Removal of suspended solids and turbidity from marble processing wastewaters by electrocoagulation: Comparison of electrode materials and electrode connection systems

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ARTICLE INFO

ABSTRACT

In this study, removal of suspended solids (SS) and turbidity from marble processing wastewaters by electrocoagulation (EC) process were investigated by using aluminium (Al) and iron (Fe) electrodes which were run in serial and parallel connection systems. To remove these pollutants from the marble processing wastewater, an EC reactor including monopolar electrodes (Al/Fe) in parallel and serial connection system, was utilized. Optimization of differential operation parameters such as pH, current density, and electrolysis time on SS and turbidity removal were determined in this way. EC process with monopolar Al electrodes in parallel and serial connections carried out at the optimum conditions where the pH value was 9, current density was approximately 15 A/m^2, and electrolysis time was 2 min resulted in 100% SS removal. Removal efficiencies of EC process for SS with monopolar Fe electrodes in parallel and serial connection were found to be 99.86% and 99.94%, respectively. Optimum parameters for monopolar Fe electrodes in both of the connection types were found to be for pH value as 8, for electrolysis time as 2 min. The optimum current density value for Fe electrodes used in serial and parallel connections was also obtained at 10 and 20 A/m^2, respectively. Based on the results obtained, it was found that EC process running with each type of the electrodes and the connections was highly effective for the removal of SS and turbidity from marble processing wastewaters, and that operating costs with monopolar Al electrodes in parallel connection were the cheapest than that of the serial connection and all the configurations for Fe electrode.

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1. Introduction

Depending on rapid developments in marble proccessing applications due to the increasing demands for marble in civil engineering applications, the number of the marble processing plants and the workshops and eventually the trading volume has increased in recent years. As a result of this increasing trading volume, the wastewaters discharged into water bodies after processing of marble blocks has also increased [1]. Marble proccessing plants and/or workshops are one of the places where the water is being used abundantly. Lack of the availability of high quality water requires a necessity for reusing the water in the process [2]. Therefore, treatment of the wastewater generating by marble processing plants and workshops via physical and/or physico-chemical methods and recirculating of these relatively high quality of waters into the proccessing after treatment is of great importance [3,4].

Wastewaters containing a high amount of suspended solids are resulted from several stages of the processing of marble such as cutting, washing, smoothing, and polishing [5]. The general application for reusing of wastewaters in small workshops is currently proceeded with purifying the wastewater through gravitational settling methods in pools and then including it into the process pipeline by pumping the supernatant [6], while physico-chemical methods are generally used in larger plants in addition to the settling [5].

For the purpose of getting high quality of marble product, high quality of water in terms of suspended solids (SS) is desired to reuse it in marble processing works. In case of using a relatively lower quality of water in the finishing and honing processes, which is not well purified, a lower quality of the product is obtained since suspended solids in the water cause scratches on the surface of the product, and, as a result of this, the competitiveness of the producer in the market decreases.

Electrocoagulation (EC) technology has been developed as an alternative for breaking of stable emulsions and suspensions of water by using of metal salts, polymers and polyelectrolytes [2]. The

Table 1
Characterization of raw marble processing wastewater.

Parameter	Value	[a]
Total SS (mg/L)	5178	100
Chromium (Cr^{6+})	Not detected	0.3
Oil and grease (mg/L)	20	10
pH	8.23	6–9
Conductivity (mS/cm)	0.44	–
Turbidity (FTU)	2640	–
TDS (g/L)	0.21	–

[a] Turkish Republic Ministry of Environment and Forestry The By law of Water Pollution and Control.

principle of EC process is based on three separation processes [7]: (i) mechanistic, (ii) electrochemistry–coagulation, and (iii) hydrodynamic. The process is capable of removing the metal ions and the soluble inorganic pollutants with the aid of dissolving of charged polymeric metal hydroxides [2]. Further, as a comparison with the conventional chemical and biological techniques, the process including an electrical field formation can effectively remove the finest colloidal particles in the case of their coagulation ability [8]. Also, this process has been established for the treatment of several types of wastewaters discharged from olive mill [9], potato chips manufacturing [10], and antibiotics production [11] and used for the removal of sulphides, sulphates, and sulphite [12]. The efficiency of EC process depends on different operational conditions such as the type of the electrode material used, solution pH and current density [13].

In the present study, both of the serial and parallel connection types have been attempted to determine the removal efficiency of the process for SS and turbidity in the marble processing wastewater by using aluminum (Al) and iron (Fe) electrodes. Depending on the experimental results obtained, optimization of different operational parameters such as pH, current density, and electrolysis time were achieved. In the final stage, required quantity of electrode (kg) per one cubic meter of treated wastewater and electrode consumption per one kg of removed SS has been determined under the optimal conditions as well as the operational costs.

2. Materials and methods

2.1. Wastewater sampling

The marble wastewater used in the study was supplied from a plant processing the Burdur Beige type of marble in Isparta, Turkey. Characterization of the wastewater is shown in Table 1.

2.2. Experimental set-up

All of the experiments were conducted in an EC reactor mainly consisted of four components: (1) a direct current (DC) power supply, (2) an electrolytic EC cell, (3) a magnetic bar, and (4) a magnetic stirrer. Schematic presentation of the reactor is shown in Fig. 1. DC power supply (MCH-303D, running between in a certain range of voltage and current, 0–30 V and 0–3 A) was used in order to handle the current and the voltage. Mixing of the solution was done by using a magnetic stirrer (J.P. Selecta, S.A., Agimatic-E) where 250 mL of a beaker including standard size of electrode sheets (45 mm × 60 mm × 0.1 mm of sheet size and 162 cm² of active electrode surface) and a plexiglass material was placed on its plate. For the experiments, two types of electrode, Al and Fe, were used in order to compare their removal efficiency. 5 mm of a distance between each electrode sheet was kept constant during the experiments.
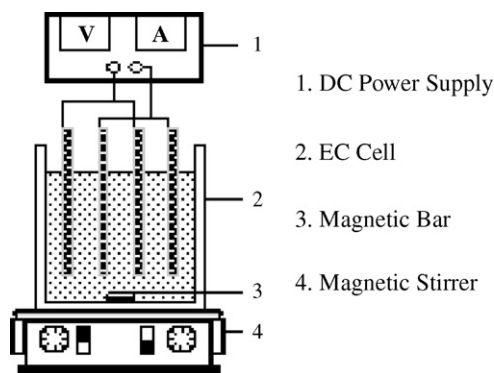

Fig. 1. Schematic presentation of the EC reactor used in the study.

1. DC Power Supply
2. EC Cell
3. Magnetic Bar
4. Magnetic Stirrer

2.3. Experiments

All of the chemicals used in the study were of analytical grade. HCl and NaOH solutions were used to adjust the pH value. No chemical was used in order to maintain the conductivity of the wastewater, however, natural conductivity of the wastewater was utilized.

All of the experiments were carried out under room temperature. Prior to the experiments, the wastewater was filtered through a filter paper having coarse pore sizes (Macharey-Nagel (MN), 751/75) in order to get a homogenized particle size distribution in the sampling. The resulted wastewater (250 mL) was added to the electrolytic cell. After the electrode sheets were dipped into the cell, electrolysis was started and a rapid mixing under 500 rpm was applied simultaneously. When electrolysis and rapid mixing was stopped, a slow mixing under 60 rpm was applied for 2 min. After this duration, 3 min of settling process was applied without any additional process. The rational for using 2 min for flocculation was determined by jar testing carried out before the experiments. Also, the optimum value of 3 min for settling procedures was choosen as a result of settling analysis conducted under different settling times ranging between 1 and 5 min. After the flocculation and settling procedures, the resulted supernatant was pipetted and again a filtration procedure (MN 751/75) was applied in order to eliminate a potential additional removal effect of the filter paper. The obtained filtrate was analyzed for its SS and turbidity content. Each of the electrode sheets was washed with acetone before the experiments, rinsed with 200 mL of formic acid solution (10%, v/v) for 3 min after the experiments in order to remove the potentially deposited residuals on the surface of the electrode. After this procedure was completed, the electrodes were washed with distilled water, dried in an oven (Nüve FN 500) for 2 h and then its final weight was measured in order to estimate the electrode consumption during the process. The used electrode was retained in a dessicator for using in the next process.

The removal efficiency of the process for SS and turbidity was calculated according to the following equation:

$$\text{Removal, } (\%) = \left(\frac{(C_0 - C)}{C_0} \right) \times 100 \tag{1}$$

where C_0 and C is the initial and final concentration of the pollutant (mg/L and FTU), respectively.

In order to make a statistical comparison between the experimental results obtained for the effect of differential parameters on removal of SS and turbidity, each of the experiments was repeated five times for all of the experimental conditions and the average mean values were considered for each experimental condition. In case of showing any data point a statistical deviation, the experiment was repeated until a confidential result is obtained and the result was included into the calculation.

2.4. Measurements

SS measurements were done as explained in the Standard Method [14]. For these measurements, the resultant filtrate, which was obtained by filtering the sample second times after electrolysis through the coarse filter paper (MN 751/15), was shaken several times and filtered through a 0.45 μm of filter paper (Whatman, ϕ 47 mm) with the aid of a vacuum effect generated by a filtration setup (KNF Neugberger D-7800). To determine the SS removal efficiency of the EC process, the filter paper was dried in an oven under 103–105 °C for 1 h, cooled in a dessicator and then measured for the weight loss.

Turbidity measurements were done according to the Absorptometric Method by a spectrophotometer (Hach DR 2000) at 450 nm wavelength. Initial and final pH value of the solutions was measured through a pH meter (Hanna Instruments HI 9321) according to the Electrometric Method and both the conductivity and TDS values were determined by using a conductivity/TDS meter (Hach 44600).

To determine the zeta potential of the dried marble powder (Burdur Beige type of marble), a zeta meter (Zeta Meter 3.0) was used. The experiments were conducted under different pH conditions ranging between 5.0 and 10.0. For this purpose, the test solution of which the solid content was 4% was prepared by adding 0.05 g of dried marble powder to 49.5 g of distilled water. pH value of the prepared solution was then adjusted to the desired value. The resultant solution was mixed by the magnetic stirrer for 2 min and then analyzed for its zeta potential. For each of the solutions, 10 zeta potential measurements were done individually and the average mean value of these 10 measurements that can be automatically calculated by the device was taken into account [15].

Imaging of the flocculates formed after electrolysis where Al and Fe electrodes were used was detected by a microscope (Olympus SZ61). 90-fold magnified images were recorded by using software (Motic Images Plus 2).

3. Results and discussion

3.1. Effect of pH on removal of SS and turbidity

The mechanism of EC process is affected by chemical features and conductivity of the environment. In addition, size of the particles and concentration of the chemical species existing in the environment also affect the mechanism of EC process [2]. However, the key factor affecting the performance of the process is pH value of the solution [16].

In case of applying an electrical potential to the wastewater during EC processes, the anode material is exposed to an oxidation reaction (as shown below in Eqs. (2) and (3)), while the cathode material is exposed to a reduction reaction (as shown below in Eqs. (4) and (5)). The reaction equations for oxidation and reduction stages are shown below [8]:

$$\text{Anode;} \quad M_{(S)} \rightarrow M_{(aq)}^{n+} + ne^- \tag{2}$$

$$2H_2O_{(I)} \rightarrow 4H_{(aq)}^+ + O_{2(g)} + 4e^- \tag{3}$$

$$\text{Cathode;} \quad M_{(aq)}^{n+} + ne^- \rightarrow M_{(S)} \tag{4}$$

$$2H_2O_{(I)} + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{5}$$

In EC process, $Al_{(aq)}^{3+}$ ions may form hydrolysis products such as $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)^{2+}$ and these hydrolysis products formed may cause to form hydroxo species and/or polyhydroxides when Al electrode is used on hydrolysis. [8,17].

Similar to the formation of Al based ions explained above, ferric ions may be formed by electrochemical oxidation of Fe elec-

trodes. As a result of this, monomeric ions, $Fe(OH)_3$ and several polymeric hydroxo species such as $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_8(OH)_2^{4+}$, and $Fe(H_2O)_6(OH)_4^{4+}$ may form depending on the pH condition of the aqueous medium [18,8]. The efficiency of these Fe based hydroxides, polyhydroxides or polyhydroxymetallic complexes is based on the concentration of Fe ions, the nature of the colloidal solution and the pH value of the solution [19].

For all of the experiments, the initial concentration of SS and turbidity was determined in the range of 1324–1652 mg/L and 705–857 FTU, respectively. The effect of pH on SS removal efficiency was investigated under the experimental conditions of 15 A/m² of current density and 1 min of electrolysis time. The results obtained from the experiments which were individually conducted by Al and Fe electrode revealed that SS removal efficiency was higher than 98% for Al electrode and 95% for Fe electrode, respectively, for both of the electrode connection systems (monopolar-parallel, MP-P, and monopolar-serial, MP-S) (Fig. 2). Similar to the obtained results of the present study, results of a former study [20], where SS removal from tannery wastewaters was investigated by electroflotation process, revealed that removal efficiency of the system was found to be 95.3% when Al and Fe electrodes were used as anode and cathode material, respectively, and to be 95.2% when Al and Fe electrodes were used as cathode and anode material, respectively. It is seen in Fig. 2 that the removal efficiency is higher when the initial pH value in the reactor becomes closer to the natural pH of the wastewater (pH 8) although almost the same removal efficiencies are resulted by Al and Fe electrodes connected as parallel. Although differences between the removal efficiencies are lower, consumption of the electrode material is higher in serial connection systems because of the high electrode potential. Since current in MP-P connection systems is divided towards electrode sheets depending on the correlation between capacitance of the electrodes, lower electrical potential is required for parallel connection systems than required for serial connection systems [21].

It can also be seen in Fig. 2 that the MP-S connection systems were more effective than the MP-P connection systems for all the SS removal efficiency cases for both of the electrode types (with an exception for MP-S connection system with Fe electrode at pH 9). In addition to that, the maximum SS removal efficiency was obtained at pH 9.0 for both of the MP-P and MP-S connection systems in case of using Al electrode, while it was obtained at pH 8.0 for both of the MP-P and MP-S connection systems in case of using Fe electrode. As a comparison of Al electrode with Fe electrode, it can be observed that MP-P and MP-S connection systems with Al electrode were more effective than that of Fe electrode at all pH values.
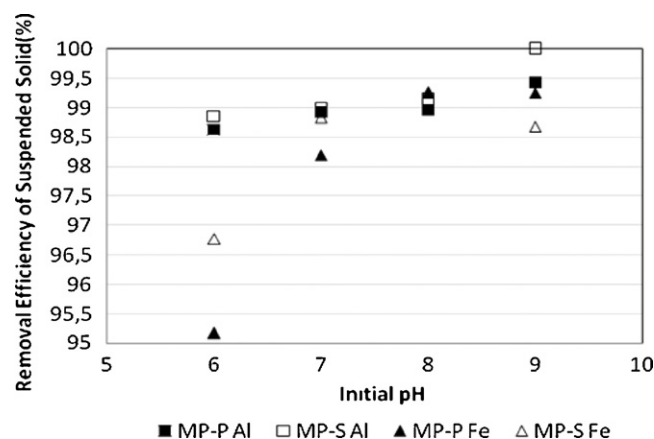

Fig. 2. Effect of pH on removal of suspended solids (current density: 15 A/m²; electrolysis time: 1 min.).
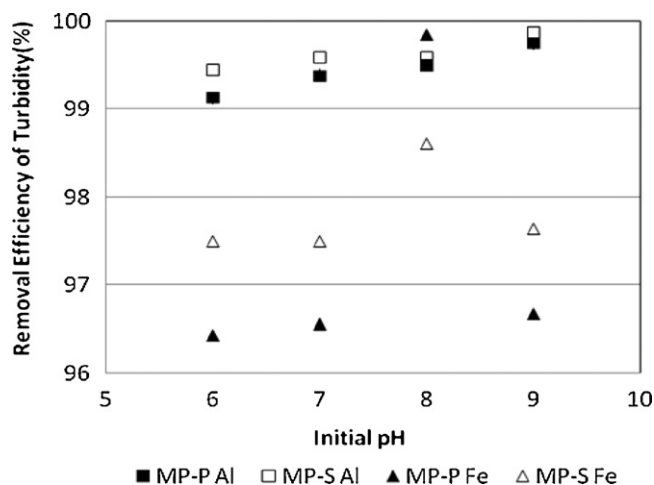
Fig. 3. Effect of initial pH on removal of turbidity (current density: 15 A/m^2; electrolysis time: 1 min.).

Fig. 4. Zeta potential of raw material.

Kobya et al. [10] stated as a result of their study focused on the treatment of potato chips manufacturing wastewater by EC process that higher SS removal efficiencies could be obtained by using of Al electrode when it was compared with Fe electrode. In the present study, obtaining of higher SS removal efficiencies for MP-S connection systems with Al and Fe electrode at all pH values is resulted from the dissolution of higher amounts of dissolved electrode materials in MP-S connection systems compared with MP-P connection systems. Therefore, it can be clearly understood that SS removal efficiency was considerably affected by pH value of the solution and that the higher removal efficiencies could be obtained at higher pH values (pH 8.0–9.0).

The effect of pH on turbidity removal efficiency was also investigated under the same experimental conditions (15 A/m^2 of current density and 1 min of electrolysis time). The effect of pH value on turbidity removal efficiency is shown in Fig. 3. According to Fig. 3, higher removal efficiencies could be obtained when Al and Fe electrode was used in MP-S connection systems, while MP-P connection systems led the both electrode types to remove lower turbidity. The maximum turbidity removal efficiency was obtained at pH 9.0 for Al electrode and at 8.0 for Fe electrode. In addition to that, the removal efficiency increased with increasing pH value for both of the connection types and for Al electrode. Kobya et al. [10] preferred to use Al electrode in their study because Fe electrode caused an additional color formation in the effluent due to the chemical features of Fe electrode.

Effect of final pH on SS and turbidity removal was also investigated in the study and the results are presented in Table 2. For all of the electrode types and connection systems, final pH value of the solution increased for pH condition of 6 and 7 and decreased for pH
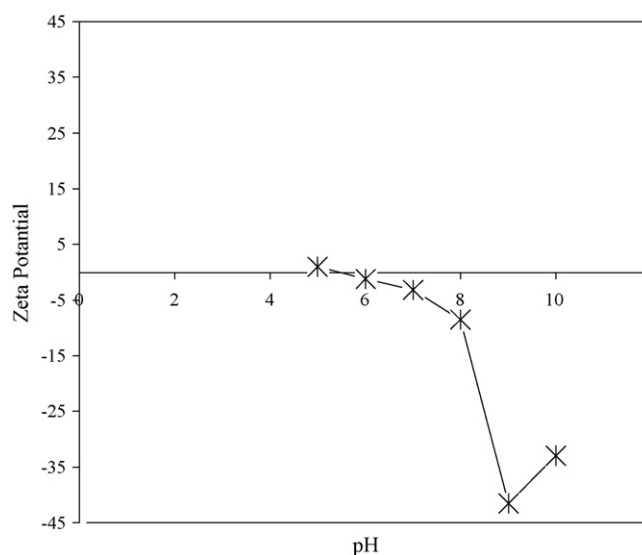
condition of 8 and 9 as per initial pH value. Recent experimental works have showed that EC process is capable of neutralizing the pH of wastewaters [22]. According to that, pH value of the medium increased during the study when the initial pH was low, and it decreased when the initial pH value was higher than 9.

3.2. Zeta potential

The zeta potential measurement is utilized in order to determine the surface charge of the particles in the solution. The colloids are dispersed into the solution through the electrostatic repulsive forces existing between the particles. The electrical double layer around the colloidal particles overlaps as a result of adding of coagulant materials to the solution, and this overlapping effect aids the removal of the pollutant through aggregation itself [7,23].

The result of zeta potential measurement for the dried marble powder is shown in Fig. 4. The results imply that the marble powder has a negative surface charge at all pH values higher than pH 5.0. The negativity of the surface charge increases with increasing pH value, reaches to a maximum value at pH 9.0, and then tends to decrease up to pH 10.0. By keeping the given information in the previous section in view, one can notice that the maximum SS removal was obtained at pH 9.0 for Al electrode and at pH 8.0 for Fe electrode. Having negative surface charge of the colloids at these pH values providing the maximum SS removal implies that the hydroxides forming by electrolysis support the destabilization mechanism through positive charges.

3.3. Effect of current density

The effect of current density on the removal efficiency is calculated according to the following equation:

$$J = \frac{I}{A} \tag{6}$$

where J is the current density (A/m^2), I is the current (A), and A is the active surface area of anode electrodes (m^2).

The effect of current density on SS removal efficiency was studied at optimal conditions (pH: 9.0 and electrolysis time: 1 min). Figs. 5 and 6 show the result of the effect of different current densities on SS and turbidity removal provided by using Al and Fe electrode in MP-P and MP-S connection systems. The results show that SS removal efficiency was found to be higher than 96% for MP-P
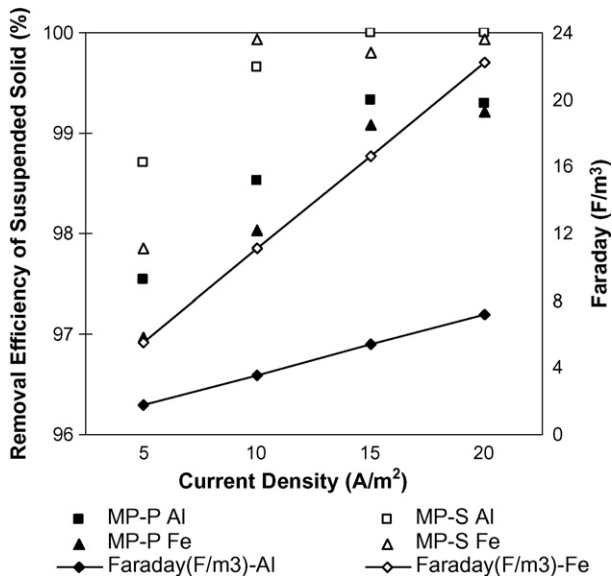
Table 2
pH change in duration of electrolysis time in the reactor.

		pH conditions			
		pH 6	pH 7	pH 8	pH 9
MP-P Al	Initial pH	6.00	7.05	8.09	9.00
	Final pH	6.96	7.28	7.94	8.31
MP-S Al	Initial pH	6.08	7.03	7.95	9.18
	Final pH	6.91	7.08	7.74	8.47
MP-P Fe	Initial pH	6.00	6.95	7.96	9.00
	Final pH	6.12	7.06	7.76	8.32
MP-S Fe	Initial pH	6.02	7.01	7.95	8.97
	Final pH	6.31	7.19	7.65	8.21

Fig. 5. Effect of current density on removal of suspended solids (pH: 9 for MP-P Al and MP-S Al, and 8 for MP-P Fe and MP-S Fe; electrolysis time: 1 min.).

and MP-S connection systems with Al electrode. Bhaskar Raju et al. [24] reported that Al electrodes were more efficient that Fe electrodes to remove SS from synthetic textile wastewaters by EC. It can be observed from Fig. 5 that 100% of removal efficiency was obtained in MP-S connection system under the conditions of 15 and 20 A/m^2 of current density. In addition to that, SS removal efficiency was found to be 99.33% for MP-P connection system when 15 A/m^2 of current density was applied. If both costs for energy and electrode are taken into account, choosing of the lower current density of 15 A/m^2 as an optimum condition is of worthwhile for the economic feasibility of the process.

The effect of current density on SS removal efficiency was studied at optimal conditions (pH: 8.0 and electrolysis time: 1 min.). According to the obtained results, maximum SS removal efficiency was obtained for MP-P connection systems by using Fe electrode under the condition of 20 A/m^2 current density whereas it was found to be 99.93% for MP-S connection system under the condi-
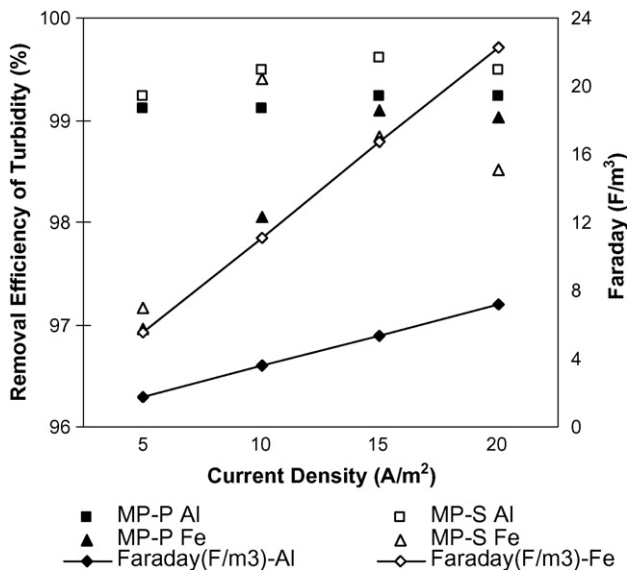
tion of 10 A/m^2 current density. It is clear that MP-S connection systems resulted in higher removal efficiency than MP-P connection systems for all current density conditions studied by using Al and Fe electrode (Fig. 5). This is due to the consumption of the electrode material was higher for serial connection systems than parallel connection systems. The removal efficiency for the pollutant is changed by directly proportional to the consumed electrode material. The amount of the consumed electrode material during the electrolysis is found to be; 0.0048–0.0068 g for Al electrode and 0.0155–0.0248 g for Fe electrode in MP-S connection system and 0.0025–0.0052 g for Al electrode and 0.0159–0.0199 g for Fe electrode in MP-P system. As mentioned before, since current in MP-P connection systems is divided towards electrode sheets depending on the correlation between capacitance of the electrodes, lower electrical potential is required for parallel connection systems than required for serial connection systems [21]. Thus, need for electrode material is higher for serial connection systems than parallel connection systems.

The mechanism of coagulation–flocculation process takes places as a result of two different formations: (i) charge neutralization occuring between cationic productions of hydrolysis and negative charged colloids, and (ii) aggregation of the impurities existing in the amorphous hydroxide precipitate (sweep coagulation–flocculation). The most important parameters having a great effect on these formations are pH and the dosage of the coagulant [25]. Bukhari [26] stated that 0.05 and 0.1 A of current applied under the condition of 5 min of electrolysis time resulted in 40–50% and 50–60% of SS removal efficiency, respectively, and that a removal efficiency was obtained in proportion to the amount of dissolved materials against each of the working times ranging between 10 and 50 min. Depending on the results, it was suggested that the crucial parameter that has a great impression on the removal mechanism was the charge neutralization. In the same study, 80–100% of SS removal efficiency was obtained for all three current conditions of 0.2, 0.4, and 0.8 A studied under the same electrolysis time condition (5 min). Similarly, the removal efficiency increased with increasing amount of the dissolved materials where the electrolysis time was examined in the range of 10–50 min but it could not be provided in proportion to the amount of dissolved materials. Consequently, it was suggested that the removal mechanism was sweep coagulation under the current conditions studied. In the present study, SS removal efficiency was found to be higher than 96% for both MP-P and MP-S connection systems under all of the current conditions studied. There was no considerable change obtained for the removal efficiency although SS removal efficiency increased with increasing amount of the dissolved materials. Therefore, it is thought that the key mechanism which has an important role on the removal of SS is sweep coagulation.

The effect of current density on the removal of turbidity by MP-P and MP-S connection systems with Al and Fe electrode is shown in Fig. 6. It can be clearly seen that the turbidity removal efficiency is relatively high for each of the current density conditions. The results for Al electrode revealed that the higher removal efficiency could be obtained through MP-S connection system. The current density where the maximum removal efficiency was obtained in MP-P and MP-S connection systems was found to be 15 A/m^2. Turbidity removal efficiency of MP-S connection systems decreased at 20 A/m^2 of current density condition while there was no change for MP-P connection systems. In case of using Fe electrode, the current density, where the maximum removal efficiency was obtained, was also found to be 20 and 10 A/m^2 for MP-P and MP-S connection systems, respectively. Fig. 6 illustrates that the removal efficiency tends to decrease after 10 A/m^2 of current density in MP-S connection systems while it tends to increase in MP-S connection systems under the same condition.

Fig. 6. Effect of current density on removal of turbidity (pH: 9 for MP-P Al and MP-S Al, and 8 for MP-P Fe MP-S Fe; electrolysis time: 1 min.).
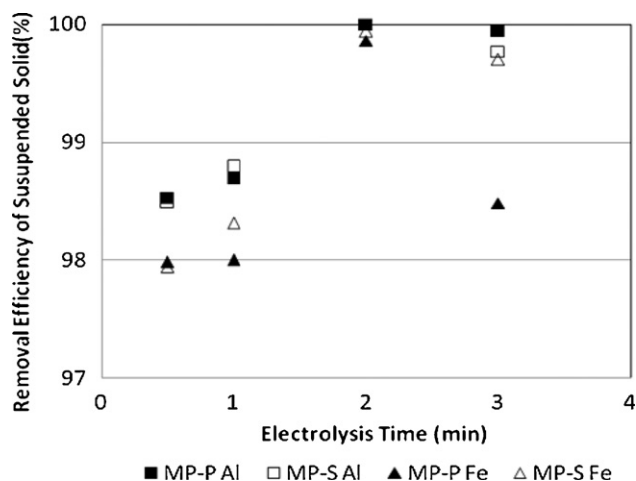
Fig. 7. Effect of electrolysis time on removal of suspended solids (pH: 9 for MP-P Al and MP-S Al, and 8 for MP-P Fe and MP-S Fe; current density: 15 A/m² for MP-P Al and MP-S Al, and 20 A/m² for MP-P Fe and 10 A/m² for MP-P Fe).

Fig. 8. Effect of electrolysis time on removal of turbidity (pH: 9 for MP-P Al and MP-S Al, and 8 for MP-P Fe and MP-S Fe; current density: 15 A/m² for MP-P Al and MP-S Al, and 20 A/m² for MP-P Fe and 10 A/m² for MP-P Fe).

It should be pointed out that there was a clean and colourless effluent in case of using Al electrode in the process, while Fe electrode caused a blurriness effluent. Chen et al. [22] who studied the purifying of restaurant wastewaters by electrocogulation process reported that a relatively clean and stable effluent could be achieved by using Al electrode in the process. On the other hand, using of Fe electrode resulted in a greenish effluent and then the colour of the effluent changed into yellow along the process, emphasizing that the electrode gives an extra turbidity loading into the effluent. As a result, it was suggested that the forming of greenish and yellow effluent after the process might be originated due to the Fe(II) and/or Fe(III) ions dissoluted from the surface of the electrode.

3.4. Effect of electrolysis time

The effect of electrolysis time on SS removal efficiency of Al and Fe electrode connected as MP-P and MP-S is represented in Fig. 7. According to the results, 2 min of an electrolysis time was found to be sufficient for both of the connection systems to get 100% of SS removal efficiency by using Al electrode under the optimum experimental conditions (pH value: 9 and current density: 15 A/m²). It was observed that SS removal efficiency decreased with increasing amount of the dissolved Al ions after 2 min of electrolysis time that was choosen as the optimum condition. The same electrolysis time condition (2 min) was also found to be sufficient under the optimal conditions of 20 A/m² of current density for MP-P connection system and 10 A/m² for MP-S connection system and of pH 8. In conclusion, SS removal efficiency was found to be 99.66% and 99.94% for MP-P and MP-S connection system, respectively.

It can be clearly seen in Fig. 7 that SS removal efficiency increased with increasing electrolysis time. In addition to that, using of Al
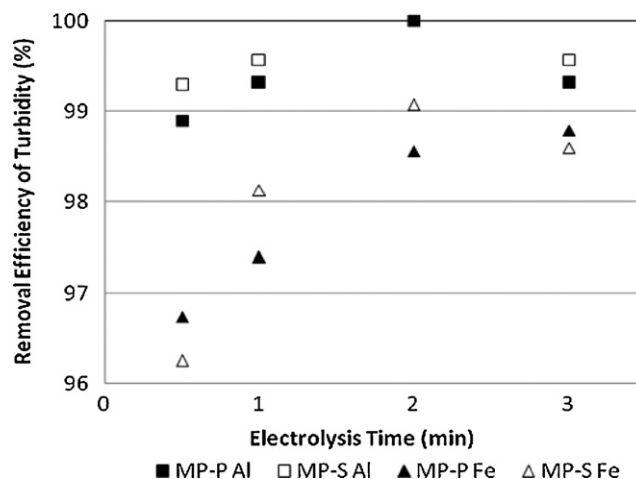
electrode in both connection systems resulted in higher removal efficiency than that of Fe electrode. İnan et al. [27] who studied purifying of olive oil mill wastewaters by EC stated that SS removal efficiency for Al electrode was higher than that of Fe electrode under different electrolysis time conditions ranging between 2 and 40 min.

Fig. 8 shows the effect of electrolysis time on turbidity removal efficiency of Al and Fe electrode in MP-P and MP-S connection systems. Similar to the result obtained for the removal of SS, 2 min of electrolysis time was found to be sufficient for both of the electrode types.

3.5. Operating cost analysis

Operating costs mainly include the cost of electrode materials and electric energy consumed [28]. In the present study, the operating cost is calculated (for each of the electrode type, $/m³, and the connection type, $/kg SS) according to the following equation:

$$\text{Operating cost} = a \times C_{\text{energy}} + b \times C_{\text{electrode}} \tag{7}$$

where a and b are the constants indicating the unit cost for Turkey's conditions in 2007 (a: 0.2 $/kWh, b: 2.2 and 4.0 $/kg for Fe and Al electrode, respectively), C_{energy} is the consumed electric energy to remove 1 kg SS or to treat 1 m³ wastewater, and $C_{\text{electrode}}$ is the amount of the sacrificed electrode to remove 1 kg SS or to treat 1 m³ wastewater.

The result obtained for the calculated operating costs and the variation of voltage is shown in Tables 3 and 4, respectively. Depending on the optimum experimental conditions, the operating cost for Al electrode was calculated to be 0.0854 and 0.2739 $/m³ for MP-P and MP-S connection systems, respectively, while it was 0.2868

Table 3

Cost analysis of EC process (under the optimal conditions of: (i) pH: 9, current density: 15 A/m², electrolysis time: 2 min for Al electrode used in both of the connection systems, (ii) pH: 8, electrolysis time: 2 min, current density: 20 A/m² for MP-P connection and 10 A/m² for MP-S connection for Fe electrode).

	MP-P Al	MP-S Al	MP-P Fe	MP-S Fe
Initial conductivity (mS/cm)	0.44	0.41	0.46	0.49
Final (conductivity (mS/cm) − temperature (°C))	0.42	0.40	0.46	0.50
Faraday (F/m³)	10.74	10.74	44.45	22.22
Energy consumption (Wh)	0.0568	0.2064	0.0757	0.0763
kg material/m³	0.01	0.0272	0.1028	0.0848
kg material/kg SS	0.0016	0.0046	0.0185	0.0128
kWh/kg SS	0.0363	0.1384	0.0546	0.0462
Operating cost ($/kg SS) (electrode material + energy)	0.0137	0.0459	0.0517	0.0375
Operating cost ($/m³) (Electrode material + energy)	0.0854	0.2739	0.2868	0.2476

Table 4
The variation of voltage on determining of optimum experimental conditions.

Experiment	The variation of voltage (V) for;			
	MP-P Al	MP-S Al	MP-P Fe	MP-S Fe
Optimum pH	4.8–16.2	6.5–26.2	2.2–6.1	6.2–24.2
Optimum current density	3.2–12.4	6.5–26.2	2.5–6.9	11.6–28.4
Optimum electrolysis time (depending on optimum current density value)	6.2–7.0 (0.24 V)	24.2-25.6 (0.24 V)	6.8–7.2 (0.32 V)	12.5–15.8 (0.16 V)

and 0.2476 \$/m^3 for Fe electrode, respectively. On the other hand, the operating cost for the removed SS was calculated to be 0.0137 and 0.0459 \$/kg SS for MP-P and MP-S connection systems for Al electrodes, respectively, while it was 0.0517 and 0.0375 \$/kg SS for Fe electrodes. If studied connection and electrode configurations are taken into account, it can be seen that MP-P/Al system is of the cost-effective system over all of the other systems.

The total change in amount of anode and cathode electrode (M_T) was calculated according to the following equation:

$$M_T = M_A + M_C \qquad (8)$$

where M_A and M_C is the change in amount of the dissolved materials from the surface of anode and cathode electrode (g), respectively.

The energy consumption (Wh) in the process was calculated according to the following equation:

$$E = V \times I \times t \qquad (9)$$

where E is the electric energy (Wh), V is the voltage (V), I is the current applied (A), and t is the time (h).

The amount of electrode materials dissolved during the process depends on the density of current applied to the electrolytic solution. The interaction between the current and the amount of the dissolved material during the reaction is explained by Faraday's law [8]. In this study, energy demand was calculated according to the Faraday equation:

$$C_e = \frac{(I \times t \times M_W)}{(F \times v \times z)} \qquad (10)$$

where C_e is the energy demand (F/m^3), F is the faraday constant (96,487 C/mol), M_W is the molecular weight of aluminium (26.98 g/mol) and iron (55.84 g/mol), and z is the electron transfer coefficient (z_{Al}: 3 and z_{Fe}: 2).

As a result, it can be said that electric potential is higher for Al and Fe electrode in serial connection systems when it is compared with parallel connection systems. The results show that Al and Fe

electrode was consumed much more 35% and 80%, respectively, in MP-S connection system than consumed in MP-P system. When operating costs for any removal efficiency resulted by the parallel and the serial connection system are considered, the parallel connection system in monopolar electrodes is more favourable than the other. Kobya et al. [29] reported that the MP-P connection system was more cost-effective than the other connection systems studied (MP-S and bipolar serial, BP-S, systems). The disadvantages of the serial connection system over the parallel connection system are the increasing of operating costs (including the cost for electrode material and energy consumption) due to the higher dissolution of the electrode material and the additional pollutant loading (higher than the amount of the pollutant that is removed) into the reactor
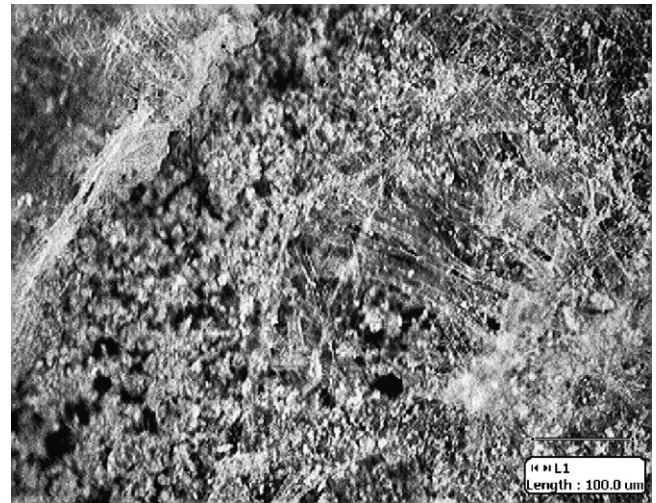
Fig. 10. Flocculates formed after electrolysis with Al electrode.
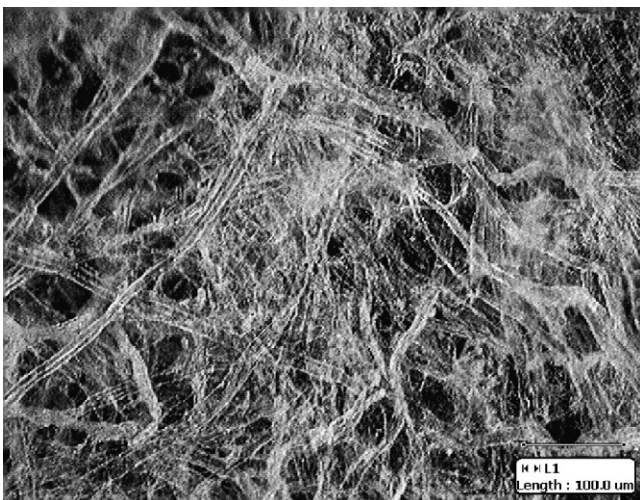
Fig. 9. Microscopic visualization of natural (unused) filter paper.
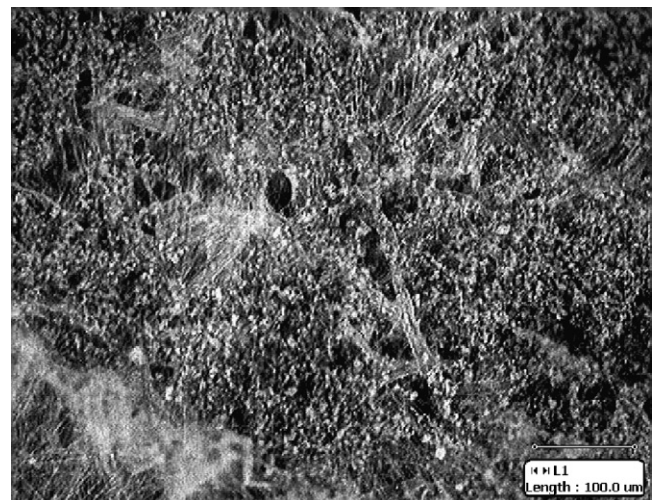
Fig. 11. Flocculates formed after electrolysis with Fe electrode.

due to the formation of additional coagulant agents in serial connection system. However, obtaining of optimum removal efficiency in shorter operation time is the advantage of the serial connection system over the parallel connection system. To address the need for suitable coagulant dosage in wastewater treatment applications, high electrolytic dissolution rates are required, and therefore serial connection systems are preferred over parallel connection systems [8].

3.6. Microscopic visualization of the flocculates

The floc formation with Al and Fe electrode during the experiment carried out under the same conditions was demonstrated by imaging the surface of the filter paper (MN 751/75) used before and after the experiments. Surface of the natural filter paper (unused in any experiment) is shown in Fig. 9. Comparison of the figures gives the impression that the size of the flocculates formed with Al electrode was larger than that of formed with Fe electrode (Figs. 10 and 11).

4. Conclusions

EC is a highly effective process to remove SS and turbidity from marble processing wastewaters by using of Al and Fe electrode materials in MP-P and MP-S connection systems. Since the wastewater treated by EC process gains a great importance to reuse it in marble processing, this makes the process a novel alternative over the conventional technologies which are currently used by marble processing workshops. Unlike Fe electrode, using of Al electrode does not cause any additional colour formation in the treatment of marble wastewaters, thus making the usage of Al electrode much easier and more advantageous over the usage of Fe electrode. Additionally, showing that the EC process is an efficient performer over a wide-range of pH conditions for the treatment of marble processing wastewaters and that the optimum pH value giving the highest removal efficiency is close to the natural pH of the wastewater (i.e., applying the process without the need for additional pH adjustment) indicates the importance of the present study. Considering the results of the study, one can point out that the EC process becomes a promising and more advantageous technology for marble processing workshops than other systems, where a high amount of natural waters are used, because of the successful treatment performance in shorter operation times.

In this study, SS and turbidity removal efficiency related to each experimental configuration examined throughout the study was found to be higher than 90% although SS removal efficiency of each configuration tended to increase with the increasing current density. The highest removal efficiency was obtained under the condition of 20 A/m^2 of current density while lower removal efficiencies were even obtained under the value of 5 A/m^2 which was the lowest current density applied. As a result of this study, it is thought that the main mechanism of the process was sweep coagulation.

Acknowledgement

References

[1] T. Onargan, H. Köse, Mermer, second ed., Sciences Press, Dokuz Eylül University, İzmir, 1997, pp. 209–220.

[2] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) – science and applications, J. Hazard. Mater. B84 (2001) 29–41.

[3] D.İ. Önenç, Tozlaşan Bloklar ve Umutlar, Mermer Doğal Taş Sektörünün Dergisi, Year: 7, Number: 30 (2001) 66–68.

[4] B. Ersoy, Mermer İşleme Tesisi Atıksu Arıtımında Kullanılan Flokların Tanıtımı, in: M. Ersoy (Ed.), Turkey National 4th Marble Symposium, 18–19 December, Afyon-Turkey, 2003, pp. 449–462.

[5] M. Kavaklı, Mermer İşletme Tesisleri Proses Atıksularının Özellikleri, Arıtılması ve Kontrolü, in: M. Ersoy (Ed.), Turkey National 4th Marble Symposium, 18–19 December 2003, Afyon-Turkey, 2003, pp. 313–326.

[6] A. Şentürk, L. Gündüz, İ.T. Tosun, A. Sarıışık, Mermer Teknolojisi, Süleyman Demirel University Engineering&Architecture Faculty Mining Engineering Department, Isparta-Turkey, 1996, p. 242.

[7] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloid Surf. A. Physicochem. Eng. Aspects 211 (2002) 233–248.

[8] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. B114 (2004) 199–210.

[9] Ü.T. Ün, S. Uğur, S. Koparal, Ü.V. Öğütveren, Electrocoagulation of olive mill wastewaters, Sep. Purif. Technol. 52 (2006) 136–141.

[10] M. Kobya, H. Hiz, E. Şentürk, C. Aydıner, E. Demirbaş, Treatment of potato chips manufacturing wastewater by electrocoagulation, Desalination 190 (2006) 201–211.

[11] C.C. Jara, D. Fino, V. Specchia, G. Saracco, P. Spinelli, Electrochemical removal of antibiotics from wastewaters, Appl. Catal. B – Environ. 70 (2007) 479–487.

[12] M. Murugananthan, G. Bhaskar Raju, S. Prabhakar, Removal of sulfide, sulfate and sulfite ions by electrocoagulation, J. Hazard. Mater. B109 (2004) 37–44.

[13] N. Adhoum, L. Monser, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, Chem. Eng. Process. 43 (2004) 1281–1287.

[14] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 19th edition, Washington D.C., 1995.

[15] A.M. Alptekin, Doğal Taş Atıksularının Flokülasyon/Koagülasyon Yöntemiyle Arıtılması, Master Thesis, Afyon Kocatepe University Institue of Natural and Applied Sciences, Afyon, Turkey, 2006, p. 73.

[16] Y. Avşar, U. Kurt, T. Gönüllü, Comparison of classical chemical and electrochemical processes for treating rose processing wastewater, J. Hazard. Mater. 148 (2007) 340–345.

[17] M. Rebhun, M. Lurie, Control of organic matter by coagulation and flocs separation, Water Sci. Technol. 27 (1993) 1–20.

[18] P.N. Johnson, A. Amirtharajah, Ferric chloride and alum as single and dual coagulants, J. AWWA 75 (1983) 232–239.

[19] O. Larue, E. Vorobiev, C. Vub, B. Durand, Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions, Sep. Purif. Technol. 31 (2003) 177–192.

[20] M. Murugananthan, G. Bhaskar Raju, S. Prabhakar, Separation of pollutants from tannery effluents by electro flotation, Sep. Purif. Technol. 40 (2004) 69–75.

[21] M. Eyvaz, M. Bayramoğlu, M. Kobya, Tekstil endüstrisi atıksularının elektrokoagülasyon ile arıtılması: Teknik ve ekonomik değerlendirme, itüdergisi/e su kirlenmesi kontrolü, Cilt: 16, Sayı: 1–3 (2006) 55–65.

[22] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol. 19 (2000) 65–76.

[23] R.D. Letterman, A. Amirtharajah, C.R. O'Melia, in: R.D. Letterman (Ed.), Coagulation and Flocculation in Water Quality and Treatment, fifth ed., McGraw-Hill, New York, 1999.

[24] G. Bhaskar Raju, M. Thalamadai 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.

[25] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface 100–102 (2003) 475–502.

[26] A.A. Bukhari, Investigation of the electro-coagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater, Bioresour. Technol. 99 (2008) 914–921.

[27] H. İnan, A. Dimoglo, H. Şimşek, M. Karpuzcu, Olive oil mill wastewater treatment by means of electro-coagulation, Sep. Purif. Technol. 36 (2004) 23–31.

[28] M. Bayramoğlu, O.T. Can, M. Kobya, M. Sözbir, Operating cost analysis of electrocoagulation of textile dye wastewater, Sep. Purif. Technol. 37 (2004) 117–125.

[29] M. Kobya, M. Bayramoglu, M. Eyvaz, Techno-economical evaluation of electrocoagulation for the textile wastewater using different electrode connections, J. Hazard. Mater. 148 (2007) 311–318.