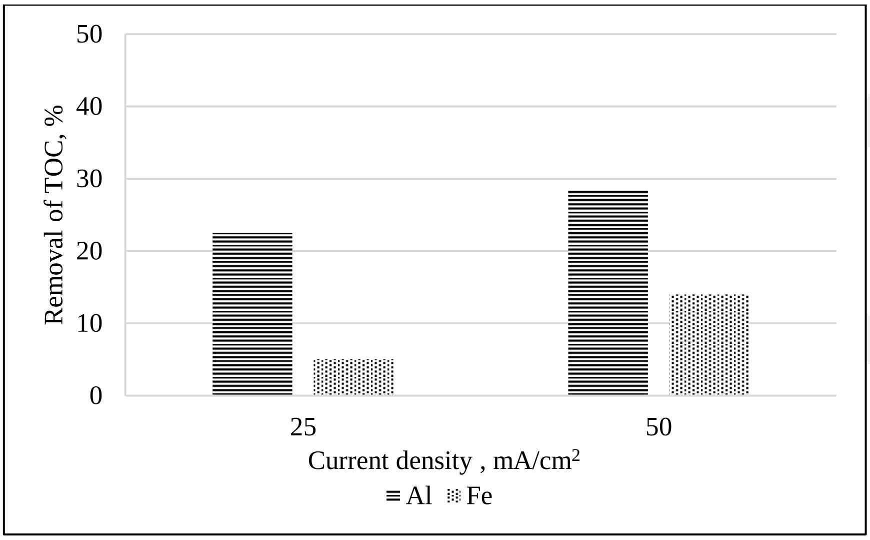


Figure 6.16. Electrode selection ([TOC]=236-253 mg/L, pH=8.3, room temp.)

Two different current densities were tested for electrode selection experiments. 22.5% and 28.5% TOC removal efficiencies were obtained using Al electrode, whereas 5% and 14% were achieved using Fe electrodes for 25 and 50 mA/cm^2 of current densities, respectively. For both current densities the TOC removal performance of Al electrode was higher than Fe electrode for both of the current densities. In addition, higher corrosion occurred in the presence of Fe electrode. Therefore, Al electrode was selected for the treatment of in-situ pre-treated textile wastewater and the parametric study was carried out in the presence of Al electrode same as Omwene and Kobya (2018), Alimohammadi et al., (2017), and Sharma et al., (2018).

6.3.2 Effect of current density

The main parameter for electrocoagulation is the amount of generated coagulant. It is directly related to current density and reaction time (Kabdaşlı et al., 2012). For this purpose, electrocoagulation process was carried out using various current densities and results are given in Figure 6.17.

The effect of current density on TOC removal efficiency was investigated by varying the current density between 12.5 and 100 mA/cm^2 at original pH and at room temperature. From Figure 6.16, it can be concluded that the removal percentage increased with increasing current density, and the maximum removal efficiency was found at 100 mA/cm^2 of current density. The lowest removal was found at 12.5 mA/cm^2. When the current density was doubled, removal efficiency was improved from 10 to 22.5%. When the current densities were 50 and 100 mA/cm^2 removal efficiencies of TOC were achieved 28.5% and 34.42%, respectively. The findings are in good accordance with the literature. Removal efficiency increases with increasing time and current density because with increasing current density generates more of metal ions which are coagulant agents and hydrogen bubbles increased (Nariyan et al., 2017; Azarian et al., 2018).

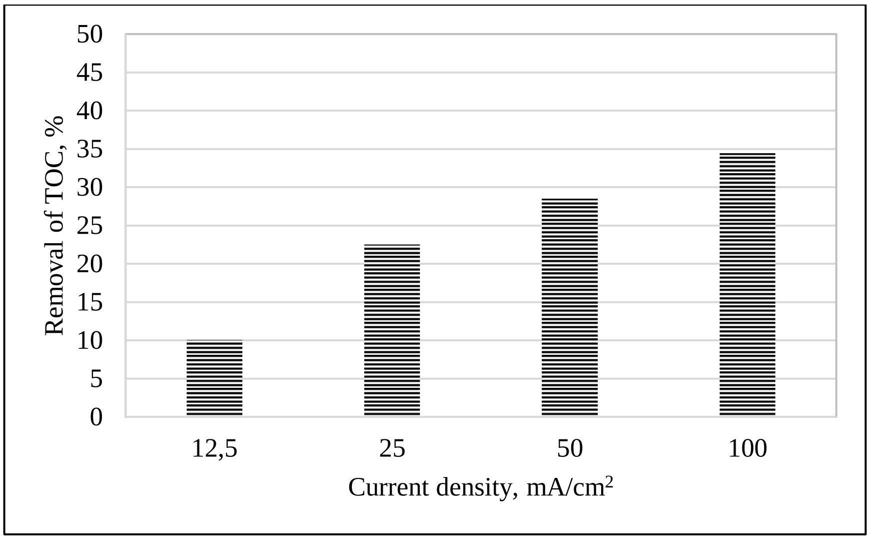


Figure 6.17. Effect of current density ([TOC]=252-256 mg/L, pH=8.3, room temp.)

Electrodes were weighed before and after the experiment and loss of mass of electrodes was also determined. The loss of mass increased from 0.06 g to 1.2 g as the current density was increased from 12.5 to 100 mA/cm^2.

According to these results, there was no significant increase in TOC removal efficiency at current values higher than 25 mA/cm^2. Since cost of the treatment increased and corrosion of electrodes was remarkable at high current densities (Zazouli and Taghavi, 2012), 25 mA/cm^2 current density was recommended as the optimum current density.

6.3.3 Effect of pH adjustment

It is well known that the EC process is highly dependent on the initial pH of the wastewater. The generation of metallic hydroxides depend on the pH of the aqueous solution and the initial pH of wastewater affects the performance of electrocoagulation (Khemila et al.,2018 Bassyouni et al., 2017).

Three different pH values were tested to investigate the effect of pH adjustmen of wastewater. During the experiments, the current density was set to 25 mA/cm^2 at room temperature. As shown in Figure 6.18, TOC removal was determined as 23 % at the original pH (7.5-8) of the pre-treated real textile wastewater. When the pH value was set to 5, 40-45% TOC removal occurred by the pH adjustment. After pH adjustment, the TOC removal was improved up to 65% by electrocoagulation at pH 5. This can be explained by the dissolved organic carbon abatement occured due to the formation of foam and precipitation of some organic compounds at pH value between 4-6.5 (Soares et al.,2014, Khorram and Fallah, 2018).

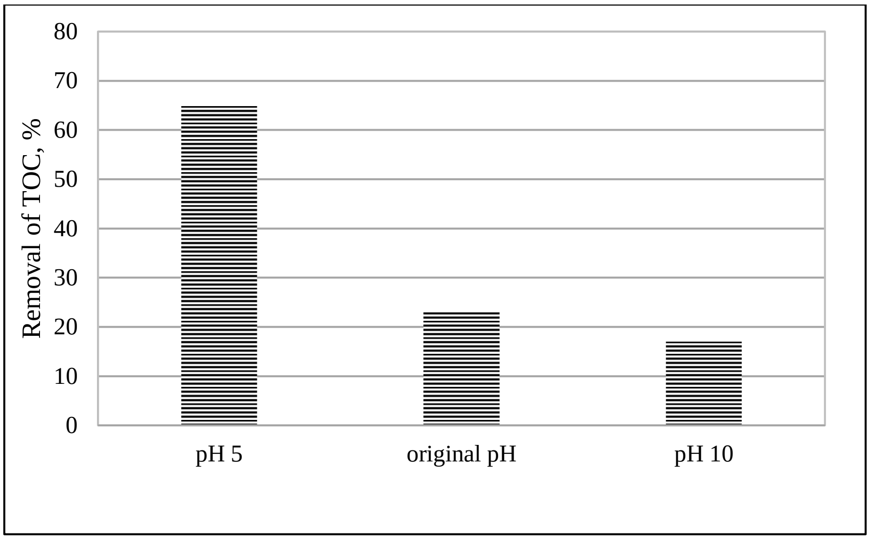


Figure 6.18. Effect of pH adjustment on total TOC removal ([TOC]=236-252 mg/L, current density = 25 mA/cm^2, room temp.)

Though the initial pH value was set to 5, final pH increased to 7-7.5 at the end of the experiment. The reason of this increase can be explained by the formation of hydrogen gas and the accumulation of hydroxide after reduction of water in the cathode (Can et al., 2003; Sahu et al., 2015; Karagözoğlu and Malkoç, 2017). Because between pH 5 and 6, the dominant aluminum species are $Al(OH)^{2+}$ and $Al(OH)^{3+}$, which act as a coagulating agent, the lowest TOC removal efficiency was evaluated at pH 10. At high pH values, the removal efficiency of this contaminant was lower due to the formation of soluble [such as $Al(OH)^{4-}$] aluminum complexes (Cerqueira et al., 2009).

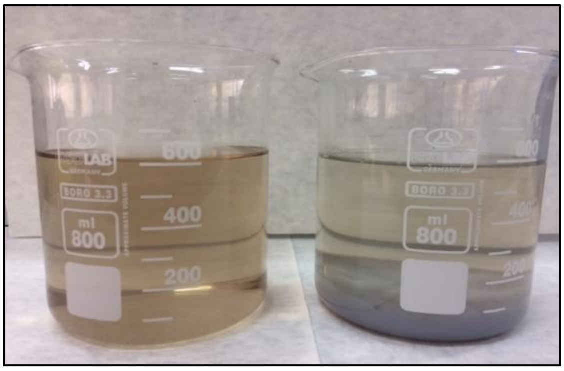
6.3.4 Evaluation of water standard values after electrocoagulation

All experiments were completed for the electrocoagulation method and optimum conditions were determined. After the optimum conditions were decided, water was subjected to the second stage which was adsorption. All the removal efficiencies by electrocoagulation are summarized below in Table 6.4. These results were obtained at optimum conditions.

After adjusting the pH, the TOC removal was found to be 64.8 % at the selected current value. An effective treatment has also been obtained in turbidity and color removal. The color values were adjusted to the water standards and the removal efficiency of turbidity value was found 83%. Before and after electrocoagulation appearance of wastewater was given in Figure 6.19.

Table 6.4. Collected wastewater after EC treatment at optimum conditions (CD: 25 mA/cm^2, pH=5, room temperature)

		Initial Value	**Final Value**	**Final Removal, %**	**Usual range in irrigation water (based on class A -class B)**
TOC (mg/L)		225.6	79.24	64.8	5-8
Turbidity (NTU)		24.3	3.8	83.5	1
Conductivity (mS/cm)		7.44	7.27	-	0.7-3
Salinity (ppt)		4.09	3.99		-
pH		8.17	7.2	-	6.5-8.5
Total Suspended Solid (mg/L)		34	12	64.7	30-20
Color (1/m)	436 nm	29	2.8	-	7
	525 nm	25	1.6	-	5
	620 nm	17.7	0.9	-	3



before after

Figure 6.19. The change of appearance of wastewater before and after EC treatment

As a conclusion, it can be said that electrocoagulation method was very effective for the removal of color and total suspended solid, especially. Also, this method can be used for the removal of total organic carbon. However, when compared with the irrigation water criteria, this method is not sufficient for the wastewater used. Therefore, it is aimed to increase the water quality with other treatment methods.

6.3.5 Solid waste in electrocoagulation

Solid waste generation is the disadvantage of the electrocoagulation method. During the electrocoagulation experiments, the generated solid amount was calculated for different current density values. It was observed that the solid amount increased as the current density increased. 0.35 g/L solid waste was generated for 12.5 mA/cm^2, and 2.96 g / L solid waste was generated for 50 mA/cm^2. The resulting solid was filtered through the solution and then dried at 105 °C. The solid formed is given in Figure 6.20;

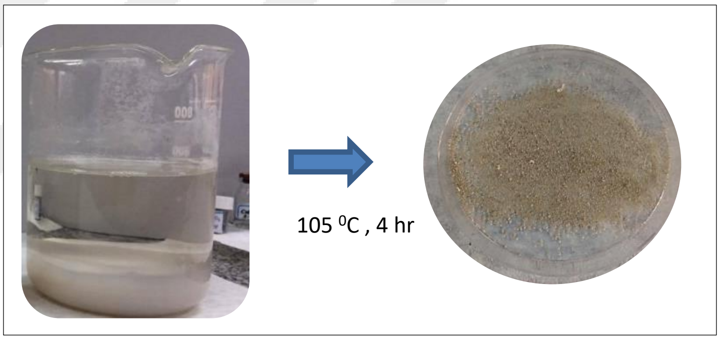


Figure 6.20. Solid waste

6.3.6 Sludge characterization in electrocoagulation

The characteristic properties of the generated sludge from EC was investigated by SEM-EDX analysis. This analysis was investigated at optimum operating conditions which were room temperature, initial pH value 5, and 25 mA/cm^2 current density.

SEM analysis was examined to determine of the sludge morphology. Also, EDX analysis was led to understanding of the elemental analysis of the generated sludge. SEM images of samples are given in Figure 6.21 with two different magnification. The images of the samples were seen as lumpy particles. According to the Figure 6.22, the EDX results, electrocoagulation sludge includes mainly Al, O, C, Mg, and Ca. The sludge includes nearly 18% Al, 53% O, and 23% C. In the literature same results were reported by researchers (Hafez et al., 2018; Nasrullah et al., 2018; Roa-Morales et al., 2014; and Elazzouzi et al., 2018). All analysis were performed at Katip Çelebi University in İzmir.

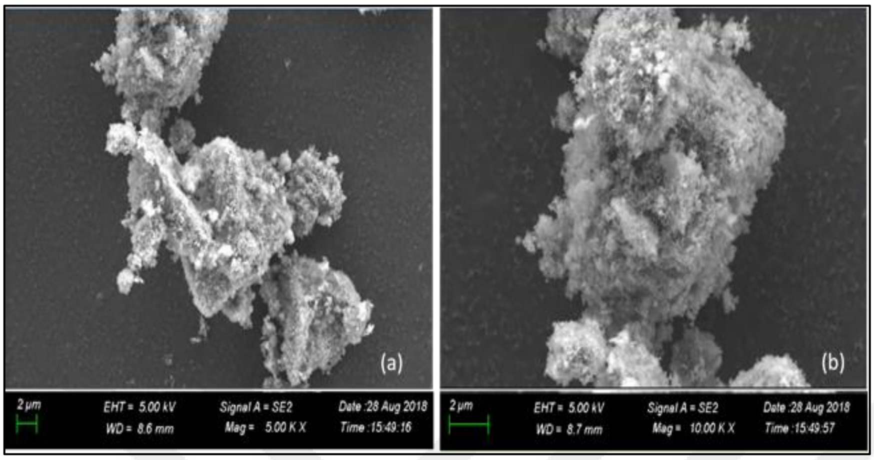


Figure 6.21. SEM analysis for sludge of electrocoagulation, (a)5000x magnification; (b)10000x magnification

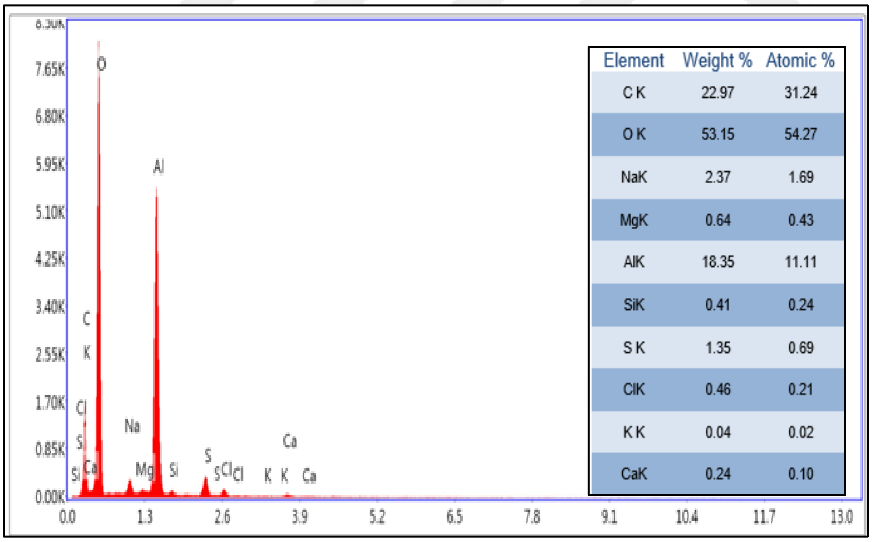


Figure 6.22. SEM-EDX analysis of electrocoagulation sludge

6.3.7 Cost analysis

Economic investigation for EC, the operating cost was calculated by considering two parameters as major cost items (Kobya et al., 2016); amount of energy and electrode material consumptions with the following equations 10,11 and 12;

$$C_{energy} = \frac{U*t*I}{V}\left(\frac{kWh}{m^3}\right) \quad (10)$$

$$C_{electrode} = \frac{I*t*MW}{z*F*V}\left(\frac{kg}{m^3}\right) \quad (11)$$

$$Total\ cost\ (\$/m^3) = x^{**} * C_{electrode} + y^{**} * C_{energy} \quad (12)$$

Where U is the applied voltage (3 Volt), I is the applied current (0.5 A), t is the time (7200 sec) and V is the volume of wastewater (0.0006 m^3), MW is the molecular weight of aluminum (27 g/Mol), z is the number of moles of electron involved in the reaction (Al = 3) and F is the Faraday constant (F = 96500C/ Mol) and ;

- $C_{electrode}$: Electrode consumption per 1 m^3 of treated water
- C_{energy} : Energy requirement per 1 m^3 of treated water
- x**: Electrode prices $/kg
- y**: Electrical energy prices $/kWh

According to the Turkish market in February 2019, prices for electrical energy were 0.12 US $/kWh, and prices for Al and Fe electrode materials were 4.5 and 3.7 US $/kg. In the following Table 6.5 the effect of current on the cost of EC method is summarized. As seen in the equations used, the current is directly proportional to the cost economy. When the current is increased, the cost of the system increases proportionally.

Table 6.5. Cost analysis for all current

Current (A)	**0.25**	**0.5***	**1**	**2**
Electrode Cost (kg/m^3)	0.275	0.55	1.1	2.2
Energy Cost (kWh/m^3)	2.08	4.16	8.32	16.64
Total Cost ($\$/\boldsymbol{m^3}$)	1.48	2.97	5.95	11.89

Operating costs for EC were calculated using selected current and electrode type and process shown below;

$$C_{electrode} = \frac{I * t * MW}{z * F * V}\left(\frac{kg}{m^3}\right) = \frac{0.5 * 2 * 3600 * 27}{3 * 96500 * 0.0006} = 0.55\,\frac{kg}{m^3\ of\ water}$$

$$C_{energy} = \frac{U * t * I}{V}\left(\frac{kWh}{m^3}\right) = \frac{2.5 * 2 * 0.5}{0.0006} = 4.16\,\frac{kWh}{m^3\ of\ water}$$

$$Total\ cost = x^{**} * C_{electrode} + y^{**} * C_{energy} = 4.5 * 0.55 + 0.12 * 4.16 = 2.97\ \$/m^3$$

6.3.8 Kinetic study for electrocoagulation

Up to this point the parameters were optimized for the electrocoagulation method.

In order the determine the suitable kinetic model, experiments were performed at various current densities such as 12.5 mA/cm^2, 25 mA/cm^2, 50 mA/cm^2, and 100 mA/cm^2. The experiments were performed at room temperature with Al electrodes. The total organic carbon data (C_{A}, mg/L) were collected at different batch times such as 30, 60, 90, 120 minutes. The collected data are given in Table 6.6.

Table 6.6. Collected data for electrocoagulation kinetic study

Time (min)	**TOC values (mg/L)**			
	12.5 mA/cm^2	**25 mA/cm^2**	**50 mA/cm^2**	**100 mA/cm^2**
0	52.0	52.0	52.0	52.0
30	50.0	48.3	47.3	43.7
60	48.2	44.2	42.6	41.6
90	47.4	42.6	40.0	36.5
120	46.0	40.0	38.2	33.0

The first and second order reaction kinetic models were proposed and the equations 13 and 14 are given below;

$$-\frac{dC_{TOC}}{dt} = k_1 C_{TOC} \qquad (13)$$

$$-\frac{dC_{TOC}}{dt} = k_2 {C_{TOC}}^2 \qquad (14)$$

The integrated forms of Equations 13 and 14 at $C_{TOC} = C_{TOC_0}\ at\ t = 0$;

$$ln\ \frac{C_{TOC_0}}{C_{TOC_t}} = k_1 t \qquad (15)$$

$$\frac{1}{C_{TOC_t}} = \frac{1}{C_{TOC_0}} + k_2 t \qquad (16)$$

where, C_{TOC_0} and C_{TOC_t} are the initial TOC and TOC at any time (t), respectively. k_1(min^{-1}) and k_2 (L/mg.min) are the first and second order reaction rate constants, respectively.

In order to observe suitability of first or second order kinetic models explain the TOC reduction, for first order model ln(C_{TOC_0}/C_{TOC_t}) versus time and for second order model (1/C_{TOC_t}) versus time at various current densities were plotted and are given Figure 6.23 and 6.24.

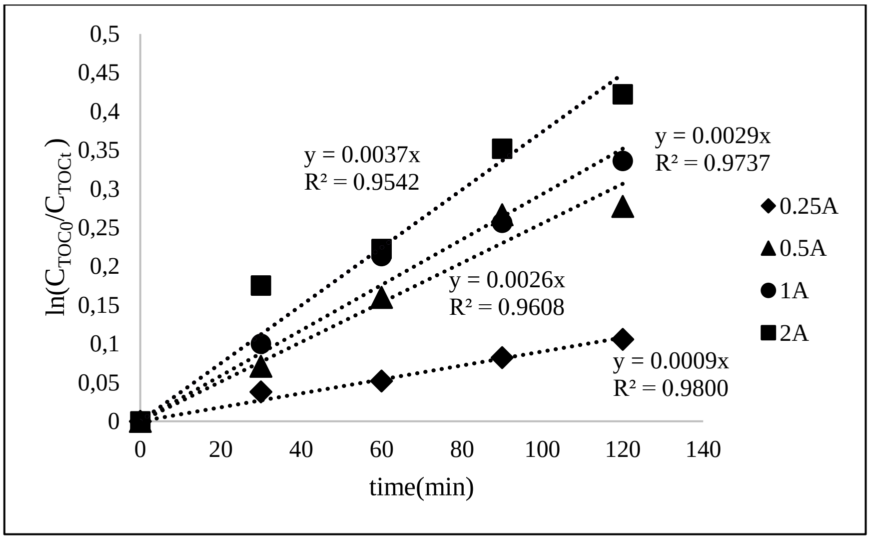


Figure 6.23. 1^{st} order kinetic model for electrocoagulation ($[TOC]_0$=50-52 mg/L, Al electrode, room temp.)

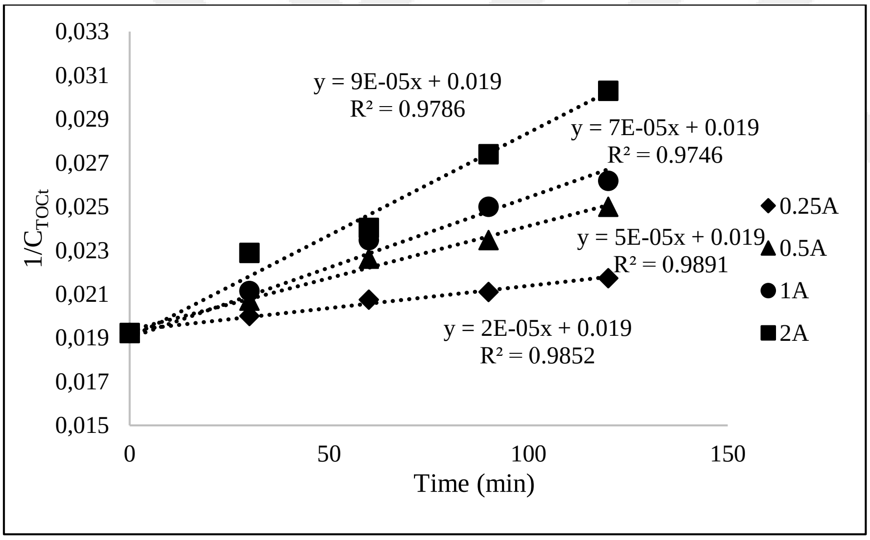


Figure 6.24. 2^{nd} order kinetic model for electrocoagulation ($[TOC]_0$=50-52 mg/L, Al electrode, room temp.)

The values of the rate constants and regression coeffcients were calculated according to these graphs and from Figure 6.23 and 6.24, TOC data fit a straight line for both models. The reaction rate constants for current densities of 12.5, 25, 50 and, 100 mA/cm^2 were evaluated as 0.009, 0.0026, 0.027 and 0.0037 min^{-1} for first order kinetic model. The second order reaction rate constants were found to be $2*10^{-5}$, $5*10^{-5}$, $7*10^{-5}$ and, $9*10^{-5}$ (L/mg.min), respectively. Rate constants increased with increasing current density for both of the kinetic models.

Also, Murthy and Parmar, Chou, and Sangal et al., reported that the reaction rate increased with increasing current densities (Murthy and Parmar, 2011; Chou, 2009; and Sangal et al., 2013). The regression coefficients were calculated in the range 0.95-0.980 and 0.974-0.989 for first and second order kinetic models, respectively. For both kinetic models, R^2 were found close to unity. The second-order kinetic model is more suitable in terms of higher regression coefficient when compared to first order regression coefficient.

To understand the relationship between the current density and reaction rate, current density are plotted against second order reaction rates values and is given in Figure 6.25. Power law relation was considered and rate constant versus current density were plotted with the following Equation 17 to find the coefficients of equation (Al-Shannag et al., 2014; El-Shazly et al., 2013);

$$k = \alpha * I^{\beta} \qquad (17)$$

Which linear form is;

$$lnk = ln\alpha + \beta lnI \qquad (18)$$

Where ;

β and α : arbitrary constants

k : rate constant, L/(mg.min)

I: current density, mA/cm^2

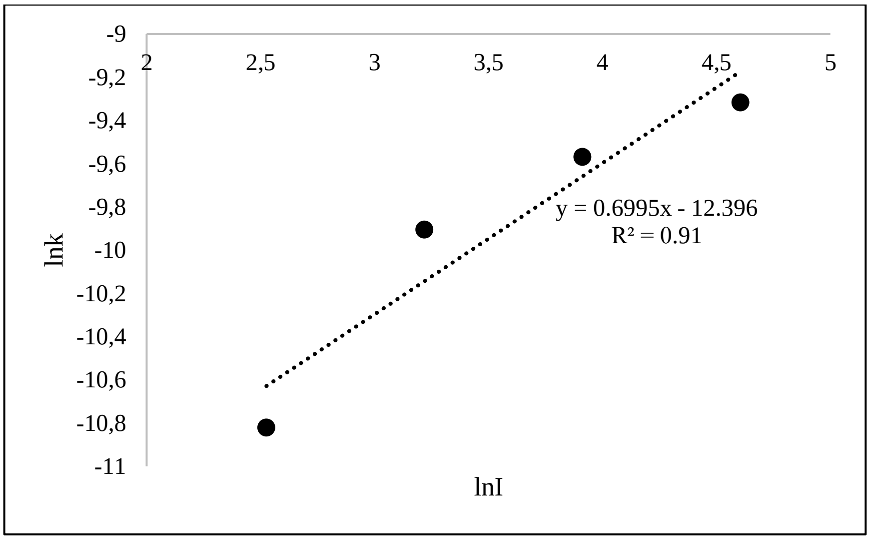


Figure 6.25. Relationship between rate constant and current density

According to the Figure 6.25 β and α were found 0.69 and $4*10^{-6}$, respectively. The Equation 18 can be expressed;

$$lnk = 0.69\, lnI - 12.396 \qquad (19)$$

$$-\frac{dC_{TOC}}{dt} = 4 * 10^{-6} * I^{0.69} * C_{TOC}^{2} \quad (20)$$

6.4 Treatment of Textile Effluent by Sequence of EC and Adsorption

The second step of the hybrid study was adsorption process. For adsorption process two different agricultural wastes were used for the preparation of the adsorbent; walnut shell and corncob. Some important parameters such as contact time, adsorbent dosage and initial pH value were investigated as parametric study.

Certain amount of the real textile wastewater were collected from the associated partner in a monthly period. As mentioned before, since different batches were obtained from different dying processes, the initial characteristic properties of the textile wastewater varied. For this reason, the experiments were repeated for electrocoagulation and it was observed that the optimum conditions did not change even though the percentages of removal varied. The initial total organic carbon value was 60-64 mg/L for the experiments of adsorption. The pH was adjusted to pH=5 by acidification prior to electrocoagulation experiments and then electrocoagulation was applied. Adsorption was applied to the effluent water of the electrocoagulation.

6.4.1 Effect of contact time

Effect of contact time experiments were performed to examine the optimum time required for adsorption and to find the equilibrium point. Experiments were continued for 24h and according to the results, it was seen that removal of TOC increased with time. The increase in the rate of removal was significant between 1-6 hours and after 6 hours removal of TOC approximately remained constant. This can be explained that, the pollutants were adsorbed by the external surface of adsorbent at the beginning of experiments, so the adsorption rate was fast. After the external surface reached the saturation point, the molecules diffused through the interior surface which took relatively long contact time (Ahmad and Hameed, 2009). The results are given Figure 6.26 and 6.27.

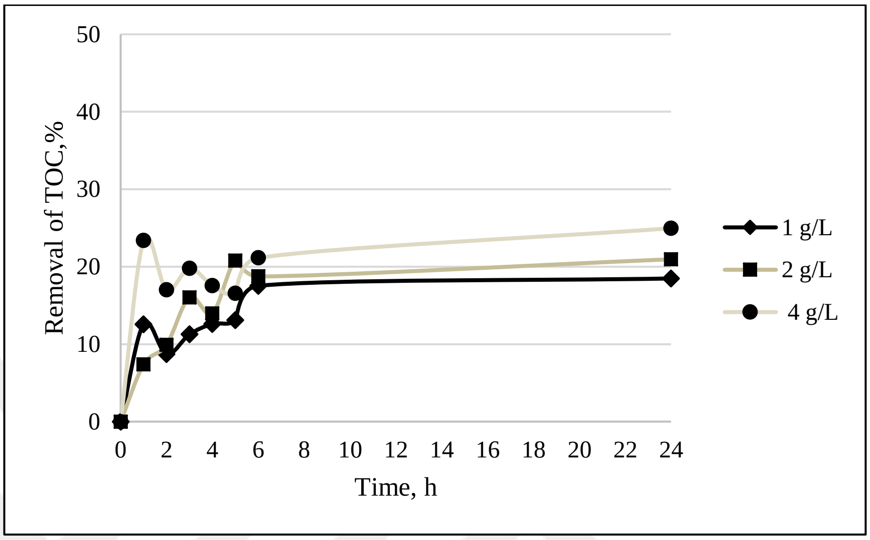


Figure 6.26. Effect of contact time to removal of TOC with corncob adsorbent ($[TOC]_0$=60-64 mg/L, room temp., original pH)

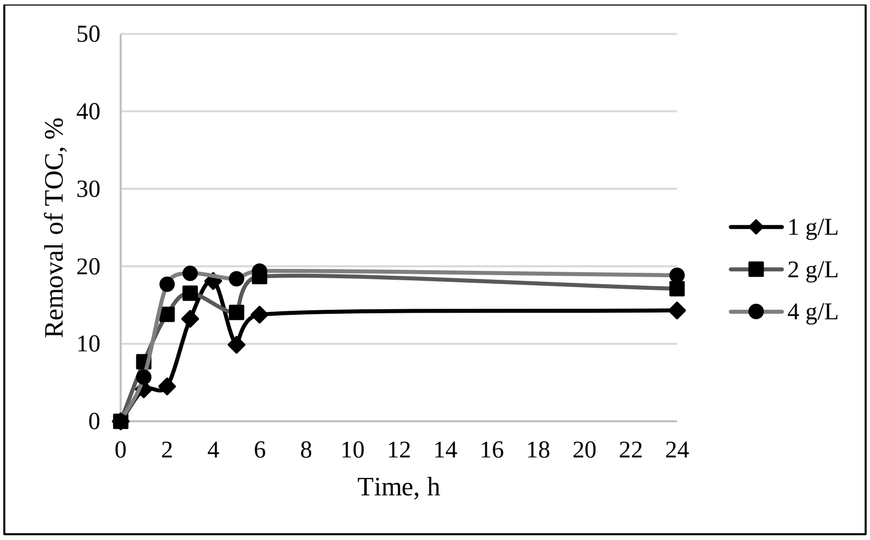


Figure 6.27. Effect of contact time to removal of TOC with walnut shell adsorbent ($[TOC]_0$=60-64 mg/L, room temp., original pH)

6.4.2 Effect of adsorbent dosage

To assess the effect of adsorbent dosage, three different adsorbent dosages were tested with two different adsorbent type. For this purpose, walnut shell and corncob based activated carbon adsorbents were tested at 1,2 and 4 g/L adsorbent dosage, additionally 0.5 g/L adsorbent dosage was used by corncob based activated carbon. The results are given in Figures 6.28 and 6.29.

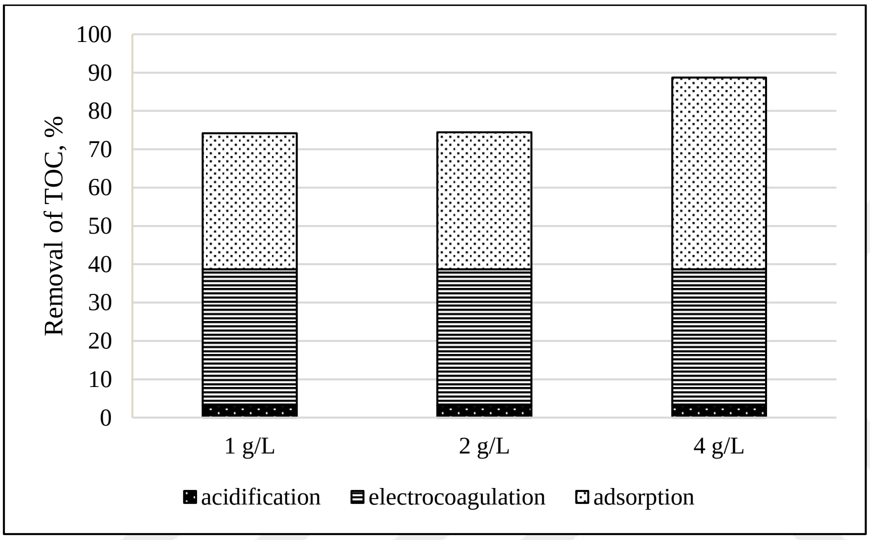


Figure 6.28. Effect of dosage of walnut shell based adsorbent ($[TOC]_0$=60-64 mg/L, room temp., original pH)

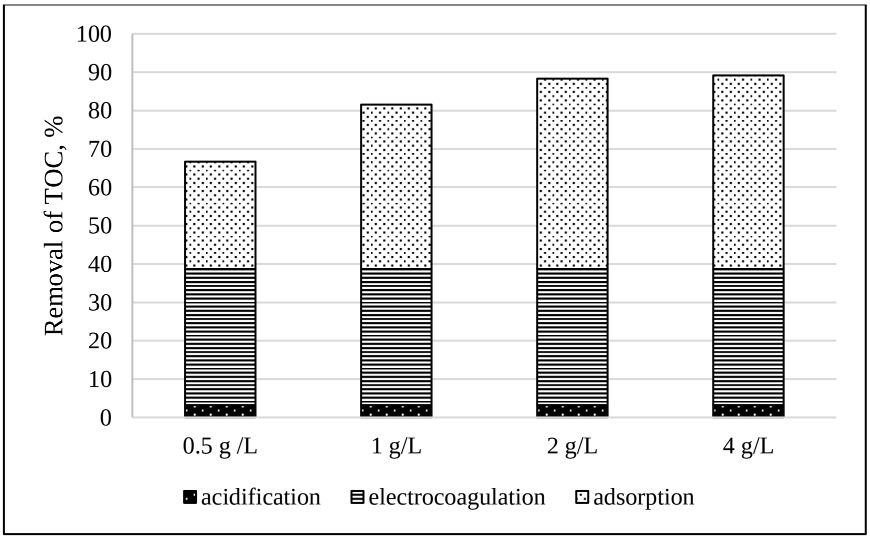


Figure 6.29. Effect of dosage of corncob based adsorbent ($[TOC]_0$=60-64 mg/L, room temp., original pH)

When the adsorbent dosage was increased, the TOC removal efficiency increased due to the higher surface area and the availability of more adsorption sites (Nazari et al., 2016). For walnut shell based activated carbon, the removal efficiencies of TOC were very close for 1 and 2g/L and the removal efficiency increased from 35.5% to 50% when adsorbent dosage was increased from 2g/L to 4g/L. For corncob based activated carbon, it was seen that there was slight difference for the removal efficiency of TOC between 2 and 4g/L. There was a slight difference when the removal efficiencies of both adsorbent for 4 g/L adsorbent dosage were compared however, for 1 and 2 g/L, removal efficiencies were higher for corncob based activated carbon than that of walnut shell.

Additionally, 0.5 g/L was tested with corncob based activated carbon to see for possible saving in the adsorbent dosage, but the adsorbent dosage was very effective. Since there was a small difference between 1 and 2 g/L for the TOC removal, 1 g/L corncob based activated carbon was selected as optimum condition with total TOC removal of 81.6%.

6.4.3 Effect of initial pH

Other important parameter for the adsorption method is the pH effect. To investigate the effect of initial pH, three different initial pH values were examined (pH 5, original pH (7-7.5), and pH 10) and results are given in Figure 6.30. The experiments were performed with the optimum dosage of 1 g of corncob based activated carbon per liter at room temperature. Total TOC removal efficiency was found 80.6 % at original pH value. When the initial pH value was decreased (pH=5), removal increased to 86% and when the initial pH value was increased to 10, total TOC removal decreased 74 %. Because of the removal efficiency increased at lower value than point of zero charge, it can be said that, the pH region in which the activated carbons are charged positively was more suitable to adsorb the negatively charged pollutants in the textile wastewater.

Because of there was a slight difference for removal of TOC between original pH and pH=5 and since acidification needs more chemical treatment which causes more cost and environmental effect, original pH was selected as the optimum initial pH value.

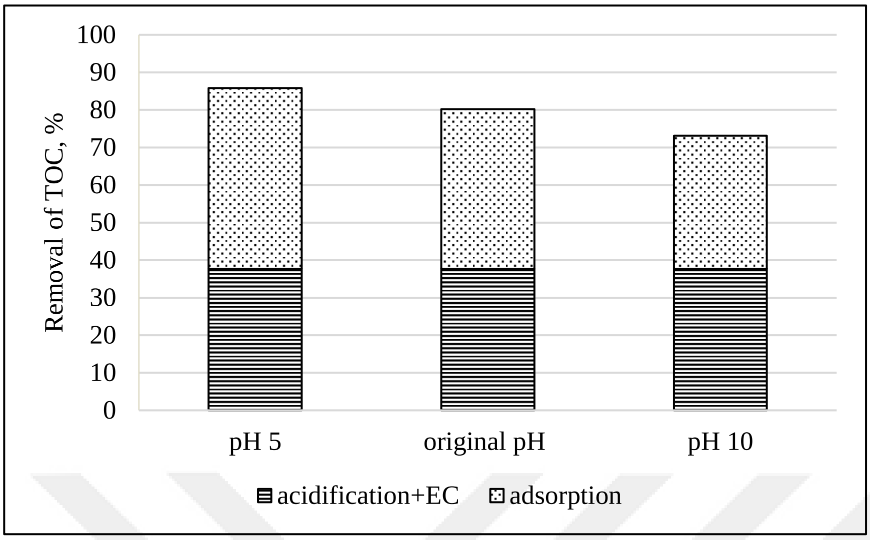


Figure 6.30. Effect of initial pH on TOC ($[TOC]_o$=60-55 mg/L, [adsorbent dosage]=1g/L, room temp.)

6.4.4 Evaluation of water standard values after EC and adsorption sequence

Adsorption process was tested after electrocoagulation by sequentially and optimum conditions were found and all analyses were examined. After the adsorption process, it was seen that the TOC, turbidity, and color were achieved the standard conditions. Total TOC removal was found between 75-80 % and turbidity removal was achieved 95%. After the adsorption textile wastewater color became clear. However the hybrid route including EC and adsorption processes were not effective for removal of salinity. All removal efficiencies are shown in Table 6.7;

Table 6.7. Wastewater properties after EC + Adsorption hybrid process at optimum condition

		Initial Value	Final Value EC+Adsorption	Final Removal (%)	Usual range in irrigation water (based on class A -class B)
TOC (mg/L)		60-64	11-13	75-80	**5-8**
COD (mg/L)		295	222-219	25-26	**25-50**
Turbidity (NTU)		15-30	1-0.6	90-95	**1**
Conductivity (mS/cm)		7-9	9	-	**0.7-3**
Salinity (ppt)		5.4	5.3	-	**-**
pH		7.5-8	7-7.5	-	**6.5-8.5**
Dissolved O_2 (mg/L)		3.42	3.35	-	**-**
Color	**436 nm**	15-30	1-1.5	85-90	**7**
	525 nm	9-20	0.8-0.5	85.5	**5**
	620 nm	7-17	0.3-0.1	88	**3**

As a result, it can be said that after the electrocoagulation method, the total organic carbon removal by the adsorption method was very effective and the final value of TOC was very close to the accepted values for the irrigation water standards. Also, the color and turbidity were completely purified. Adsorption method was very effective for total organic carbon removal but the final values of salinity and chemical oxygen demand were still high for the irrigation reuse. The initial and final appearance of the wastewater is given in Figure 6.31.

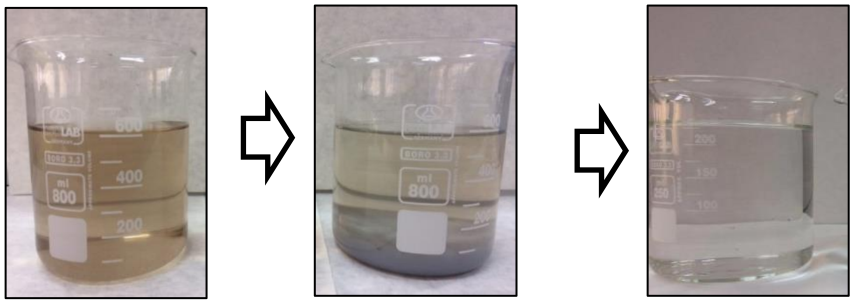


Figure 6.31. Appearance of wastewater befor and after treatment

6.4.5 Adsorption isotherms

The adsorption isotherm defines the distribution of total organic carbon between solid phase and the solution at the equilibrium point. Also, the adsorption isotherm is an equation which related to the amount of adsorbed onto the adsorbent (q_e) and the equilibrium concentration of the solution (C_e) (Aljeboree et al., 2017).

The isotherm study was performed using the total organic carbon concentration data obtained in the parametric study on adsorption performed after 24h. The experiments were performed five different adsorbent dosage (0.5, 1, 2, 4, and 8 g/L) at room temperature. The collected data are given in Table 6.8. The equilibrium adsorption capacities, q_e, were found 24, 21, 15, 8.87, and 4.98 mg/g for 0.5, 1, 2,4, and 8 g/L adsorbent dosage, respectively.

Table 6.8. Collected data for adsorption isotherms

Adsorbent dosage (g/L)	TOC initial (mg/L)	TOC final (mg/L)	q_e (mg/g)
0.5	44	32	24.00
1	44	23	21.00
2	44	14	15.00
4	44	8.5	8.87
8	44	4.15	4.98

Adsorption capacity was calculated using following equation;

$$q = \frac{C_{TOC_0} - C_{TOC_t}}{m} * V$$

where C_{TOC_0} and C_{TOC_t} are the total organic carbon concentration at initial and at any time, m is the adsorbent dosage (g), V is the volume of the wastewater (L).

In this study, four different adsorption isotherms models (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich) were tested. Linear equations and constants for each model are summarized in the Table 6.9.

Table 6.9. Adsorption isotherms

Isotherm Models	Equation	Linearized form	Parameters
Langmuir	$q_e = \frac{q_L * b * C_e}{1 + b * C_e}$	$\frac{1}{q_e} = \frac{1}{b * C_e * q_L} + \frac{1}{q_L}$	• b (L/mg) • q_L (mg/g)
Freundlich	$q_e = K_f * C_e^{\frac{1}{n_f}}$	$\ln q_e = \ln K_f + \frac{1}{n_f} * \ln C_e$	• K_f (mg/g) • n_f
Temkin	$q_e = \frac{R * T}{B} lnK_T C_e$	$q_e = \frac{R * T}{B} * lnK_T + \frac{R * T}{B} * lnC_e$	• K_T (L/mg) • B (J/ mol)
Dubinin-Radushkevich	$q_e = q_s e^{-K_{ad}\epsilon^2}$	$\ln q_e = \ln q_s - K_{ad}\epsilon^2$	• q_s (mg/g) • K_{ad} (mol^2/kJ^2)

- **Langmuir Isotherm;**

Langmuir isotherm has the linear form as the following Equation 21;

$$\frac{1}{q_e} = \frac{1}{b * C_e * q_L} + \frac{1}{q_L} \qquad (21)$$

where;

- b is Langmuir isotherm constant (L/mg),
- q_L is maximum monolayer adsorption (mg/ g)
- Ce is the equilibrium concentration of solute in the bulk solution (mg/L)

To calculate the q_L and b, according to the linearized form of equation, $1/q_e$ versus $1/C_e$ was plotted and given in Figure 6.32. The values of b and q_L can be obtained from the intercept, which is ($\frac{1}{q_L}$), and from the slope, which is ($\frac{1}{b*q_L}$) .

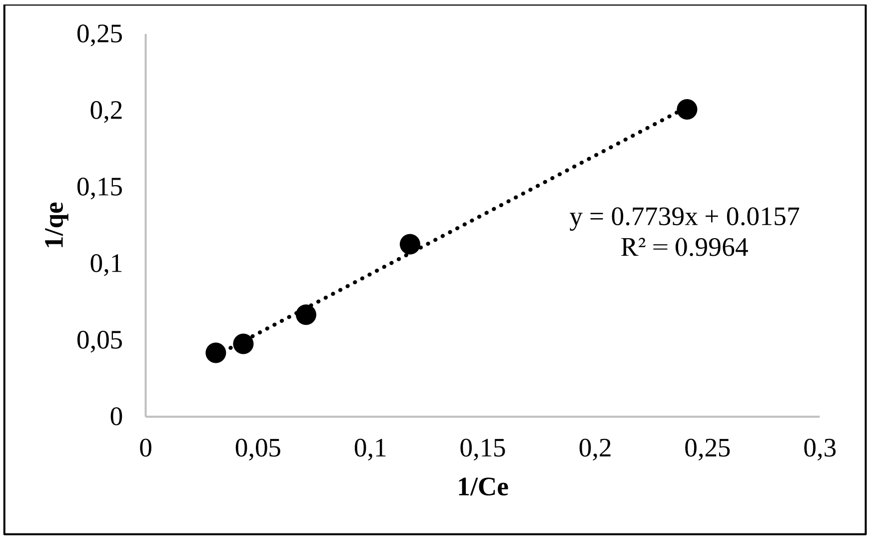


Figure 6.32. Linear plot of Langmuir isotherm model for TOC removal

According to the Figure 6.32, the parameters of Langmuir isotherms were found 0.02 L/mg and 63.69 mg/g for b and q_L, respectivelly. The final equation and correlation factor (R^2) were found;

$$q_e = \frac{1.27C_e}{1 + 0.02C_e}$$

.

- **Freundlich Isotherm;**

Freundlich isotherm has the linear form as the following Equation 22;

$$lnq_e = lnK_f + \frac{1}{n_f} * lnC_e \qquad (22)$$

where;

- q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g),
- C_e is the equilibrium concentration of solute in the bulk solution (mg/L),
- K_F is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g)
- $1/n_F$ is the heterogeneity factor.

To determine the parameters of Freundlich isotherms, K_F and n_F, lnq_e versus lnC_e was plotted and given in Figure 6.33. The values of K_F and n_F can be obtained from the intercept, which is (lnK_F) and from the slope, which is ($\frac{1}{n_F}$),

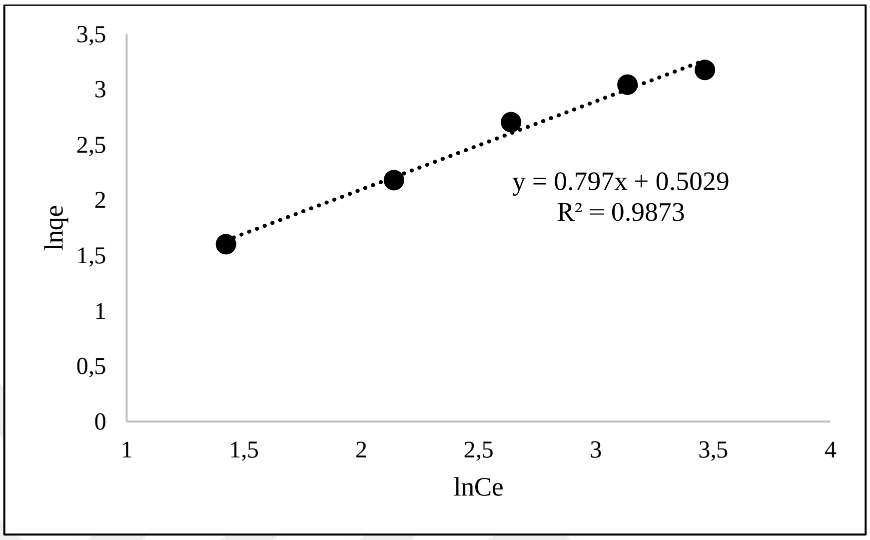


Figure 6.33. Linear plot of Freundlich isotherm model for TOC removal

According to the Figure 6.33, the parameters of Freundlich isotherms were found 1.25 and 1.66 mg/g for n_F and K_F, respectivelly. The final equation and correlation factor were found;

$$q_e = 1.66 * C_e^{\frac{1}{1.25}}$$

- **Temkin Isotherm**

Temkin isotherm has the linear form as the following Equation 23;

$$q_e = \frac{R * T}{B} * lnK_T + \frac{R * T}{B} * lnC_e \qquad (23)$$

where;

- R is the ideal gas constant (8.314 J/molK),
- K_T is the Temkin isotherm equilibrium binding constant (L/mg),
- B (J mol-1) is the Temkin constant and T is the temperature (room temperature) (K).

To determine the parameters of Temkin isotherms, K_T and B, q_e versus lnC_e was plotted and given in Figure 6.34. The values of K_T and B can be obtained from the intercept, which is ($\frac{RT}{B} lnK_T$), and from the slope, which is ($\frac{RT}{B}$).

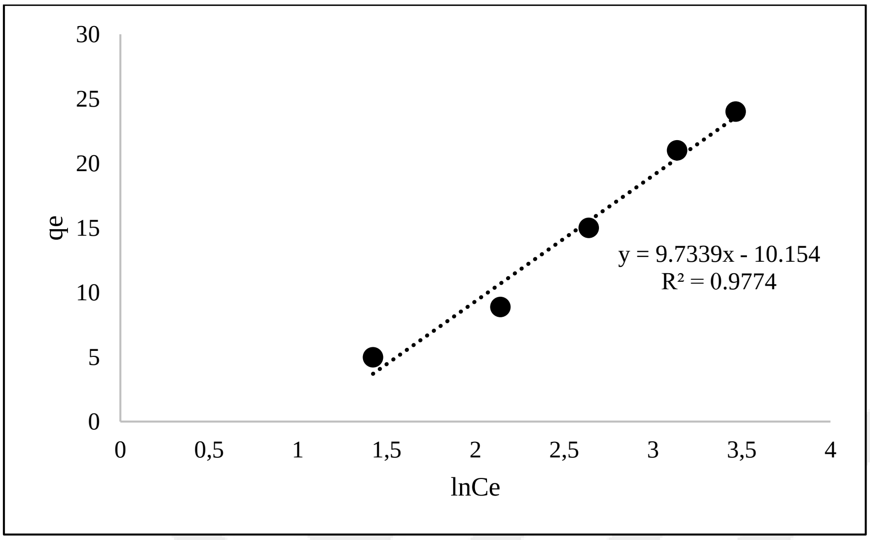


Figure 6.34. Linear plot of Temkin isotherm model for TOC removal

According to the Figure 6.34, the parameters of Temkin isotherms were found 254.92 J/mol and 0.352 L/mg for B and K_T, respectivelly. The final equation was found;

$$q_e = 9.72\ln(0.352C_e)$$

- **Dubinin-Radushkevich**

Dubinin- Radushkevich isotherm has the linear form as the following Equation 24;

$$\ln q_e = \ln q_s - K_{ad}\epsilon^2 \qquad (24)$$

$$\epsilon = RTln\left(1 + \frac{1}{C_e}\right) \qquad (25)$$

where;

- q_s adsorption capacity (mg/g),
- C_e the adsorbate equilibrium concentration (mg/L),

- K_{ad} (mol^2/kJ^2) is the Dubinin–Radushkevich isotherm constant and ε is the Polanyi potential (kJ/mol)
- R is the reaction gas constant (0.008314 kJ/molK) and T is the temperature (298 K)

To calculate the q_s and K_{ad}, according to the linearized form of equation, lnq_e versus ε^2 was plotted and given in Figure 6.35. The values of q_s and K_{ad} can be obtained from the intercept, which is (lnq_s), and from the slope, which is (K_{ad})

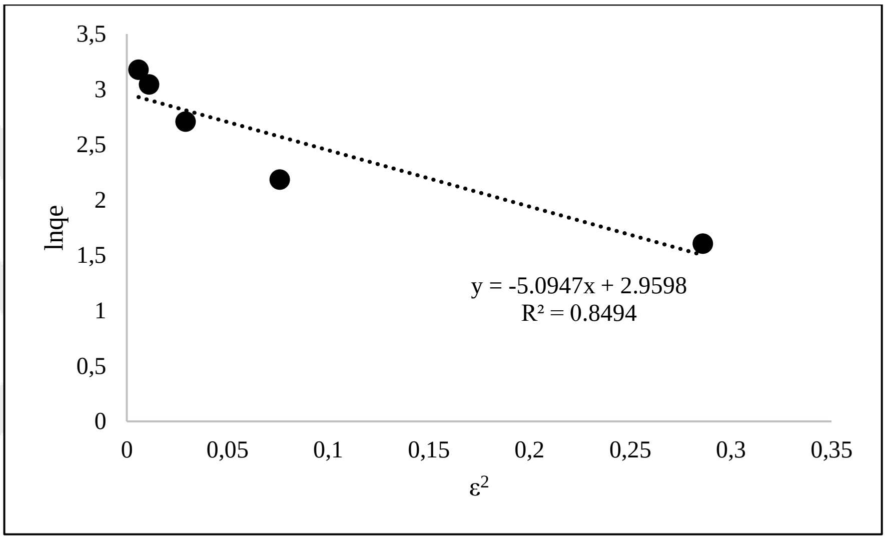


Figure 6.35. Linear plot of Dubinin-Radushkevich isotherm model for TOC removal

According to the Figure 6.35, the parameters of Dubinin-Radushkevicch isotherms were found 5.1 mol^2/kJ^2 and 19.29 mg/g for K_{ad} and q_s , respectivelly. The final equation and correlation factor (R^2) were found;

$$q_e = 19.29e^{-5.1\epsilon^2}$$

The values of correlation factors very close to the unity for all models. However, the results showed that Langmuir isotherm model gave the best fit for the organic carbon adsorption by corncob based activated carbon with $R^2 = 0.9964$. The maximum adsorption capacity was found 63.69 mg/g and the equilibrium constant were found 0.02 L/mg. In the literature, there are some studies to find the adsorption capacities of the different adsorbents. The values found in this study are in the same order of magnitude with the values of the studies in literature such as 55.56 mg/g

(Igwegbe et al.,2015), 30.3 mg/g (Heibati et al., 2015) 59.88 mg/g (Dehghani et al., 2016) 132-77 mg/g (Ocinski et al., 2016), 62.06 mg/g (Aljeboree et al., 2017), and 66 mg/g (Rashid et al., 2018) for the Langmuir isotherm model.

The parameters and correlation factor for three different isotherm models are summarized in Table 6.10.

Table 6.10. Parameters of adsorption isotherms

Isotherm	Parameters	Value
Langmuir	q_L (mg/g) b (L/mg) R^2	63.69 0.02 0.9964
Freundlich	n_f K_F (mg/g) R^2	1.25 1.66 0.9873
Temkin	B (J/mol) K_T (mg/g) R^2	254.92 0.352 0.9774
Dubinin-Radushkevich	q_s (mg/g) K_{ad} (mol^2/kJ^2) R^2	19.29 5.1 0.8494

6.4.6 Adsorption kinetic study

The time-dependent experimental batch adsorption data were used for the kinetic modelling. The first order and second order kinetic models were tested to find the kinetic parameters (Sartape et al., 2017; Montero et al., 2018).

<u>Collecting the Kinetic Data</u>

The kinetic study was performed using the total organic carbon concentration (C, mg/L) data obtained in the parametric study on adsorption performed at hourly. The experiments were performed 0.25 g/250 mL adsorbent dosage at room temperature. The collecting data is given in Table 6.11. According to the Table 6.11, the equilibrium adsorption capacity, q_e, was found 21.16 mg/g.

Table 6.11. Collecting data for adsorption kinetic study

Time (h)	TOC (mg/L)	Adsorption capacity (q, mg/g)
0	43	0
1	28.9	14.1
2	25.53	17.47
3	25.25	17.75
4	24.5	18.5
5	23.3	19.7
6	22.25	20.75
7	21.3	21.7
24	21.84	**21.16**

Adsorption capacity was calculated using following equation;

$$q = \frac{C_{TOC_0} - C_{TOC_t}}{m} * V$$

where C_{TOC_0} and C_{TOC_t} are the organic carbon concentration at initial and at any time, m is the adsorbent dosage (g), V is the volume of the wastewater (L).

First-Order Kinetic Model;

First order kinetic model can be expressed by Equation 26;

$$\frac{dq}{dt} = k_1(q_e - q) \qquad (26)$$

The equation 26 can be integrated by applying the boundary conditions;

$$\int_0^{qt} \frac{dq}{(q_e - q)} = \int_0^t k_1 dt \qquad (27)$$

The integrated form of Equation 27 becomes;

$$-\ln(q_e - q_t) + lnqe = k_1 t \qquad (28)$$

Equation 28 can be rearranged to obtain the first order kinetic model;

$$\ln(q_e - q_t) = lnq_e - k_1 t \qquad (29)$$

where q_t and q_e are the amount adsorbed at any time and at equilibrium (mg/g) and k_1 is the first-order rate constant (min^{-1}).

Second-Order Kinetic Model;

The second order kinetic model can be expressed by Equation 30:

$$\frac{dq}{dt} = k_2(qe - q)^2 \qquad (30)$$

$$\frac{dq}{(qe-q)^2} = k_2 dt \qquad (31)$$

The Equation 31 can be linearized by taking integration at the boundary conditions t=0, q=0, and t=t, q=q_t;

where q_e-q=u , -dq=du

The integrated form of Equation 31 becomes;

$$\frac{1}{q_e - q} - \frac{1}{q_e} = k_2 t \qquad (32)$$

Equation 32 can be rearranged to obtain;

$$q_t(1 + q_e * k_2 t) = q_e^2 * k_2 t \qquad (33)$$

The equation 33 becomes;

$$\frac{(1 + q_e * k_2 t)}{q_e^2 * k_2} = \frac{t}{q_t} \qquad (34)$$

Finally, the Equation 34 can be rearranged and the second order kinetic model can be expressed by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (35)$$

where q_t and q_e are the amount adsorbed at any time and at equilibrium (mg/g), and k_2 is the second order rate constant (g/mg.min).

According to the Equation 29 and 35, the plots of log (q_e-q_t) versus t for first order and the plots of t/qt versus t for second order model are shown in Figures 6.36 and 6.37, respectively.

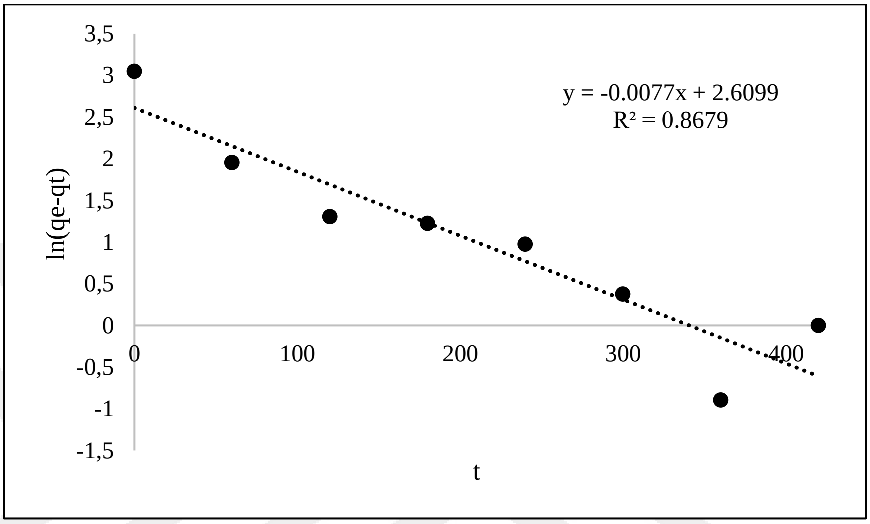


Figure 6.36. The linear plot of first order kinetic model for adsorption

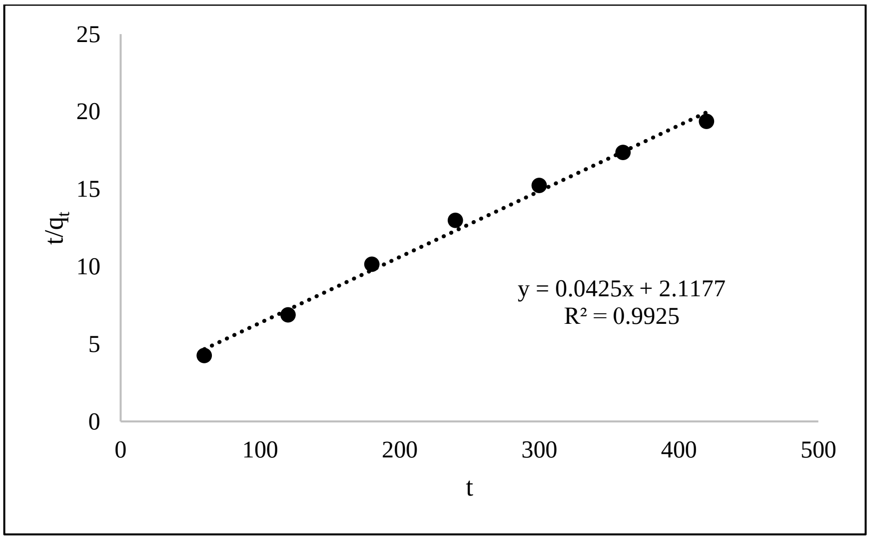


Figure 6.37. The linear plot of second-order model for adsorption

The kinetic parameters for first and second order kinetic models were calculated from slope and intercept of plots. The results are given in Table 6.12.

Table 6.12. Results of kinetic study for adsorption

Kinetic models	Parameters	Value
First order	k_1(l/min)	0.0078
	R^2	0.8679
Second order	k_2 (mg/g.min)	0.000853
	R^2	0.9925

It can be said that the second order model was fitted better according to the regression coefficient R^2=0.9925 same as the literature (Dede, 2018; Bonilla-Petriciolet et al., 2017; Wu et al., 2001; Bhattacharya et al., 2008; Cao et al., 2014; Ghaedi et al., 2016; Simonin, 2016; Alshameri et al., 2018).

6.5 Treatment of Textile Effluent by Sequence of EC and Adsorption and Photo-Fenton Like Oxidation

Photo-Fenton like oxidation was the third step of the hybrid process. For this method, $BiNiO_3$ and $BiFeO_3$ supported by corncob based activated carbon catalysts were tested. Firstly, catalyst screening experiments were investigated and then parametric study experiments were carried out with the selected catalyst.

6.5.1 Catalyst screening experiments

In order to assess the performances of the catalysts, 0.25 and 0.5 g/L of catalyst loadings were compared on the TOC removal efficiency at original pH and pH 3. During the experiments the hydrogen peroxide concentration was 2 mM. The experimental results are given in Figures 6.38 and 6.39. According to the Figure 6.38, the TOC removal efficiency was higher with $BiNiO_3$/corncob AC catalyst for both catalyst loadings. Although there was a slight difference in TOC removal between the two catalysts at 0.25 g / L catalyst loading, this difference increased slightly when 0.5 g / L was tested. For 0.5 g/L TOC removal was found 10.9 % for $BiNiO_3$ and 7.67 % for $BiFeO_3$ catalyst, respectivelly. Total TOC removal increased from 75.23 % to 86.13% with 0.5 g/L $BiNiO_3$ catalyst. In addition, according to the Figure 6.39, when the initial pH value was decreased (pH=3), there was a slight increase for the TOC removal, so that it can be said that effect of initial pH was not effective for the screening experiments.

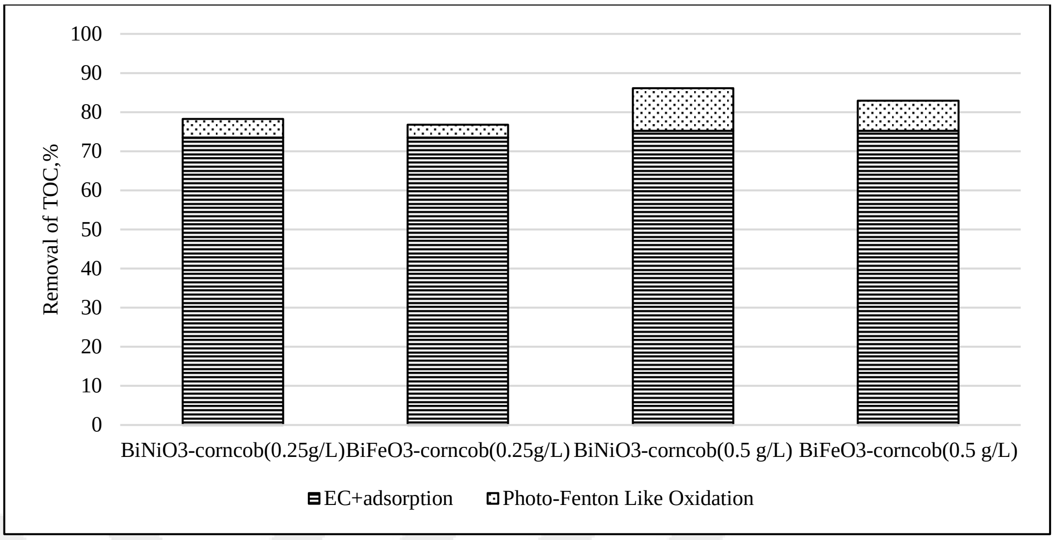


Figure 6.38. Catalyst screening experiments effect of catalyst loading ($[TOC]_0$=11-13 mg/L after EC+ adsorption, room temp., $[H_2O_2]_0$= 2mM, 100 W light power, original pH)

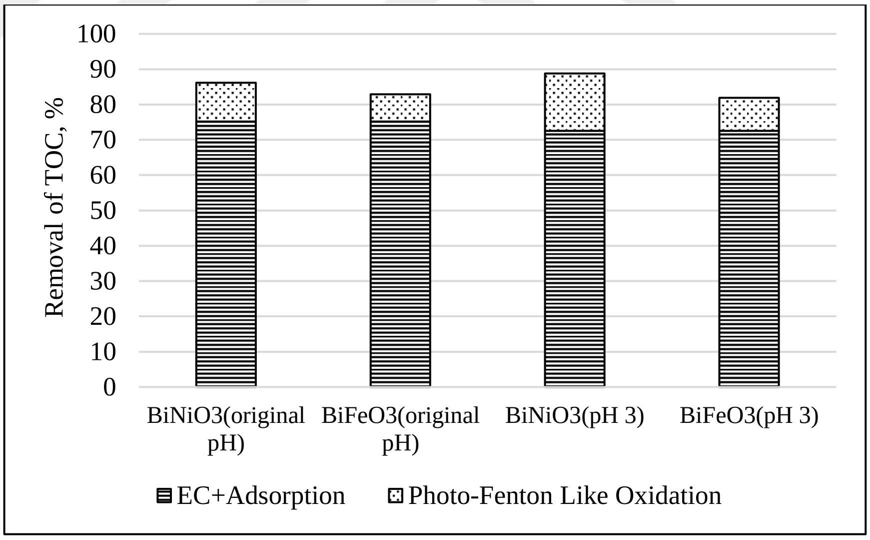


Figure 6.39. Catalyst screening experiments effect of initial pH ($[TOC]_0$=11-13 mg/L after EC+ adsorption, room temp., $[H_2O_2]_0$= 2mM, 100 W light power, catalyst loading=0.5 g/L)

As a result, $BiNiO_3$/corncob activated carbon was selected as the optimum catalyst due to the performance it has shown.

6.5.2 Parametric study

The effect of catalyst loading, initial pH and initial hydrogen peroxide concentration on the TOC removal efficiency were investigated with $BiNiO_3$/corncob AC catalyst according to the screening experiments.

6.5.2.1 Effect of catalyst loading

The effect of catalyst loading experiments showed that the removal efficiency of TOC increased with increasing catalyst loading and results of catalyst loading experiments are given in Figure 6.40.

The effect of catalyst loading experiments were investigated between 0.25 and 1 g/L catalyst loading. In addition, an experiment without using catalyst was tested. According to the Figure 6.40, there was no significant difference between no catalyst and 0.25 g/L catalyst loading. Further increase in loading increased the TOC removal efficiency. This can be explained that the increase of the catalyst amount increases the number of active sites on the photocatalyst surface so that the number of hydroxyl and superoxide radicals increase (Akpan and Hameed, 2009; Djaneye-Boundjou et al., 2012). When catalyst loading were increased to 0.5 g/L, TOC removal efficiency increased by nearly 8% and total removal of TOC was evaluated as 75.5%, but this was not enough to achieve irrigation water standards. Because of this reason 0.75 and 1g/L catalyst loadings were tested. With 0.75 g/L, final TOC value was found 7-7.5 mg/L which is suitable for irrigation. In addition to TOC, when COD removal efficiency were analyzed, it was observed that there was an increase in removal with increasing catalyst loading. According to the initial value of the wastewater, after the photo-fenton step the total COD removal was found to be 32% with 0.5 g/L catalyst loading and 49% with 0.75 g/L catalyst loading. Hence the optimum catalyst loading was selected as 0.75 g/L with a total TOC removal efficiency nearly 84%.

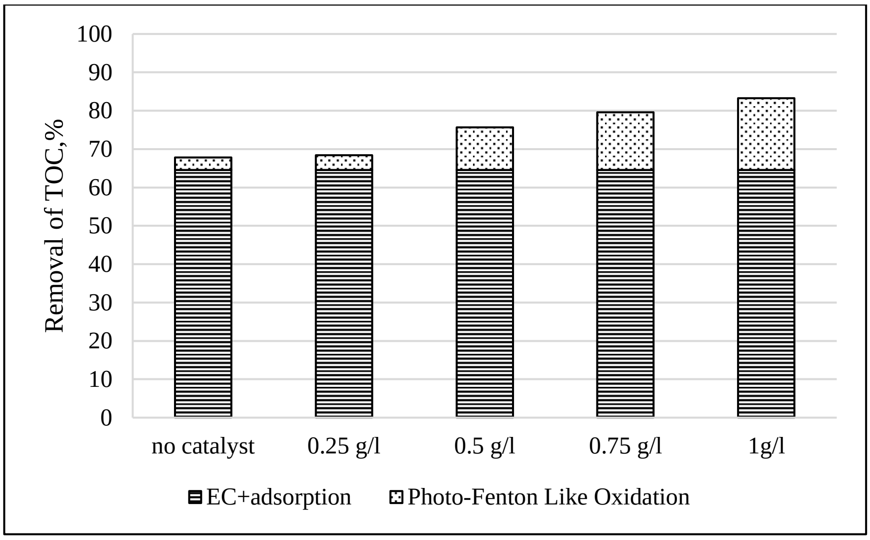


Figure 6.40. Effect of catalyst loading ($[TOC]_0$=11-13 mg/L after EC+ adsorption mg/L, room temp., $[H_2O_2]_0$= 2mM, 100 W light power, original pH)

6.5.2.2 <u>Effect of initial pH value</u>

In order to investigate the effect of the initial pH on the TOC removal, the initial pH of pre-treated textile wastewater was adjusted to 3 and 5. Results of the experiments are given in Figure 6.41. During experiments 2 mM hydrogen peroxide concentration, 0.75g/L catalyst loading and the room temperature were kept constant with 100 watt light power.

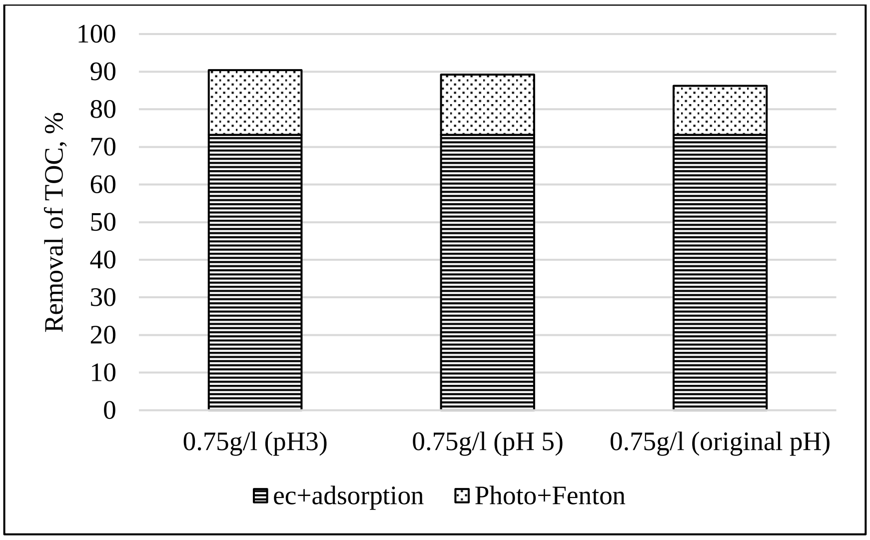


Figure 6.41. Effect of inital pH ($[TOC]_0$=11-13 mg/L after EC+ adsorption, room temp., [catalyst loading] =0.75 g/L)

Investigating the results obtained from the experiments showed that pH was not very effective on TOC removal efficiency. According to the Figure 6.41 with decreasing pH value, TOC removal increased slightly. Maximum TOC removal efficiency was evaluated at pH 3 with total 90% removal but there was no significant difference whem compared with the alkaline medium. At original pH the TOC removal was 86.24%. In general, iron catalysts in Fenton processes give better results in acidic conditions (Elmorsi et al., 2010; Nesic et al., 2014). However, the results of experiments showed that the initial pH value is not necessary to be acidic. Thus, it was shown in literature that it can be work in the wider pH range with the iron free catalyst used (Bokare and Choi, 2014; Pachhade et al., 2009). As a result, optimum pH value was selected as the original pH (7-7.5) value.

6.5.2.3 Effect of hydrogen peroxide concentration

To examine the effect of hydrogen peroxide concentration 2,4 and 8 mM hydrogen peroxide concentrations were tested. During experiments, catalyst loading (0.75 g/L), light power (100 watt), and temperature (room temperature) were kept constant. Also, an experiment without addition of hydrogen peroxide was investigated. The results are given Figure 6.42 and 6.43.

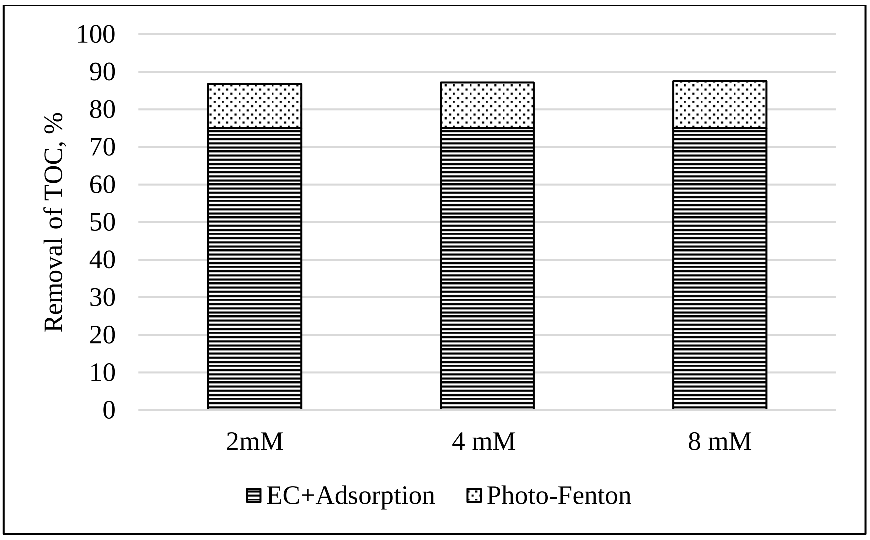


Figure 6.42. Effect of hydrogen peroxide concentration ($[TOC]_0$=11-13 mg/L after EC+ adsorption, room temp., [catalyst loading]=0.75 g/L, original pH)

According the Figure 6.43, the results showed that the hydrogen proxide concentration was not effective on TOC removal efficiency. When hyrogen peroxide concentration were increased from 2 mM to 8 mM total TOC removal efficiency increased only nearly 1%. Also, according to the Figure 6.43, in the absence of H_2O_2 and light, total TOC removal was found 77.5% and in the absence of H_2O_2, total TOC removal was evaluated 85.5% by the effect of the catalyst and visible light (photocatalytic degradation).

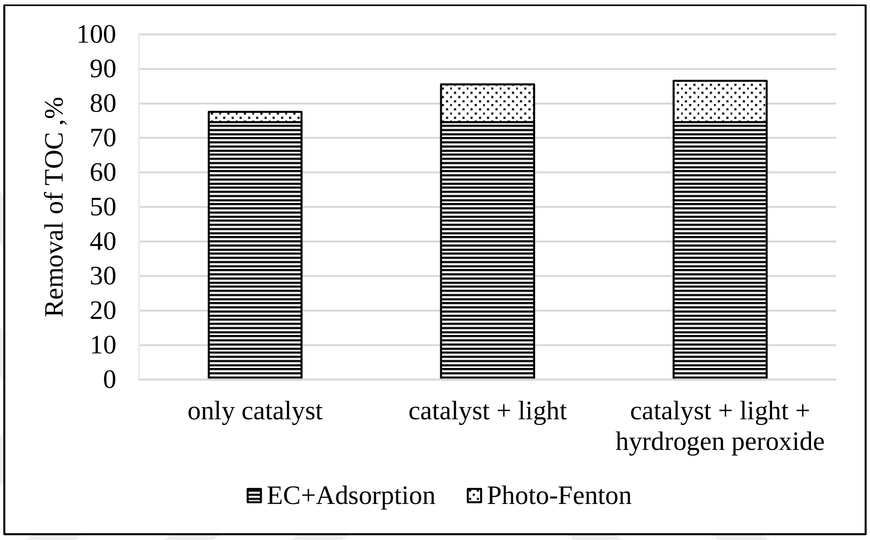


Figure 6.43. Fenton reaction performance on different conditions ($[TOC]_0$=11-13 mg/L after EC+ adsorption, room temp., [catalyst loading]=0.75 g/L, original pH)

Wastewater properties after Electrocoagulation/Adsorption/Photo-Fenton Like Oxidation are given in Table 6.13.

Table 6.13. Wastewater properties after EC/Adsorption/photo-Fenton like oxidation

		Initial Value	Final Value EC+Adsorption+photo-Fenton like oxidation	Final Removal (%)	Usual range in irrigation water (based on class A -class B)
TOC (mg/L)		55-60	7-7.5	87	**5-8**
COD (mg/L)		295	150-160	49-45	**25-50**
Turbidity (NTU)		15-30	0.6	90-95	**1**
Conductivity (mS/cm)		7-9	8-9	-	**0.7-3**
Salinity (ppt)		5.4	5.3	-	**-**
pH		7.5-8	7-7.5	-	**6.5-8.5**
Dissolved O_2 (mg/L)		3-3.5	3.3	-	**-**
Color	**436 nm**	30-15	1-0.8	96.6-94.6	**7**
	525 nm	20-9	0.7-0.5	96.5-94.4	**5**
	620 nm	17-7	0.3-0.1	98.5—98.2	**3**

After the EC+ adsorption+ photo-Fenton step, in addition to other methods, it can be said that, foto-Fenton like oxidation step is more effective for the COD removal. Nearly 50% COD removal was achieved after this step.

6.6 Treatment of Textile Effluent by Sequence of EC and Adsorption and Photo-Fenton Like Oxidation and MFC

To asses to the effect of microbial fuel cell and electric generation, after the photo-Fenton step, finally MFC was tested at original pH (7-7.5) and room temperature conditions and the ratio of sodium acetate / textile wastewater is 3: 1 by volume and the external resistance was kept constant at 220 Ω.

Experiments were continued 7 days and at the end of the 7th day, TOC, COD, turbidity, conductivity, and color analyses were examined. It can be said that this method had no benefit for the removal efficiencies as a final step. The COD and the turbidity values increased when compared the value found after the photo-Fenton process. After the Photo-Fenton prosess COD value was 150-160 mg/L, but this value increased to 180-190 after MFC. Also, this system was not effective to generate electrical energy. These results can be explained due to the MFC is useful method when the the wastewater includes high organic pollutants.

6.7 Toxicity Analysis

A toxicity test was applied on real textile wastewater exposed to hybrid process which includes electrocoagulation, adsorption, and photo-Fenton like oxidation. The lengths of the Lepidium sativum roots growing in the textile wastewater, distilled wastewater, and treated textile wastewater at the end of the hybrid process are given in Figure 6.44. The average lengths of the roots growing in the textile wastewater, distilled water, and treated textile wastewater were calculated as 1.175, 3.625 and 3.620 cm, respectively. The growth inhibition was evaluated as 0.13 %. According to the toxicity tests, no remarkable growth inhibition was observed in the treated textile wastewater by hybrid process. This result indicates that the pollutants is decomposed into non-toxic end products at the end of the hybrid process.

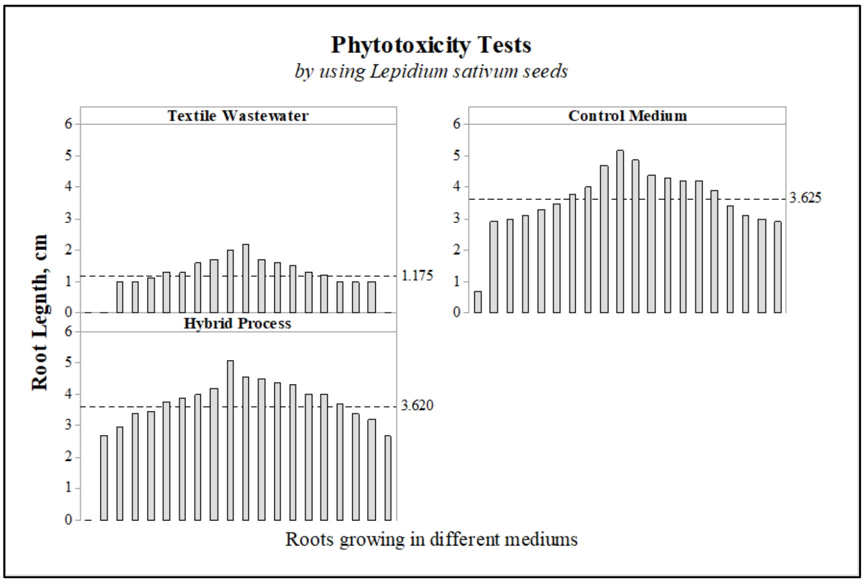


Figure 6.44. Results of Toxcitiy Tests by Using Lepidium Sativum Seeds

Application of Reverse Osmosis Method for Salinity Removal

At the end of all hybrid applications, since irrigation water standard values were not provided in terms of salinity and conductivity, reverse osmosis method was applied to the effluent of hybrid processes.

Hybrid process effluent was simulated in terms of salinity and conductivity values, a synthetic wastewater was prepared and the experiment was carried out in the laboratory of another research group in our department. In this system, GE Sepa CF CA (Thin Film) NF CK membrane supplied by GE Infrastructure Water and Process Technologies was used. The experiments were performed with a 191x140 mm membrane for 2.5 hours under 15 bar pressure. Conductivity, salinity and total dissolved matter removal were calculated for the samples taken from feed stream, concentrated stream and permeate stream. At the end of 15 minutes, salinity and conductivity values reached the standard values of irrigation water.

7. CONCLUSIONS

This study aims the treatment of the pre-treated real textile wastewater by a hybrid process which includes various physical, chemical and biological methods for reuse it as irrigation water. Considering environmental and economic factors, the adsorbents used during the treatment are obtained from corn and walnut agricultural wastes as a low cost and environmental adsorbent. These adsorbents were also used as support materials in catalysts.

The results obtained by the experiments can be evaluated separately for each method.

Electrocoagulation

In the present work, the efficiency of electrocoagulation process for the treatment of real textile wastewater was investigated. Firstly, the efficieny of the two different electrode materials, Al and Fe, were tested. Then, effect of current density and the initial pH were investigated. In addition to the parametric study, to understand the characteristic properties of the solid waste, SEM, and BET analyses were examined. Finally, cost analysis and first and second order kinetic model were investigated. These investigations were led to the following results.

- ***Electrode Selection***

When Fe electrode was used, too much inconsistency in the results were observed. Besides these problems, TOC removal is better when the Al electrode is used so that Al electrode was selected and the parametric study experiments were continued with this electrode.

- ***Current Density***

As current density increased from 12.5 to 100 mA/cm^2, TOC removal increased from 10 to 34.42%. Removal efficiency increased when the current was changed 12.5 to 100 mA/cm^2. The maximum efficiency was reached at 100 mA/cm^2. Because the corrosion was directly related to current, 25 mA/cm^2 was selected the optimum.

- ***pH***

After the current density was decided, initial pH value was changed and acidic medium was investigated. The results in the acidic medium, pH=5, were better than the original pH value. Removal of TOC increased from 22.5 to 41.42%. Significant effects was also obtained in color and turbidity removal.

- ***Cost***

Cost equation relating electrode and operating cost was expressed as a function of current density. Total cost at the optimum conditions was calculated as 2.97 $\$/m^3$ of treated water.

- ***Kinetic Study***

First and second order kinetic models were tried for the kinetic study. For first order model ln(C_{TOC_0}/C_{TOC_t}) versus time and for second order model ($1/C_{TOC_t}$ - $1/C_{TOC_0}$) versus time at various current densities were plotted and it was seen that rate constants increased with increasing current density for both of the kinetic models. The second-order kinetic model gave better results when the regression coefficients are compared.

In general, based on the results of this study, the TOC removal by electrocoagulation using aluminum electrode seems to be a very efficient but not enough to meet the discharge standards. Hence, electrocoagulation combined with other technologies such as adsorption, AOP and etc. were tested as the following steps.

<u>Adsorption</u>

For adsorption process agricultural wastes (corncob and walnutshell) were used for the preparation of activated carbon as adsorbents. The adsorbents were characterized by SEM, BET, and TGA-FTIR analyses. The characterization results of the prepared activated carbon showed that both activated carbons have high surface area and porous structure. The corncob based activated carbon had higher surface area. BET analysis results showed that surface area of 1433 and 1364 m^2/g for corncob and walnutshell based acitivated carbon, respectively. According to the

TGA results, it can be said that weight loss of activated carbon slightly changed so that thermal stability is very high. The weight loss walnut shell based activated carbon total weight loss were found 6.6 % and 8.6% at 950 °C for corncob and walnut shell based activated carbon, respectively, which are considered as very low with similar studies in literature.

The effect of adsorbent type, dosage, and initial pH as parametric study, and four different isotherm models and two different kinetic model were investigated. This investigation was led to the following results.

- ***Adsorbent type and dosage***

1, 2, and 4 g/L adsorbent dosages were tested for both adsorbent. The results showed that the removal efficiency of TOC was higher with low amount of adsorbent dosage for corncob based activated carbon. As the adsorbent dosage was increased, the increase in the removal efficiency was not much, 1 g/L corncob based activated carbon was selected as the optimum condition with total TOC removal of 80%, approximately.

- ***Initial pH***

After selection of the adsorbent type and dosage, the initial pH value was changed and acidic and alkaline medium were investigated. It was seen that, when the pH value was decreased, removal efficiency slightly increased. Also, the point of zero charge of activated carbons were examined and it was found 7 and because of the removal efficiencies increased in acidic medium, it can be said that the pH region in which the activated carbons are charged positively was more suitable to adsorb the negatively charged pollutants in the textile wastewater. Because of the differences of the removal efficiencies between original pH (7-7.5) and pH 5 were insignificant, original pH was selected as optimum condition to reduce the total organic carbon.

So that, 1 g/L corncob based activated carbon at original pH was found to be the optimum condition for adsorption process.

- ***Isotherm and Kinetic study***

The experimental isotherm results were analyzed using The Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms models. The results showed that the Langmuir isotherm was the best fit amoung the four models with R^2 = 0.9964. The maximum adsorption capacity and equilibrium constant were found to be 63.69 mg/g and 0.02 L/mg, respectively. The adsorption capacity had a higher value when when the similar studies in the literature were compared.

To understand the adsorption mechanism, first and second order kinetic models were examined. The constants were found 0.0078 l/min and 0.000853 mg/g.min for first and second order kinetic models, respectively. When compared the R^2 value, second order kinetic model fitted the more suitable model with higher R^2 (R^2>0.99).

Photo-Fenton Like Oxidation

In the catalyst screening experiments, the performances of $BiNiO_3$/corncob based AC and $BiFeO_3$/corncob based AC were compared by changing the catalyst loading and initial pH. The results of catalyst screening experiments for photo-Fenton-like oxidation showed that $BiNiO_3$/corncob based AC catalyst was more successful and the parametric study experiments were carried out with $BiNiO_3$/corncob based AC catalyst.

For parametric study experiments, the effect of catalyst loading (no catalyst to 1g/L), initial pH (pH 3, pH 5, original pH (7-7.5)), and initial H_2O_2 concentration (2-8 mM) were compared. When different catalyst loadings were performed, it was seen that, the removal efficiency increased as the catalyst loading was increased and 0.75 g/L was selected as the optimum catalyst loading. The effect of initial pH and the initial H_2O_2 concetration was not remarkable for the removal efficiency as catalyst loading. To increase the concentration of H_2O_2 was led to a slight increase in treatment. In the experiments performed to compare the effect of catalyst, light and concentration of the H_2O_2, only 3,11, and 12-13% removal efficiency were observed with only catalyst, with catalyst and light, and with catalyst, light and H_2O_2, respectively.

General Conclusions

For general, the results obtained from this study can be expressed as;

- Corn cob as an agricultural waste, is an efficient source for low-cost and environmentally raw material of activated carbon.

- The electrocoagulation method is an effective method for the treatment of textile wastewater, especially for color, turbidity, and suspended solids. It is observed that it is more effective in high pollution wastewater. In terms of organic pollution removal, the adsorption method has the highest efficiency. With the activated carbon obtained from agricultural wastes, very high removal efficiency was provided. In Photo-Fenton-like oxidation method, catalyst loading was the most effective parameter. Because of the wastewater contains low organic pollution, the percentage of the removal efficiency was less when compared to other methods.

- At the end of the hybrid process, 87% of the TOC removal (25-30% by electrocoagulation, 40-45% by adsorption and 12-15% by fenton), 49% COD (18-20% by electrocoagulation, 8-10% by adsorption and 24 % by photo-Fenton), 96-98% turbidity (more than 90% by electrocoagulation, nearly 7% by adsorption and 1-2% by photo-Fenton), around 90% color (nearly 50-55% by electrocoagulation, 35-40 % by adsorption and nearly 2% by photo-Fenton), and around 95-97% suspended solids removal (70 % by electrocoagulation, nearly 20-25 % by adsorption and 5% by photo-Fenton) were achieved.

- These physical, chemical and biological methods applied in wastewater treatment were effective to achieve the irrigation water standards of wastewater except for salinity and chemical oxygen demand.

- In textile wastewater treatment, instead of a single method, multiple methods can be applied as a hybrid process by improving the conditions.

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