Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.21257

93 (2017) 214–228
October

A consecutive electrocoagulation and electro-oxidation treatment for pulp and paper mill wastewater

Baran Özyurt*, Şule Camcıoğlu, Hale Hapoglu

Ankara University, Faculty of Engineering, Department of Chemical Engineering, 06100, Tandoğan/Ankara/Turkey, Tel. +90-312-203-34-65, email: bozyurt@ankara.edu.tr (B. Özyurt), camcioglu@eng.ankara.edu.tr (S. Camcıoğlu), hapoglu@eng.ankara.edu.tr (H. Hapoglu)

Received 15 March 2017; Accepted 25 July 2017

ABSTRACT

In this work, electrocoagulation (EC), electro-oxidation (EO_x), consecutive electrocoagulation electro-oxidation (EC&EO_x) and combined electrocoagulation electro-oxidation (EC/EO_x) treatment methods were executed for the pulp and paper mill wastewater. The performances of the methods were compared in terms of pollutant removal and energy consumption amounts. Batch electro-reactor was used with Al and Fe electrodes for EC stage and graphite electrodes for EO_x stage. The initial process conditions were electrical conductivity in 2.10 mS/cm, pH in 5.82, temperature in 20°C and constant current intensity in 1.22 A. The highest removal of turbidity, color and chemical oxygen demand (COD) was obtained as 99%, 100% and 90% respectively for both EC & EO_x and EC/EO_x processes with the utilization of Al electrodes. Although EC&EO_x method was found to be more energy efficient with 26.23% less energy consumption than EC/EO_x method, usage of a single reactor for EC/EO_x technique has been considered as a more feasible method for treatment because of the initial investment cost and ease of application. Effects of initial pH, electrical conductivity, temperature and current intensity on pollutant removal and energy consumption by means of EC/EO_x technique were also investigated and optimal operational parameters were determined as 6, 5 mS/cm, 20°C and 1A respectively.

Keywords: Chemical oxygen demand (COD) removal; Electrocoagulation; Electro-oxidation; Graphite electrode, Pulp and paper mill wastewater

1. Introduction

The pulp and paper industry has high pollutant discharges to the receiving environment. As one of the most water demanding industry, it positions third in the world by producing over 60 m^3 of wastewater per ton of paper, and by resulting in large amounts of wastewater generation after the primary metals and the chemical industries [1–3]. Pulp and paper wastewater contains chlorinated compounds; fatty acids such as oleic acid and linoleic acid; tannins; resin acids such as abietic acid and dehydroabietic acid; phenols, lignin, and sulphur compounds that are responsible for high total organic carbon (TOC), chemical oxygen demand (COD), color, turbidity and low biodegradability index [4,5]. Discharge of these wastewaters into receiving environment without treatment cause several problems such as color, slime growth, thermal impacts and scum formation. They also affect the ecosystem, enlarge the quantity of toxic substances in the receiving water and pollute scenic beauty [6–9].

It is reported that the most commonly used treatment methods of pulp and paper effluent are physical adsorption [10], chemical oxidation [11], wet oxidation [12] and biochemical [13,14] methods. The low biodegradability index of pulp and paper wastewater indicates that this kind of effluent cannot be treated effectively through biochemical methods [3–5]. On the other hand, chemical methods generate considerable amount of sludge which needs further treatment [15]. Although wet air oxidation reduces COD in a large extent, the high energy consumption and the usage of high-pressure reactors makes the treatment uneconomical [1]. Due to these disadvantages, there has been an

---

*Corresponding author.

Presented at the 3rd International Conference on Recycling and Reuse, 28–30 September 2016, Istanbul, Turkey

increasing interest in the use of electrochemical technologies for the treatment of pulp and paper effluent.

High removal yield is achieved using electrocoagulation (EC) method without adding any chemical coagulant or flocculants, thus reducing the amount of sludge, which must be disposed [16]. In recent years, EC was considered as a simple, efficient and economical method that can successfully treat different effluents, such as boron containing wastewater [17], municipal wastewater [18], textile wastewater [19], dairy wastewater [20], industrial area wastewater [21], tannery wastewater [22], heavy metal removal [23] and pulp and paper mill wastewater [1,3–6,24]. EC involves the generation of coagulants in situ by electrically dissolving either aluminium or iron ions from the respective metal electrodes. The metal ion generation takes place at the anode, while hydrogen gas is produced at the cathode. The metal ions form flocculates which trap colloidal and suspended contaminants, while the hydrogen gas floats these particles [25]. Reactions at the Al and Fe electrodes and in the bulk wastewater were explained in detail by Uğurlu et al. [26]. Despite these advantages, EC is an inefficient method for the removal of stable and dissolved organic pollutants. Reaction mechanism of EC is given in Table 1.

Electro-oxidation (EO_x) was evaluated as one of the most promising technologies for the treatment of wastewater containing soluble organic compounds [25,27]. In EO_x process, small organic pollutants can be directly and indirectly oxidized [28,29]. Indirect electro-oxidation process uses chlorine to generate hypochlorite at anode to destroy organic pollutants [30]. Contaminants can also be degraded by electrochemically generated hydrogen peroxide. Direct anodic oxidation of pollutants can also occur directly on anodes by generating hydroxyl radicals, which are the most powerful oxidizing agent for the treatment of wastewater. The hydroxyl radicals can oxidize substantially all of the organic compounds with an oxidation rate 109 times higher than that of ozone. Pollutant removal efficiency is highly affected by the electrode material. Stainless steel, $RuO_2/IrO_2/TaO_2$ coated titanium, activated carbon fiber, boron doped diamond, commercial graphite felt, carbon felt, graphite, reticulated vitreous carbon and carbon sponge are some examples of the electrode materials used in recent wastewater treatment studies. Due to low cost, graphite stands out among other materials [31,32]. EO_x does not require added chemicals or oxygen and does not produce secondary pollutants or require complicated accessories [33]. EO_x was successfully applied for the treatment of fruit-juice production wastewater [29], textile industry wastewater [30,32], leachate of oil-drilling mud [31], olive oil wastewater [34], fertilizer production wastewater [35] and soft drinking wastewater [27]. Reaction mechanism of EO_x was explained in detail by Israilides et al. and Körbahti et al. [34,36]. Although EO_x provides full mineralization of the organic matter contained in the wastewater, if the colloidal and suspended solids are present, required treatment time is prolonged

Table 1
EC mechanism

Anode	Cathode
$4OH^- + 4e^- \rightarrow 2H_2O + O_{2(g)}$	$2H_3O^+ + 2e^- \rightarrow H_{2(g)} + 2H_2O(at\ acidic\ conditions)$
$2H_2O + 4e^- \rightarrow O_{2(g)} + 4H^+$	$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-(at\ alkaline\ conditions)$
$2Cl^- + 2e^- \rightarrow Cl_{2(g)}$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
$Cl_{2(g)} + H_2O \rightarrow HOCl + H^+ + Cl^-$	
Al-electrode	
$Al_{(s)} + 3e^- \rightarrow Al_{(aq)}{}^{3+}$	$Al_{(s)} + 4OH^- \rightarrow Al(OH)_4{}^- + 3e^-(at\ pH > 9)$
$Al_{(aq)}{}^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$	
Fe-electrode	
$Fe_{(s)} + 2e^- \rightarrow Fe_{(aq)}{}^{2+}$	
$Fe_{(aq)}{}^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H_2O$	$Fe(OH)_3 + OH^- \rightarrow \left[Fe(OH)_4\right]^-$
$Fe(OH)_2 + HOCl \rightarrow Fe(OH)_3 + Cl^-$	$Fe(OH)_4{}^- + 2OH^- \rightarrow \left[Fe(OH)_6\right]_3^-(at\ pH > 9)$
$Fe^{2+} + e^- \rightarrow Fe^{3+}$	
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$	

and the energy consumption is increased. Reaction mechanism of EO_x is given in Table 2.

Here, S symbolizes the active sites of the anode surface, R represents the organic matter. It is reported that, with the aid of hydrogen peroxide formation during EO_x, electro-fenton (EF) can also be used as an electrochemical treatment method [29]. EF methods broadly include electrochemical reactions that are used to generate in situ one or both of the reagents for the Fenton reaction according to the following mechanism given in Table 3.

Since EC is a fast but incomplete process and EO_x is a complete but slow process, coupling these two processes offers a practical hybrid. COD removal mechanism of a combined EC and EO_x process includes following steps.

1. Metal ions generation [26].
2. Hydrolysis of metal ions and production of metal hydroxides and polyhydroxides [24].
3. Production of small bubbles of oxygen and hydrogen at the anode and the cathode, respectively, which leads to floatation of pollutants [49].
4. Destabilization of pollutants, suspension of particles, emulsion breakage and aggregation of destabilized phases to form flocks [24].
5. Precipitation of pollutants [24].
6. Generation of adsorbed hydroxyl radicals [36].
7. Electrochemical combustion of organic pollutants by adsorbed hydroxyl radicals [35].
8. Production of indirect oxidizing agents such as chlorine, hypochlorite and hydrogen peroxide on the anode [34].
9. Oxidation of organic pollutants by oxidizing agents [36].

Table 3
EF mechanism

Electrodic Reactions	Reactions in liquid
$Fe_{(s)} \rightarrow Fe_{(aq)}{}^{2+} + 2e^-$	$H_2O_2 + Fe_{(aq)}{}^{2+} \rightarrow Fe_{(aq)}{}^{3+} + OH^- + [OH^\bullet]$
$2H_2O \rightarrow 4H^+ + O_2 + 2e^-$	$RH + [OH^\bullet] \rightarrow ROH + H^+$
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	
$Fe_{(aq)}{}^{3+} + e^- \rightarrow +Fe_{(aq)}{}^{2+}$	

Table 2
EO_x mechanism

Anode	Cathode
Direct Oxidation	
$H_2O + S \rightarrow S[OH^\bullet] + H^+ + e^-$	$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O(\textit{at acidic conditions})$
$R + S[OH^\bullet] \rightarrow S + RO + H^+ + e^-$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-(\textit{at alkaline conditions})$
$H_2O + S + Cl^- \rightarrow S[ClOH^\bullet] + H^+ + 2e^-$	
$R + S[ClOH^\bullet] \rightarrow S + RO + H^+ + Cl^-$	
$H_2O + S[OH^\bullet] \rightarrow S + O_2 + 3H^+ + 3e^-$	
$O_2 + S[OH^\bullet] \rightarrow S + O_3 + H^+ + e^-$	
$H_2O + S[OH^\bullet] \rightarrow S + H_2O_2 + H^+ + e^-$	
$H_2O + S[ClOH^\bullet] + Cl^- \rightarrow Cl_2 + S + O_2 + 3H^+ + 4e^-$	
$H_2O + S[ClOH^\bullet] + Cl_2 \rightarrow S + ClO_2 + 3H^+ + 2Cl^- + e^-$	
Indirect Oxidation	
$2Cl^- \rightarrow Cl_2 + 2e^-$	$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$
$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^-$	
$HOCl \rightleftarrows H^+ + OCl^-$	
$6OCl^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + \frac{3}{2}O_2 + 6e^-$	

A simple strength and weakness analysis of EC and EO$_x$ processes are illustrated in Fig. 1. Several studies coupling EC and EO$_x$ were reported in previously published work. EC&EO$_x$ treatment of synthetic textile wastewater were performed by Raju et al. [32] and 91.3% COD removal was achieved using Al electrodes for EC and graphite electrodes for EO$_x$ processes. Hernandez et al. [25] achieved complete COD removal from industrial wastewater using Fe electrodes for EC and boron-doped diamond (BDD) anode and Fe cathode for EO$_x$ processes. Hernandez et al. [27] reduced COD of the soft drink wastewater by 85% using Cu electrodes for EC, BDD anode and Cu cathode for EO$_x$ processes. EC/EO$_x$ treatment of domestic wastewaters was reported by Daghrir et al. [28] and 78% of COD removal was achieved using graphite as monopolar (MP) electrodes and Al as bipolar (BP) sacrificial electrodes. Urban wastewater treatment was performed and complete turbidity and *E. coli* removal was achieved by means of BDD MP electrodes and Al BP sacrificial electrodes [37]. From textile wastewater, COD removal of 93.5% was obtained by using MP Ti and BP Al electrodes [38]. Esfandyari et al. [39] reported 96% COD removal from olive mill wastewater using RuO_2/Ti anode, stainless steel cathode and Al as BP sacrificial electrodes.

In the present work, EC, EO$_x$, EC&EO$_x$ and EC/EO$_x$ techniques were performed for pulp and paper mill wastewater treatment by using Al and Fe electrodes for EC and graphite electrodes for EOx processes.

2. Materials and methods

2.1. Wastewater characteristics and analytical method

The wastewater samples used in this study were obtained from paper production process of a pulp and craft paper plant located in Turkey. Samples were stored in containers which were kept at 4°C. The characterization of pulp and paper mill wastewater is given in Table 4.

COD, color and turbidity analyses were performed according to the standard methods SM 5220 D, SM 2120 C and SM 2130 B respectively [40]. COD and color were measured at 600 nm and 456 nm wavelengths respectively by using a spectrophotometer (PG Instruments T60V). Turbidity was determined by using a turbidity meter (Aqualytic AL250T-IR). A pH meter, a conductivity meter and a thermocouple (Mettler Toledo M200 Easy) were immersed into the wastewater for on-line pH, conductivity and temperature monitoring during treatment.

2.2. Experimental setup and procedure

A batch 1.3 L electro-reactor made of plexiglass was constructed with 6 rectangular Al or Fe electrodes in MP arrangement for EC. EO$_x$ was carried out using 6 graphite electrodes with MP arrangement. EC/EOx treatments were

Table 4
Characterization of pulp and paper mill wastewater

Parameter	Sedimentation status	Value
pH	After	5.82 ± 0.05
Electrical conductivity (mS/cm)	After	2.10 ± 0.1
Color (Pt-Co)	Before	1549 ± 1
	After	722 ± 1
COD (mg/L)	Before	1045 ± 20
	After	413 ± 20
	Dissolved	114.93 ± 20
Turbidity (NTU)	Before	99 ± 1
	After	49 ± 1
Total suspended solids (mg/L)	Before	86.71 ± 5
	After	44.25 ± 5

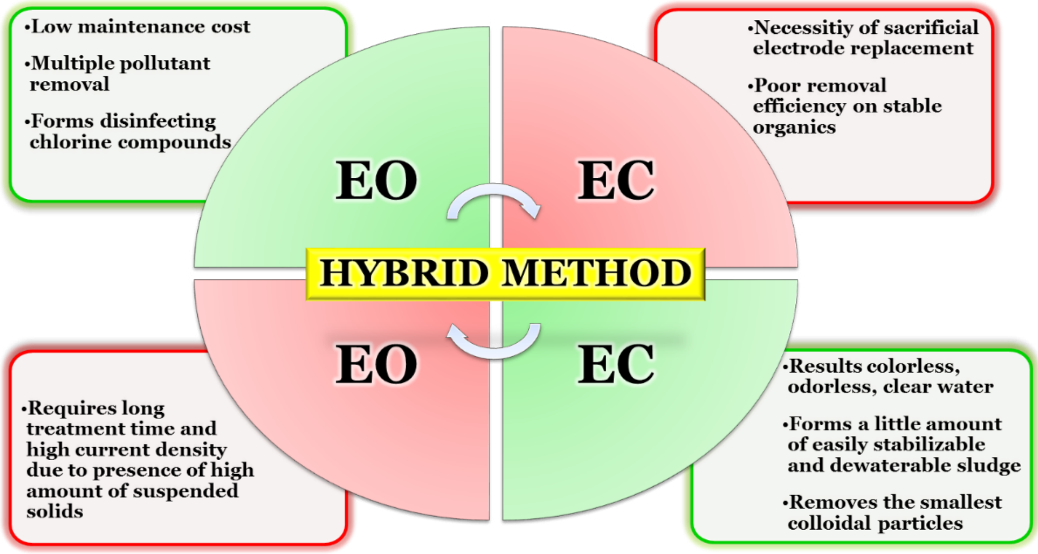


Fig. 1. Strength and weakness analysis of EC and EO$_x$.

performed using 4 graphite electrodes with MP arrangement and 3 Al or Fe electrodes with BP arrangement. Electrode specifications and configurations are given in Table 5 and Fig. 2, respectively.

A direct current power supply (MAY 11-PS constant current power supply) working in 0–2 ampere range was used to conduct experiments at constant current intensity. Uniform concentration distribution in the reactor was provided by a stirrer (MTOPS MS3200), which is operating at predetermined speed of 600 rpm. A pH meter, conductivity meter and a thermocouple (Mettler Toledo M200 Easy) were immersed into the reactor for on-line monitoring during treatment. On-line signals from pH meter, conductivity meter and thermocouple were sampled and transferred to computer through data acquisition device (MAY 11-ESA electrophoresis control unit). Experimental setup is given in Fig. 3.

In each run, initial values of electrical conductivity and pH of the medium was adjusted to the specified values using 1 M HCl, 1 M NaOH and saturated NaCl solution. To avoid considerable increments in the mixture volume of batch electro-reactor and pollutant dilution, the minimum amount of NaCl solution addition is aimed. 10 ml of samples were taken with variable intervals during the studies. At the end of the run, 250 ml sample was taken and settled at 4°C for 6 h [41]. The settling conditions were chosen by considering SM5220D in which maximum sample holding time is 28 days at 4°C [40]. The settled samples were analyzed in terms of COD, color and turbidity to determine removal efficiencies according to standard methods [40] except for EC&EO$_x$ treatment after 15 min. For this exceptional treatment period, all samples were directly analyzed as no settlements occurred. EC&EO$_x$ experiments were conducted according to the procedure given in Fig. 4. To remove impurities, electrode surfaces were scrubbed under tap water after each run. All removal efficiency and energy consumption calculations were made on the basis of wastewater characteristics after sedimentation. Energy consumption values were calculated per kg of COD removed using the logged voltage-time data considering Eq. (1) given as follows:

$$Energy\,consumption\,(kWh\,/\,kg\,COD_r) = \frac{I \times V_m \times t \times 1000}{([COD]_0 - [COD]_t) \times V_E} \qquad (1)$$

where, I is the applied current intensity in A, V_m is the mean potential difference applied in V, t is the duration of treatment in h, $[COD]_0$ and $[COD]_t$ are the initial and

Table 5
Electrode specifications

Treatment method	Material	Shape	Size (cm)	Thickness (cm)	Number of electrode	Spacing (cm)	Arrangement	Effective area (cm^2)
EC	Al	Rectangular	7 × 10	0.3	6	1	Monopolar parallel	504
	Fe	Rectangular	7 × 10	0.3	6	1	Monopolar parallel	504
EO$_x$	Graphite	Rectangular	7 × 10	0.3	6	1	Monopolar parallel	504
EC&EO$_x$	Al	Rectangular	7 × 10	0.3	6	1	Monopolar parallel	504
	Graphite	Rectangular	7 × 10	0.3	6	1	Monopolar parallel	504
EC&EO$_x$	Fe	Rectangular	7 × 10	0.3	6	1	Monopolar parallel	504
	Graphite	Rectangular	7 × 10	0.3	6	1	Monopolar parallel	504
EC/EO$_x$	Al	Rectangular	7 × 10	0.3	3	1	Bipolar parallel	378
	Graphite	Rectangular	7 × 10	0.3	4	1	Monopolar parallel	378
EC/EO$_x$	Fe	Rectangular	7 × 10	0.3	3	1	Bipolar parallel	378
	Graphite	Rectangular	7 × 10	0.3	4	1	Monopolar parallel	378

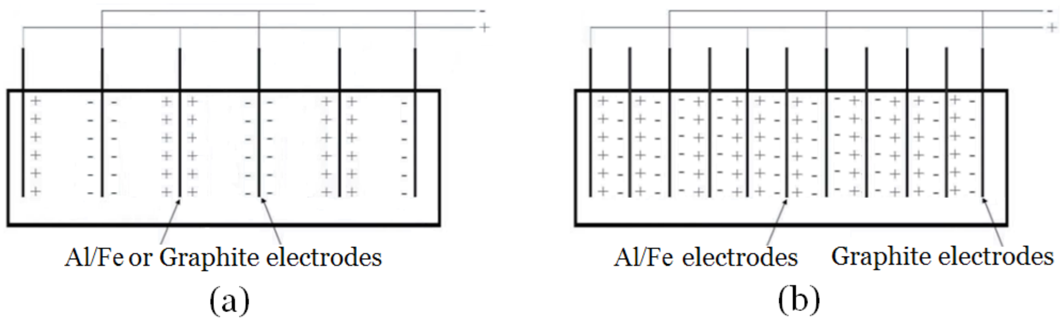


Fig. 2. Electrode configurations (a) MP arrangement (b) BP arrangement.

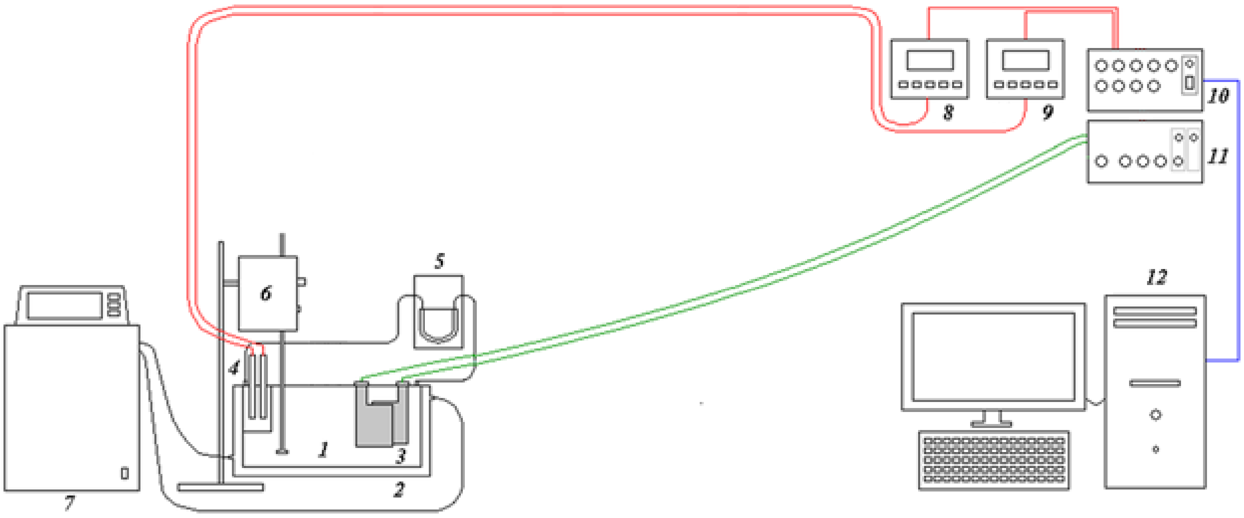


Fig. 3. Experimental system (1: EC reactor, 2: heating/cooling jacket, 3: electrodes, 4: pH meter, conductivity meter, thermocouple, 5: sample circulation pump, 6: mechanical stirrer, 7: heating/cooling water circulator, 8: pH and temperature display, 9: conductivity display, 10: control unit, 11: power supply, 12: computer).

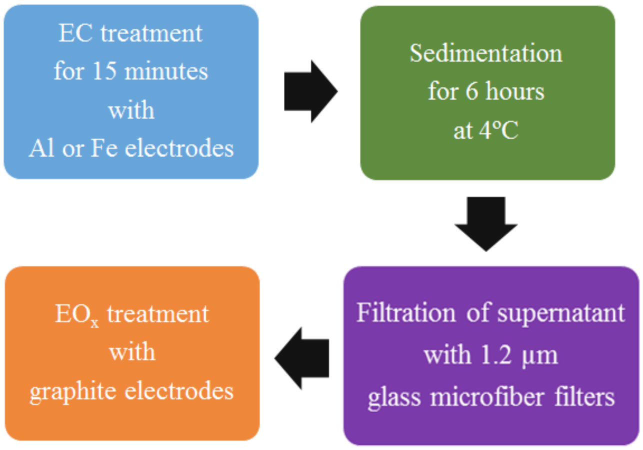


Fig. 4. Experimental procedure of EC&EO$_x$.

final COD values of the wastewater in mg/L, V_E is the volume of treated wastewater in L and COD$_r$ is the COD removed.

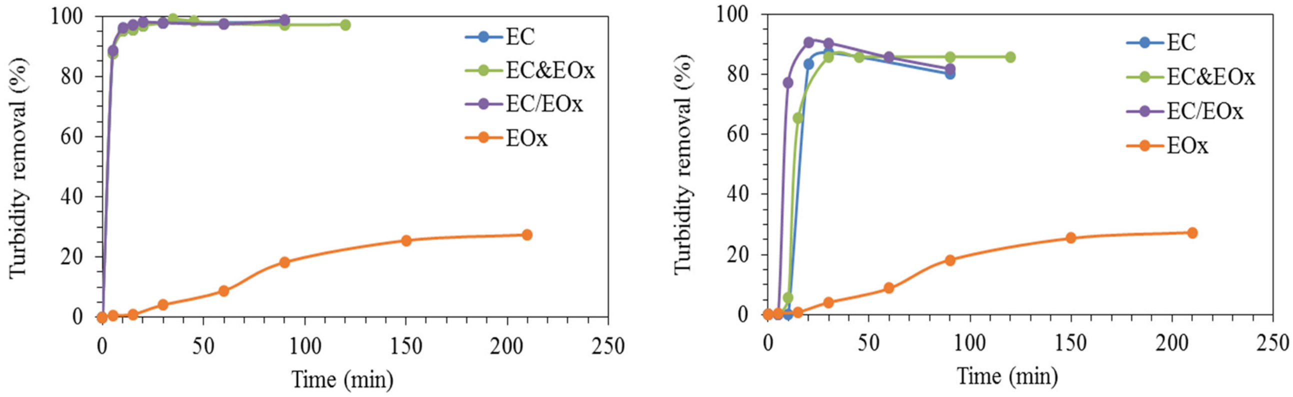
3. Results and discussion

3.1. Effect of different treatment methods on pollutant removal and energy consumption

Batch treatments of pulp and paper mill wastewater by means of EC, EO$_x$, consecutive EC&EO$_x$ and combined EC/EO$_x$ were carried out using Al or Fe as sacrificial electrodes at initial conditions of 5.82 pH, 2.10 mS/cm electrical conductivity, 1.22 A current intensity, 20°C temperature. Turbidity, COD and color removal results of EC, EO$_x$, EC&EO$_x$ and EC/EO$_x$ are given in Figs. 5–7, respectively. Results show that EC&EO$_x$ and EC/EO$_x$ treatments were both yielded 90% COD removal in 75 min with sacrificial Al electrodes. In addition, when Fe was used as the sacrificial electrode, 85% and 80% COD removal was obtained with EC/EO$_x$ and EC&EO$_x$ treatments in 90 min, respectively. EC treatment of pulp and paper mill wastewater yielded 73% and 58% removal of COD for Al and Fe electrodes, respectively, while EO$_x$ yielded only 54% COD removal in 210 min. Results show that with 15 min of treatment, EC achieved the highest COD removal value for both Al and Fe electrodes, with no increase in pollutant removal efficiency after this time due to the presence of soluble organic pollutants in pulp and paper mill wastewater. In addition, during 210 min of EO$_x$ treatment, pollutant removal tended to level off a lower value due to the presence of suspended solids.

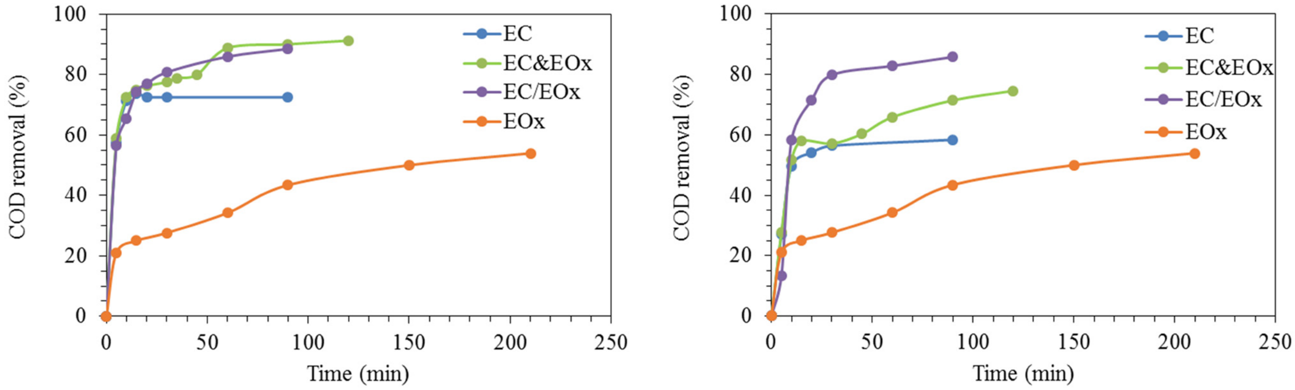
Turbidity and color removal by means of EC&EO$_x$ and EC/EO$_x$ with sacrificial Al electrodes were obtained as 98% turbidity and 100% color removal in 10 min of treatment, while EC yielded 98% turbidity and 95% color removal in 10 min. EO$_x$ removed only 27% of turbidity and 44% of color in a 210 min treatment. The certain amount of organic suspended solids in about 87 mg/L of the pulp and paper mill wastewater decreased the removal rate of EO$_x$ due to mass transfer resistances. When Fe was used as the sacrificial electrode, 90% turbidity and color removal was achieved in 30 min with EC/EO$_x$, which was 10% higher than that of the maximum removal obtained with both EC and EC&EO$_x$. After 30 min treatment, it was noted that the turbidity and color removal results of EC and EC/EO$_x$ were decreased due to formation of rust.

By applying EO$_x$ treatment, 27% turbidity and 44% color removal was reached in 210 min. Electrical conductivity, temperature and pH variations during EC, EO$_x$, EC&EO$_x$ and EC/EO$_x$ treatments with Al and Fe sacrificial electrodes are illustrated in Fig. 8.



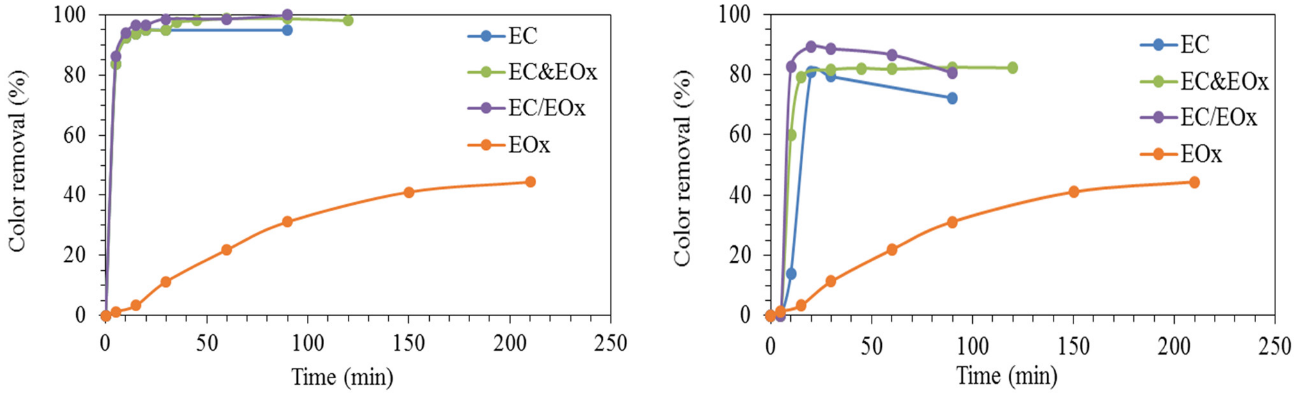
(a) (b)

Fig. 5. Turbidity removal results of various treatment methods for (a) Al electrodes (b) Fe electrodes.



(a) (b)

Fig. 6. COD removal results of various treatment methods for (a) Al electrodes (b) Fe electrodes.



(a) (b)

Fig. 7. Color removal results of various treatment methods for (a) Al electrodes (b) Fe electrodes.

As can be seen from Fig. 8a, with the usage of Al sacrificial electrodes, a 0.06 mS/cm decrease in electrical conductivity, 1.17 units of increase in pH were monitored for EC, while 1.30 mS/cm reduction in electrical conductivity, 1.05 units of pH drop and 6.20°C rise in temperature were observed for EO$_x$. EC was processed at 1.22 A current intensity and 18.2 V mean potential difference. During the 90 min treatment period, the lowest 4°C of temperature rise among the others was observed at 20°C room temperature conditions due to low energy con-

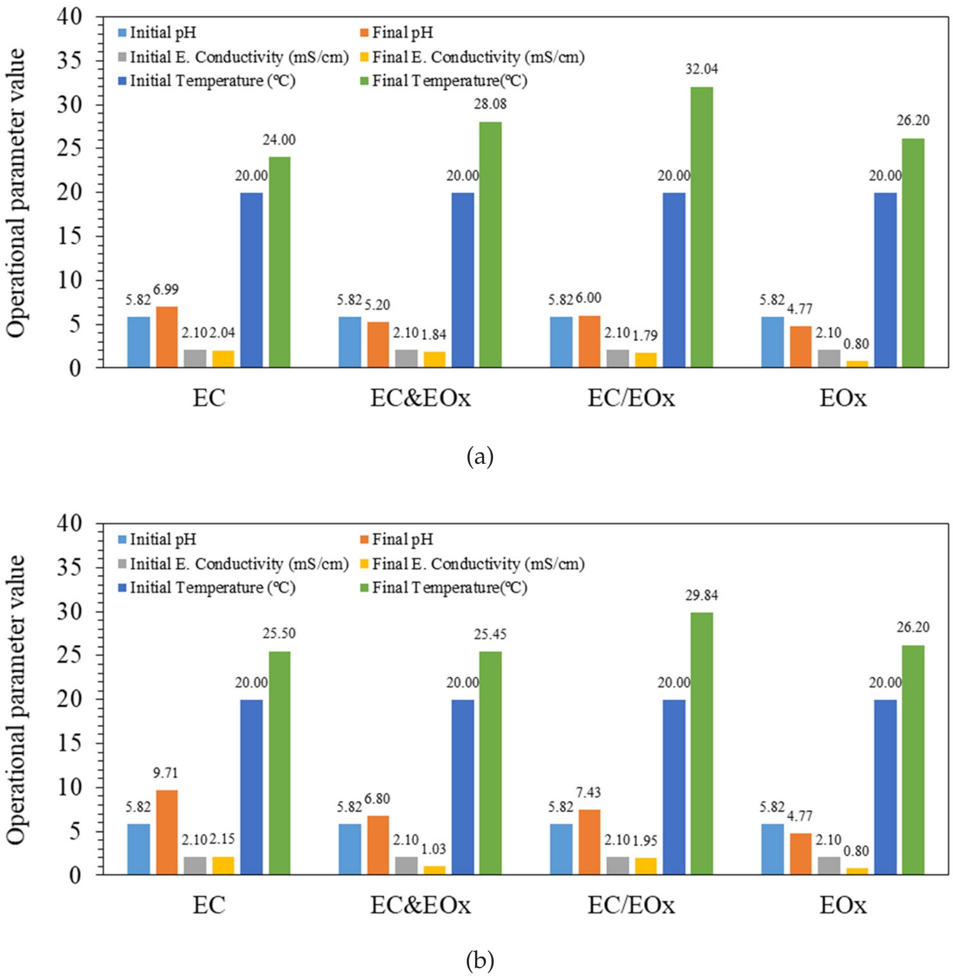


Fig. 8. Variation of operational parameters with various treatment methods for (a) Al electrodes (b) Fe electrodes.

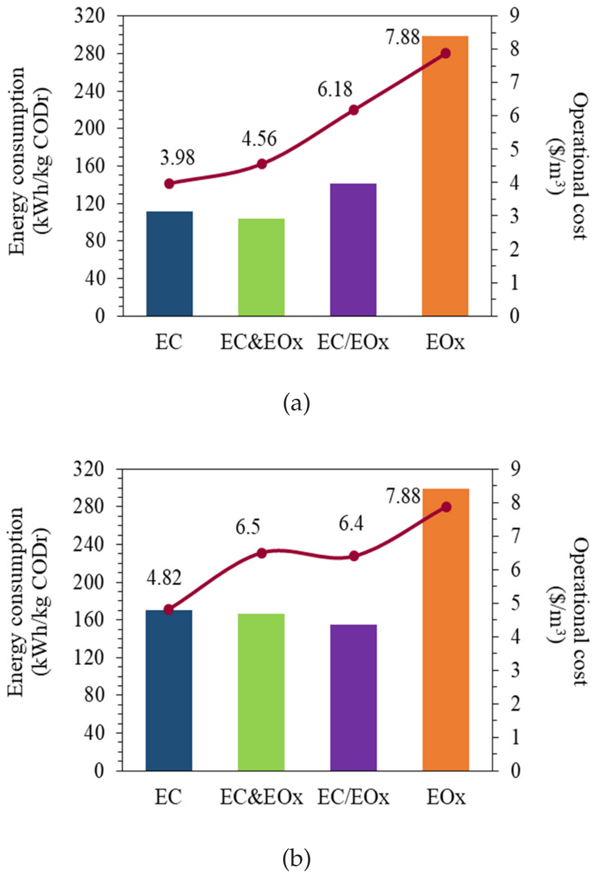
sumption. Throughout EC&EO$_x$ treatment, it was noted that electrical conductivity and pH values decreased by 0.26 mS/cm and 0.62 units respectively. A temperature increase of 8.08°C was also observed for EC&EO$_x$. During EC/EO$_x$ treatment, 0.31 mS/cm electrical conductivity reduction and 12.04°C temperature increase were found. The pH value was remained constant at about 6.

Fig. 8b shows that, with Fe electrodes, electrical conductivity, pH and temperature were increased by 0.05 mS/cm, 3.89 units and 5.5°C respectively for EC treatment, while 1.07 mS/cm reduction in electrical conductivity, 1 unit of pH increase and 5.45°C rise in temperature was observed for EC&EO$_x$. During EC/EO$_x$ treatment, 0.15 mS/cm electrical conductivity reduction, 1.61 units of pH and 12.04°C of temperature increase were observed.

Energy consumptions per kg of COD$_r$ and operational costs are illustrated for EC, EO$_x$, EC&EO$_x$ and EC/EO$_x$ treatments with the usage of Al and Fe electrodes (see Fig. 9). When Al was used as sacrificial electrode, energy consumption of EC process was calculated as 111.5 kWh/kg COD$_r$, which is 187.4 kWh/kg COD$_r$ lower than the energy consumption of the EO$_x$. Energy consumption of EC/EO$_x$ was calculated as 140.8 kWh/kg COD$_r$, which is 158 kWh/kg COD$_r$ less than that of the EO$_x$. This shows that the combination of EC and EO$_x$ has an interactive effect. Therefore, the combined process may remove more pollutant by consuming less energy. The least energy consumption of 103.9 kWh/kg COD$_r$ was evaluated for EC&EO$_x$ with Al electrodes among other treatment methods.

Additionally, by using Fe as sacrificial electrode, energy consumptions of EC and EC&EO$_x$ were calculated as 170.6 kWh/kg COD$_r$ and 166.47 kWh/kg COD$_r$ with the constant current power supply MAY 11-PS, respectively. Those values were found to be 34.6% and 37.6% higher than the values obtained with Al electrodes due to lower removal performance of Fe electrodes under the same initial operating conditions. Energy consumption of EC/EO$_x$ with Fe electrodes were the lowest among other treatment methods and calculated as 154.6 kWh/kg COD$_r$. If an economical evaluation is made, it will be seen that EO$_x$, which was performed using graphite electrodes has the highest operating cost as 7.88 \$/m^3, while EC using Al electrodes has the lowest operating cost as 3.98 \$/m^3.

When all the results obtained were taken into account, with 98% turbidity, 100% color, 90% COD removal and 103.9 kWh/kg COD$_r$ energy consumption, EC&EO$_x$ treatment using Al electrodes is the most adequate method than



(a)

(b)

Fig. 9. Energy consumptions and operational costs of various treatment methods with (a) Al electrodes (b) Fe electrodes.

the others studied. EC removed the suspended organic pollutants in 15 min. For the further time period, EO_x removed the remaining soluble organic pollutants in a relatively short treatment time domain. However, sedimentation and filtration steps of EC & EO_x did not make the process feasible in terms of investment and operating costs. On the other hand, EC/EO_x with Al electrodes has the same pollutant removal potential with slightly higher energy consumption in a single process. It is also noted that, increasing the efficiency of pollutant removal and reducing energy consumption simultaneously by determination of the optimal values of operating parameters such as pH, electrical conductivity, current intensity and temperature may be possible.

3.2. Effect of EC/EO_x operating parameters on pollutant removal and energy consumption

3.2.1. pH effect

Chemical dissolution of metal electrodes is strongly influenced by the pH of the solution. The dissolved metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate suspended particles or precipitate and adsorb dissolved contaminants [42,43]. At low pH (2–3) cationic monomeric species Al^{3+} and $Al(OH)^{+2}$ dominate. When pH is between 4 and 9, the Al^{3+} and OH^- ions generated by the electrodes react to form various monomeric species such as $Al(OH)^{+2}$, $Al(OH)_2^{2+}$, and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ that finally transform into insoluble amorphous $Al(OH)_{3(s)}$ through complex precipitation kinetics [44]. When pH is higher than 10, the monomeric $Al(OH)^{4-}$ anion concentration increases [45]. Chlorine formed at the electrode as the product of the EO_x reactions can react in the solution to form hypochlorous acid and hypochlorite ion, depending on whether the pH is low or high, respectively. Chlorine, hypochlorous acid and hypochlorite ions are strong oxidizing species that are often collectively referred as active chlorine [46].

In order to investigate the effect of pH on COD removal, color removal and energy consumption of the EC/EO_x process, batch treatments of pulp and paper mill wastewater were implemented at varying initial pH between 3 and 9, at the operating conditions of 5 mS/cm electrical conductivity, 1 A current intensity, and 20ºC temperature during 90 min. Pollutant removal and energy consumption results are given in Fig. 10.

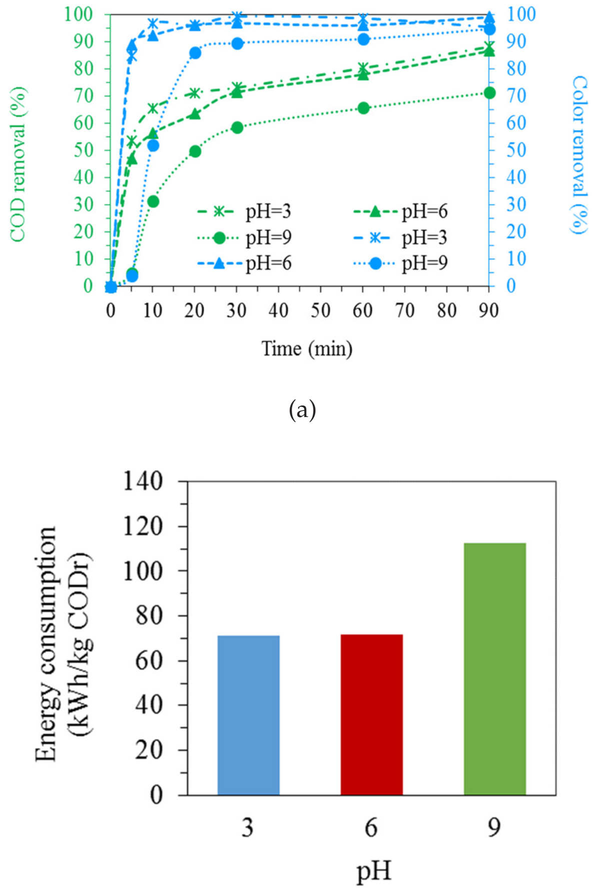
Results show that maximum pollutant removal and minimum energy consumption values were obtained at pH 3 as 88% COD removal, 97% color removal and 71.0 kWh/kg COD_r. After 90 min of EC/EO_x treatment at the initial pH values of 3, 6 and 9, the final pH values were measured as 9.43, 9.60 and 9.95, respectively. The increase of pH from the initial value of 3, depending on the OH^- formed in the cathode, resulted in similar pollutant removal amounts compared with the initial pH of 6. Also, 2.70 mS/cm reduction of electrical conductivity at pH 3, which was 0.75 mS/cm higher than the electrical conductivity drop at pH 6, indicates more active chlorine formation which causes higher organic pollutant removal via oxidation. Variations of operational parameters are shown in Fig. 11. According to the similar pollutant removal results, the initial pH value of 6 was considered to be the most appropriate value for safe and economical process operation.

3.2.2. Electrical conductivity effect

Electrical conductivity depends on ion concentrations and the temperature of a solution. Due to Ohm's law of resistance, high values of electrical conductivity reduces the resistance, the potential difference and power consumption of the EC process under constant current conditions [47]. Serikawa et al. [48] observed strong catalytic effect of chloride ion on oxidation of organic pollutants. Indirect EO_x involving active chlorine is a predominant process in removing organic pollutants from chloride medium [32].

Effect of initial electrical conductivity on COD removal, color removal and energy consumption of the EC/EO_x process was investigated by conducting batch treatments of pulp and paper mill wastewater at varying initial electrical conductivity values between 3 mS/cm and 7 mS/cm at the operating conditions of pH 6, 1 A current intensity, and 20ºC temperature for 90 min. Pollutant removal and energy consumption results are given in Fig. 12.

Results show that maximum pollutant removal values were obtained at 5 mS/cm electrical conductivity as



(a)

(b)

Fig. 10. Effect of pH on EC/EO$_x$ process in terms of (a) COD and color removal; (b) energy consumption.

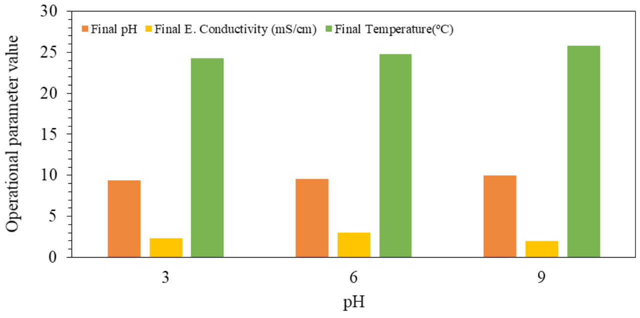
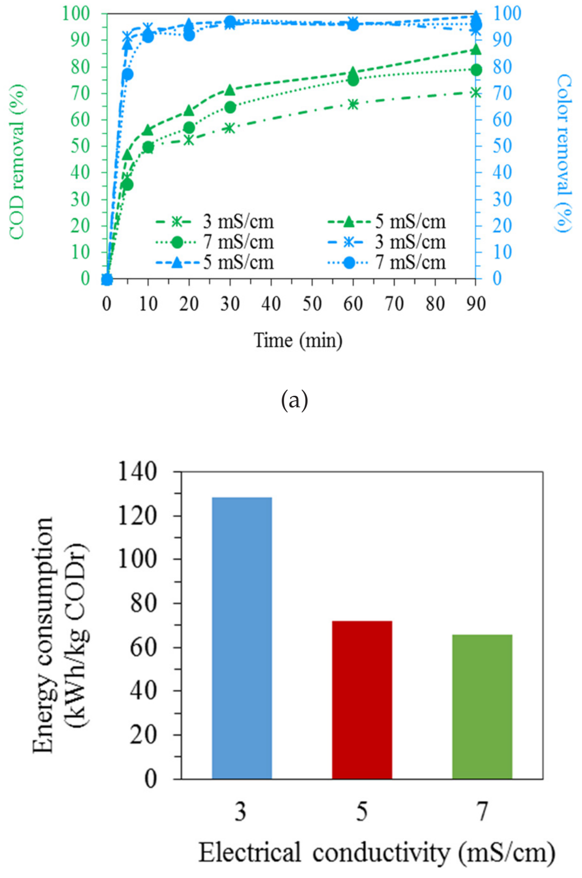


Fig. 11. Variation of operational parameters with initial pH.

87% COD removal, 99% color removal. Energy consumption at 5 mS/cm was calculated as 71.8 kWh/kg COD$_r$, which was very close to the value that was calculated as 66.0 kWh/kg COD$_r$ at 7 mS/cm. After 90 min of EC/EO$_x$ treatment at the initial electrical conductivity values of 3mS/cm, 5 mS/cm and 7 mS/cm, final electrical conductivities were measured as 2.03, 3.05 and 4.21 respectively. Variations of operational parameters are shown in



(a)

(b)

Fig. 12. Effect of electrical conductivity on EC/EO$_x$ process in terms of (a) COD and color removal; (b) energy consumption.

Fig. 13. Electrical conductivity decrease of 1.95 mS/cm from its 5 mS/cm initial value, which was nearly 1 mS/cm higher than the electrical conductivity reduction from the initial value of 3, indicates more active chlorine formation. Although there was a decrease of 2.79 mS/cm in electrical conductivity during treatment at the initial value of 7 mS/cm, pollutant removal was lower than that was obtained at the initial value of 5 mS/cm. At 25ºC and normal atmospheric pressure, $Cl_{2(g)}$ that liberated from anode can dissolve in water to the extent of 6.413 g/L. If its solubility is exceeded locally at the electrode surface, then Cl_2 bubbles may form [32]. Furthermore, salinity decrease was noted by EC/EO$_x$ which was attributed to reduction of some anions and cations using coagulation mechanism [49]. Therefore, at 7 mS/cm initial electrical conductivity the active chlorine formation was lower than that at 5 mS/cm. According to the obtained results, the electrical conductivity value of 5 mS/cm was considered to be the most appropriate value.

3.2.3. Current intensity effect

As the current intensity increases in the EC/EO$_x$ process, the amount of dissolved sacrificial BP electrode

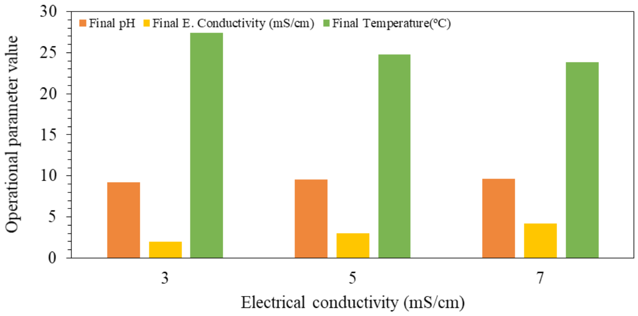


Fig. 13. Variation of operational parameters with initial electrical conductivity.

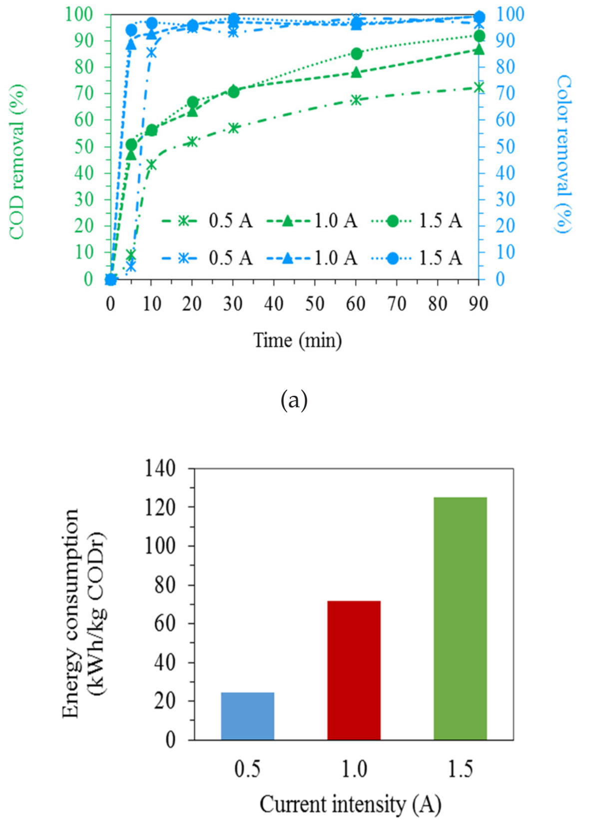
increases and the dissolution of significant amounts of sacrificial electrode material at high current densities increases the amount of contaminants removal from the wastewater. In the EC/EO$_x$ process, not only the amount of dissolved metal, but also the rate of formation of active chlorine, hydroxyl radicals, gas bubbles (H_2, Cl_2) and the size of the flocks which will affect the yield of the process depend on the current intensity. As the current intensity increases, the amount of oxidant and the number of gas bubbles increase, causing the pollutants to be removed more and faster.

In order to investigate the effect of current intensity on COD removal, color removal and energy consumption of the EC/EO$_x$ process, batch treatments of pulp and paper mill wastewater were conducted at varying current intensities between 0.5 A and 1.5 A at the operating conditions of 5 mS/cm electrical conductivity, pH 6, and 20ºC temperature for 90 min. Pollutant removal and energy consumption results are given in Fig. 14.

Maximum pollutant removal values were obtained at 1.5 A current intensity as 92% COD removal, 99% color removal. Energy consumption at 1.5 A was calculated as 125.1 kWh/kg COD$_r$, which was found to be higher than the value that was calculated as 71.8 kWh/kg COD$_r$ at 1 A (87% COD removal, 99% color removal). In order to evaluate the effect of current intensity on pollutant removal, instantaneous current efficiency (ICE) was utilized. ICE values were calculated using Eq. (2) given below.

$$ICE(\%) = \frac{([COD]_0 - [COD]_t) \times F \times V_E}{3600 \times 1000 \times 8 \times I \times t} \tag{2}$$

Here, $[COD]_0$ and $[COD]_t$ stand for the initial and final COD value of the wastewater in mg/L, F represents the Faraday constant (96485 C/mole), V_E symbolizes the volume of treated wastewater in L, I is the applied current intensity in A and t is the duration of treatment in *h*. Variation of ICE with current intensity is shown in Fig. 15.



(a)

(b)

Fig. 14. Effect of current intensity on EC/EO$_x$ process in terms of (a) COD and color removal (b) energy consumption.

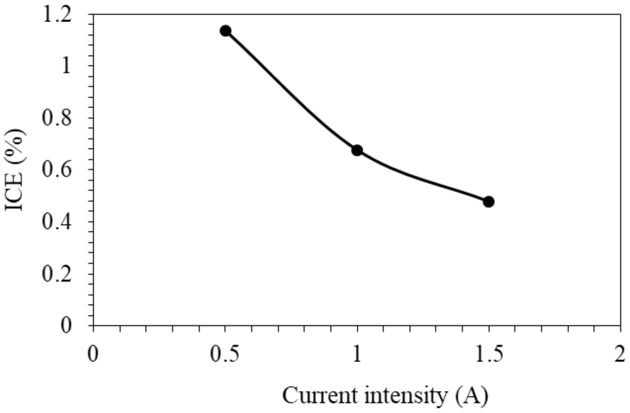


Fig. 15. Variation of ICE with current intensity.

Considering the calculated values, increasing current intensity reduced ICE. After 90 minutes of EC/EO$_x$ treatment at the current intensities of 0.5A, 1 A and 1.5 A, final electrical conductivities were measured as 3.50 mS/cm, 3.05 mS/cm and 2.88 mS/cm, respectively. Variations of operational parameters are shown in Fig. 16. At 1.5 A, an electrical conductivity decrease of 2.12 mS/cm was observed, which is close to the electrical conductivity reduction of 1.95 mS/cm at 1 A. The results indicate that, similar active chlorine formation occurred at 1 A and 1.5 A current intensities. Targeting adequate pollutant removal, higher ICE results and less energy consumption (see Fig. 14b), the current intensity range of 0.5–1 A was considered to be appropriate for process operation cases.

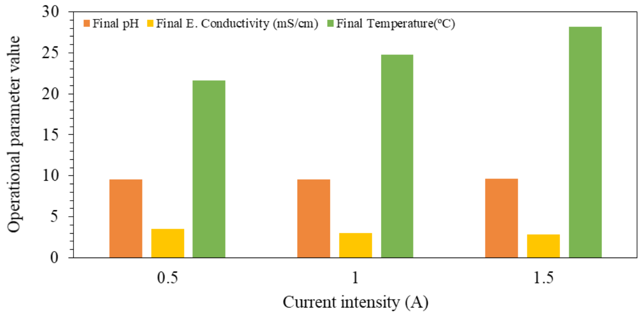
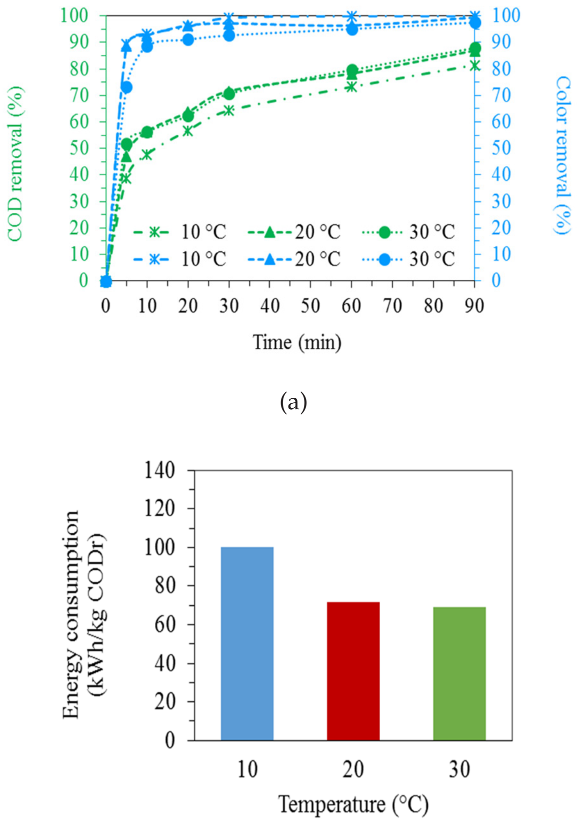


Fig. 16. Variation of operational parameters with current intensity.

3.2.4. Temperature effect

Temperature affects the pollutant removal with respect to rate of reactions, solubility of metal hydroxides, liquid conductivity and kinetic energy of gas bubbles [50]. In order to investigate the effect of temperature on COD removal, color removal and energy consumption of the EC/EO$_x$ process, batch treatments of pulp and paper mill wastewater were conducted at varying temperatures between 10ºC and 30ºC at the operating conditions of 5 mS/cm electrical conductivity, pH 6 and 1 A current intensity for 90 min. Pollutant removal and energy consumption results are given in Fig. 17.

Results show that maximum pollutant removal and minimum energy consumption values were obtained at 20ºC and 30ºC as 88% COD removal, 98% color removal and 70.5 kWh/kg COD_r with the constant current power supply MAY 11-PS. After 90 min of EC/EO$_x$ treatment at the initial temperature values of 10ºC, 20ºC and 30ºC, final pH and electrical conductivity values were found to be very close for 20ºC and 30ºC as about 9.40 and 3.07 mS/cm, respectively. Although temperature change was observed during 90 min of treatment, a constant 10°C temperature difference was remained between the initial and final temperatures. Variations of operational parameters are shown in Fig. 18. At 10ºC, final pH and electrical conductivity values were measured as 9.98 and 4.23 mS/cm respectively. Thus, the monomeric Al(OH)$^{4-}$ formation depending on pH value and low amount of active chlorine formation depending on electrical conductivity drop leads to lower pollutant removal. The 10°C difference between the end points of wastewater treatments given in Fig. 18 has no significant effect on pollutant removal and energy consumption for EC/EO$_x$ process. Thus any temperature over 10ºC may be appropriate for process operation.



(a)

(b)

Fig. 17. Effect of temperature on EC/EO$_x$ process in terms of (a) COD and color removal (b) energy consumption.

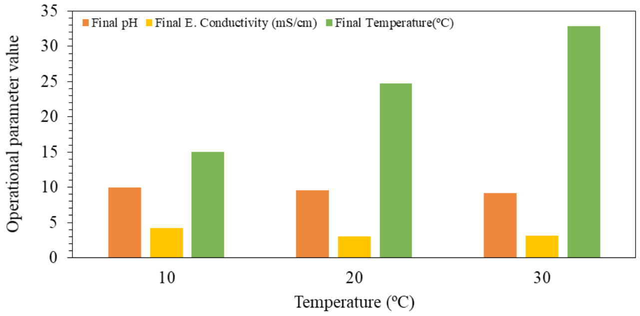


Fig. 18. Variation of operational parameters with temperature.

4. Conclusion

This research noted successful applications of EC, EO$_x$, EC & EO$_x$ and EC/EO$_x$ techniques to the treatment of pulp and paper mill wastewater using Al or Fe electrodes for EC stage and graphite electrodes for EO$_x$ stage. The efficiency of the methods was assessed by using COD, turbidity, color removal and energy consumption per kg removed COD amounts. Results showed that application of 15 min EC reached the highest COD removal value for both Al and Fe electrodes, with no increase in pollutant removal efficiency after this time due to the presence of stable organic pollutants in pulp and paper mill wastewater. In addition, during 210 min of EO$_x$ treatment, pollutant removal has increased slowly but consistently due to the presence of suspended solids. EC has the ability to remove pollutants quickly but not completely. EO$_x$ is able to remove pollutants slowly but consistently. EC&EO$_x$ and EC/EO$_x$ are combining the best abilities of EC and EO$_x$ processes with fast and complete

Table 6
Comparison of industrial pulp and paper wastewater treatments

Reference	Treatment method	Electrode material	Parameters	Optimum conditions	COD removal	Energy consumption	Operational cost
[1]	EC	Al	Electrolysis time Current density Initial pH NaCl concentration Stirring speed Inter-electrode distance	20 min 15 mA/cm^2 7 1 g/L 100 rpm 3 cm	90 %	11.055 kWh/m^3	1.56 $/m^3
[4]	EC	Al	Initial pH Current density Inter-electrode distance Electrolysis time	7 115 mA/cm^2 1.5 cm 75 min	77 %	–	–
[5]	EC	Al/Fe	Electrolysis time Voltage Initial pH Current density	60 min 10 V 5 4.167 mA/cm^2	85 %	8.334 kWh/m^3	–
[3]	EC	–	Current density Initial pH Initial COD conc. Electrode combination Inter-electrode distance	0.40 A/dm^2 7 2500 mg/L Fe/Fe 1 cm	85 %	5.16 kWh/m^3	–
[7]	EC	Fe	Supporting electrolyte conc. Current density Initial pH Stirring speed	0.03 M Na_2SO_4 30 mA/cm^2 3 50 rpm	88.5 %	11.5 kWh/m^3	–
[49]	EC	Fe	Initial pH Current density Electrolysis time	6.38 5.55 mA/cm^2 33.7 min	61.2 %	2.98 kWh/m^3	
[51]	EO_x	Cathode: graphite Anode: Ti /Co /SnO_2-Sb_2O_5+AC	Initial pH Current density	11 167 mA/cm^2	90 %	650 kWh/kg COD_r	–
[52]	EO_x	Graphite	Initial pH Current density Catalyst dose	3 70 mA/cm^2 90 g/L	96.8 %	8 kWh/kg COD_r	
[53]	EO_x	Cathode: Stainless steel Anode: RuOx –IrOx–TiOx coated titanium substrate insoluble anode	Electrolysis time Supporting electrolyte conc. Current density	5 h 3 g/L 2.5 A/dm^2	68 %	38.66 kWh/kg COD_r	–
[54]	EC	Cathode: Stainless steel Anode: Mild steel	Electrolysis time Current density Initial pH	35 min 1.05 A/dm^2 7.5	59.86 %	5.14 kWh/kg COD_r	0.48 $/m^3
	EO_x	Cathode: Stainless steel Anode: RuOx –IrOx–TiOx coated titanium anode	Electrolysis time Current density Initial pH	110 min 1.4 A/dm^2 7.5	53.41 %	26.85 kWh/kg COD_r	1.41 $/m^3
	EC&EO_x & Biological	Same as used in both EC and EO_x	Same as used in both EC and EO_x	Same as used in both EC and EO_x	94.91 %	14.856 kWh/kg COD_r	1.55 $/m^3
Present study	EC/ EO_x	MP Graphite BP Al	Initial pH Electrical Conductivity Current intensity Temperature	6 5 mS/cm 1 A 20ºC	87 %	31.6 kWh/kg COD_r	1.33 $/m^3

pollutant removal. When all the results obtained were taken into account, with 98% turbidity, 100% color and 90% COD removal and 103.9 kWh/kg COD_r energy consumption, EC&EO_x treatment using Al electrodes stands out as the most suitable method. However, sedimentation and filtration steps of EC&EO_x made the process inadequate in terms of investment and operating costs. Moreover, EC/EO_x with Al electrodes has the same pollutant removal potential with slightly higher energy consumption in a single process and it is possible to increase the efficiency of pollutant removal and reduce energy consumption simultaneously by optimizing operating parameters. Effects of initial pH, electrical conductivity, temperature and current intensity on pollutant removal and energy consumption by means of EC/EO_x were also investigated, optimal operational parameters are determined as, 6, 5 mS/cm, 20°C and 1 A respectively. Under optimum conditions, turbidity and color were completely removed, whereas 87% COD removal on the basis of sedimented wastewater was achieved. The energy of 71.8 kWh/kg COD_r and 31.6 kWh/kg COD_r were consumed with the use of constant current power supplies MAY 11-PS and SUNLINE PS 305D respectively.

Various electrochemical treatment results of pulp and paper mill wastewaters obtained from different sources in the previously published work were roughly compared with the present study in Table 6. Sridhar et al. [1] reported that energy consumption of EC for treatment of pulp and paper industry bleaching effluent was 11.055 kWh/m^3 for 20 min treatment under 150 A/m^2 current density and the operational cost of 90% COD removal was found as 1.56$/$m^3$. Similarly, Un et al. [7] obtained 88.5% COD removal from tissue paper wastewater using EC treatment with 11.5 kWh/m^3 energy consumption under 300 A/m^2 current density conditions. EO_x of paper mill wastewater was performed by Wang et al. [51] and 90% COD removal with the energy consumption of 650 kWh/kg COD_r was obtained. Soloman and Balasubramanian [54] reported operational costs of 0.48 \$/m^3, 1.41 \$/m^3 and 1.55 \$/m^3 with 59.86%, 53.41% and 94.91% COD removal efficiencies for EC, EO_x and EC & EO_x and biological treatment of bleaching effluent, respectively.

It was observed that the operational ranges were well-suited with the ones in literature.The energy consumption of 31.6 kWh/kg COD_r and operational cost of 1.33 \$/m^3 obtained under current density of 13.23 A/m^2 in 90 minutes using the constant current power supply SUNLINE PS 305D were considered to be highly competitive when compared with those reported in the literature. Although the cost of the present work with the constant current power supply MAY 11-PS might not be the adequate one, the operating cost of EC/EO_x is reduced from 6.18 \$/m^3 to 3.04 \$/m^3 by using suitable operating parameters and it is noted that with the use of a more energy efficient power supply such as SUNLINE PS 305D, highly competitive results were obtained.

Acknowledgments

This research was supported by Ankara University Scientific Research Projects Coordination Unit [grant numbers 16B0443001 and 14L0443005].

References

[1] R. Sridhar, V. Sivakumar, V. P. Immanuel, J. P. Maran, Treatment of pulp and paper industry bleaching effluent by electrocoagulant process, J. Hazard. Mater., 186(2) (2011) 1495–1502.

[2] N. Li, H. Ma, B. Wang, Advanced treatment of paper millwastewater by catalytic vacuum distillation, Desal. Water Treat., 16 (2010) 298–303.

[3] P. Asaithambi, Studies on various operating parameters for the removal of COD from pulp and paper industry using electrocoagulation process, Desal. Water Treat., 57(25) (2016) 11746–11755.

[4] R. Shankar, L. Singh, P. Mondal S. Chand, Removal of COD, TOC, and color from pulp and paper industry wastewater through electrocoagulation, Desal. Water Treat., 52(40–42) (2014) 7711–7722.

[5] M.A. Aghdam, H.R. Karimina, S. Safari, Removal of lignin, COD, and color from pulp and paper wastewater using electrocoagulation, Desal. Water Treat., 52(21) (2016) 9698–9704.

[6] D. Pokhrel, T. Viraraghavan, Treatment of pulp and paper mill wastewater - a review, Sci. Total. Environ., 333 (2004) 37–58.

[7] U. T. Un, S. Topal F. Ates, Electrocoagulation of tissue paper wastewater and an evaluation of sludge for pyrolysis, Desal. Water Treat., 57(59) (2016) 28724–28733.

[8] R. Behrooz, H.H. Abadi, B. Mohebby, Turbidity and BOD removal of a paper recycling mill effluent by electro-coagulation technique, Desal. Water Treat., 28 (2011) 65–68.

[9] J. Jafari, A. Mesdaghinia, R. Nabizadeh, M. Farrokhi, A.H. Mahvi, Investigation of anaerobic fluidized bed reactor/aerobic moving bed bio reactor (AFBR/MMBR) system for treatment of currant wastewater, Iran. J. Public Health, 42(8) (2013) 860.

[10] A. Shawwa, D. Smith, D. Sego, Color and chlorinated organics removal from pulp mills wastewater using activated petroleum coke, Water Res., 35(3) (2001) 745–749.

[11] M.M. Hassan, C.J. Hawkyard, Decolorisation of aqueous dyes by sequential oxidation treatment with ozone and Fenton's reagent, J. Chem. Technol. Biotechnol., 77(7) (2002) 834–841.

[12] S. Verenich, A. Laari J. Kallas, Wet oxidation of concentrated wastewaters of paper mills for water cycle closing, Waste Manage., 20(4) (2000) 287–293.

[13] A. Raj, M.M.K. Reddy, R. Chandra, Decolorisation and treatment of pulp and paper mill effluent by lignin-degrading Bacillus sp., J. Chem. Technol. Biotechnol., 82:4 (2007) 399–406.

[14] K. V. Rajeshwari, M. Balakrishnan, A. Kansal, K. Lata V. V. N. Kishore,State-of-the-art of anaerobic digestion technology for industrial wastewater treatment Renewable Sustainable Energy Rev., 4(2) (2000) 135–156.

[15] Ş. Camcıoğlu, B. Özyurt, Z. Zeybek, H. Hapoglu, Experimental application of one step ahead advanced pH control to water-based paint wastewater treatment, J. Fac. Eng. Archit. Gazi, 31(3) (2016) 655–664.

[16] K.S.P. Kalyani, N. Balasubramanian, C. Srinivasakannan, Decolorization and COD reduction of paper industrial effluent using electro-coagulation, Chem. Eng. J., 151(1) (2009) 97–104.

[17] Y. Xu, J.Q. Jiang, K. Quill, J. Simon K. Shettle, Electrocoagulation: a new approach for the removal of boron containing wastes, Desal. Water Treat., 2 (2009) 133–140.

[18] H. Moreno, J.R. Parga, A. J. Gomes, M. Rodríguez, Electrocoagulation treatment of municipal wastewater in Torreon Mexico, Desal. Water Treat., 51(13–15) (2013) 2710–2717.

[19] N.M. Mahmoodi, A. Dalvand, Treatment of colored textile wastewater containing acid dye using electrocoagulation process, Desal. Water Treat., 51(31–33) (2013) 5959–5964.

[20] F. Benaissa, H. Kermet-Said, N. Moulai-Mostefa, Optimization and kinetic modeling of electrocoagulation treatment of dairy wastewater, Desal. Water Treat., 57(13) (2016) 5988–5994.

[21] A. K. Yadav, L. Singh, A. Mohanty, S. Satya, T.R. Sreekrishnan, Removal of various pollutants from wastewater by electrocoagulation using iron and aluminium electrode, Desal. Water Treat., 46 (2012) 352–358.

[22] G. Varank, S.Y. Guvenc, G. Gurbuz, G.O. Engin, Statistical optimization of process parameters for tannery wastewater treatment by electrocoagulation and electro-Fenton techniques, Desal. Water Treat., 57(53) (2016) 25460–25473.

[23] S. Vasudevan, J. Lakshmi, G. Sozhan, Studies on the removal of arsenate from water through electrocoagulation using direct and alternating current, Desal. Water Treat., 48 (2012) 163–173.

[24] S. Camcioglu, L. C. Pekel, K. Polat, H. Hapoglu, Experimental Design of Wastewater Treatment with Electro-coagulation, Manag. Environ. Qual. Int. J., 25 (2014) 86–95.

[25] I.L. Hernández, C. Barrera-Díaz, B. Bilyeu, P.J.G. Rojas, E. Campos-Medina, A combined electrocoagulation–electrooxidation treatment for industrial wastewater, J. Hazard. Mater., 175(1) (2010) 688–694.

[26] M. Uğurlu, A. Gürses, Ç. Doğarand, M. Yalçın, The removal of lignin and phenol from paper mill effluents by electrocoagulation, J. Environ.Manage., 87 (2008) 420–428.

[27] I.L. Hernández, C.B. Díaz, M.V. Cerecero, P.T.A. Sánchez, M.C. Juárez, V.L. Lugo, Soft drink wastewater treatment by electrocoagulation–electrooxidation processes, Environ. Technol., 38(4) (2017) 433–442.

[28] R. Daghrir, P. Drogui, F. Zaviska, Effectiveness of a hybrid process combining electro-coagulation and electro-oxidation for the treatment of domestic wastewaters using response surface methodology, J. Environ. Sci. Heal. A., 48(3) (2013) 308–318.

[29] O.T. Can, COD removal from fruit-juice production wastewater by electrooxidation electrocoagulation and electro-Fenton processes,Desal. Water Treat., 52(1–3) (2014) 65–73.

[30] R. Bhatnagar, H. Joshi, I.D. Mall, V.C. Srivastava, Electrochemical oxidation of textile industry wastewater by graphite electrodes, J. Environ. Sci. Heal. A., 49(8) (2014) 955–966.

[31] P.V. Nidheesh, R. Gandhimathi, Removal of Rhodamine B from aqueous solution using graphite–graphite electro-Fenton system, Desal. Water Treat., 52(10–12) (2014) 1872–1877.

[32] G.B. Raju, M.T. Karuppiah, S.S. Latha, S. Parvathy, S. Prabhakar, Treatment of wastewater from synthetic textile industry by electrocoagulation–electrooxidation, Chem. Eng. J., 144 (2008) 51–58.

[33] K. Ighilahriz, M.T. Ahmed, H. Djelal, R. Maachi, Electrocoagulation and electro-oxidation treatment for the leachate of oil-drilling mud, Desal. Water Treat., 52(31–33) (2014) 5833–5839.

[34] C.J. Israilides, A.G. Vlyssides, V.N. Mourafeti, G. Karvouni, Olive oil wastewater treatment with the use of an electrolysis system, Bioresource Technol., 61(2) (1997) 163–170.

[35] O.T. Can, Removal of TOC from fertilizer production wastewater by electrooxidation, Desal. Water Treat., 53(4) (2015) 919–927.

[36] B. Körbahti, K. Artut, Electrochemical oil/water demulsification and purification of bilge water using Pt/Ir electrodes, Desalination, 258(1–3) (2010) 219–228.

[37] S. Cotillas, J. Llanos, P. Canizares, S. Mateo, M.A. Rodrigo, Optimization of an integrated electrodisinfection/electrocoagulation process with Al bipolar electrodes for urban wastewater reclamation, Water Res., 47(5) (2013) 1741–1750.

[38] A.S. Naje, S. Chelliapan, Z. Zakaria, S.A. Abbas, Enhancement of an electrocoagulation process for the treatment of textile wastewater under combined electrical connections using titanium plates, Int. J. Electrochem. Sci., 10 (2005) 4495–4512.

[39] Y. Esfandyari, Y. Mahdavi, M. Seyedsalehi, M. Hoseini, G. H. Safari, M. G. Ghozikali, H. Kamani, J. Jaafari, Degradation and biodegradability improvement of the olive mill wastewater by peroxi-electrocoagulation/electrooxidation-electroflotation process with bipolar aluminum electrodes, Environ. Sci. Pollut. Res., 22 (2015) 6288–6297.

[40] APHA, Standard Methods for the Examination of Water and Wastewater, A.D. Eaton, L.S. Clesceri, E.W. Rice, M.A.H. Franson (Eds.), twenty-first ed., American Public Health Association (APHA), American Water Works Association (AWWA) and the Water Environment Federation (WEF), Washington DC, 2005.

[41] C.L. Lai, S.H. Lin, Treatment of chemical mechanical polishing wastewater by electrocoagulation: system performances and sludge settling characteristics, Chemosphere, 54(3) (2004) 235–242.

[42] B. Merzouk, B. Gourich, A. Sekki, K. Madani, C. Vial, M. Barkaoui, Studies on the decolorization of textile dye wastewater by continuous electrocoagulation process, Chem. Eng. J., 149(1) (2009) 207–214.

[43] P. Canizares, M. Carmona, J. Lobato, F. Marinez, M.A. Rodrigo, Electrodissolution of aluminum electrodes in electrocoagulation processes, Ind. Eng. Chem. Res., 44(12) (2005) 4178–4185.

[44] M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, Operating cost analysis of electrocoagulation of textile dye wastewater, Sep. Purif. Technol., 37(2) (2004) 117–125.

[45] A. Alinsafi, M. Khemis, M.N. Pons, J.P. Leclerc, A. Yaacoubi, A. Benhammou, A. Nejmeddine, Electrocoagulation of reactive textile dyes and textilewastewater, Chem. Eng. Process., 44(4) (2005) 461–470.

[46] L. Szpyrkowicz, S.N. Kaul, R.N. Neti, S. Satyanarayan, Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater, Water Res., 39(8) (2005) 1601–1613.

[47] E. Terrazas, A. Vázquez, R. Briones, I. Lázaro, I. Rodríguez, EC treatment for reuse of tissue paper wastewater: Aspects that affect energy consumption, J. Hazard. Mater., 181(1) (2010) 809–816.

[48] R.M. Serikawa, M. Isaka, Q. Su, T. Usui, T. Nishimura, H. Sato S. Hamada, Wet electrolytic oxidation of organic pollutants in wastewater treatment, J. Appl. Electrochem., 30(7) (2000) 875–883.

[49] N. Jaafarzadeh, M. Omidinasab, F. Ghanbari, Combined electrocoagulation and UV-based sulfate radical oxidation processes for treatment of pulp and paper wastewater, Process Saf. Environ. Prot., 102 (2016) 462–472.

[50] C. Phalakornkule, J. Mandmeemak, K. Intrachod, B. Nuntakumjorn, Pretreatment of palm oil mill effluent by electrocoagulation and coagulation, Science Asia, 36(2) (2010) 142.

[51] B. Wang, W. Kong, H. Ma, Electrochemical treatment of paper mill wastewater using three-dimensional electrodes with Ti/Co/SnO_2-Sb_2O_5 anode, J. Hazard. Mater., 146(1) (2007) 295–301.

[52] B. Wang, L. Gu, H. Ma, Electrochemical oxidation of pulp and paper making wastewater assisted by transition metal modified kaolin, J. Hazard. Mater., 143(1) (2007) 198–205.

[53] P.A. Soloman, C.A. Basha, M. Velan, N. Balasubramanian, Electrochemical degradation of pulp and paper industry waste-water, J. Chem. Technol. Biot., 84(9) (2009) 1303–1313.

[54] P.A. Soloman, N. Balasubramanian, Optimization of Integrated Electro-Bio Process for Bleaching Effluent Treatment, Ind. Eng. Chem. Res., 51(14) (2012) 8211–8221.