Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 148 (2007) 340–345
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Comparison of classical chemical and electrochemical processes for treating rose processing wastewater

Yasar Avsar*, Ugur Kurt, Talha Gonullu

Yildiz Technical University, Environmental Engineering Department, 34349 Besiktas, Istanbul, Turkey

Received 2 July 2006; received in revised form 8 February 2007; accepted 16 February 2007
Available online 23 February 2007

Abstract

In this study, the treatability of rose processing wastewater was investigated by using electrocoagulation (EC) methods compared to classical chemical (CC) and Fenton application (FA) processes. High chemical oxygen demand (COD) and dissolved solids contents were detected in the wastewater. Among these treatment applications, it was found that the EC unit is the most effective treatment technique for removal of both COD and turbidity. The removal efficiencies of COD and turbidity were as high as 79.8% and 81.4%, respectively, and the reaction time was 20 min for EC methods.

Keywords: Rose processing wastewater; Electrocoagulation; Fenton; Chemical treatment

1. Introduction

Turkey is the one of the leading producers of roses and rose oil in the world. Yearly production is about 22,000 tonnes per year [1]. Isparta is the most productive city in Turkey, and about 62.4% (12,000 tonnes) of the rose flowers grown there are processed into oil. The annual wastewater originating from the rose processing industry is estimated at 21,100 m^3 in Isparta city. All of the wastewater produced during rose oil processing in the Isparta area is discharged to the environment without any pretreatment, causing severe pollution of both groundwater and surface water.

1.1. Rose processing

In the rose oil extraction phase, the rose flowers to water ratio is approximately 1/3 (500 kg of rose flowers per L water). After loading of the rose flowers into the boilers, steam is streamed into the boiler at an extraction pressure of about 2–3 atm. From the boiler unit, the mixed rose oil and water vapor are sent into the cooling unit to distill water and rose oil at 40 °C temperature. After the cooling system rose oil is generated in a different container and wastewater in another [2].

1.2. Electrocoagulation (EC) technique on treatability of wastewater

Wastewater recycling has become an absolute necessity, thus, there is an urgent need to develop more efficient and cost-effective techniques for treatment of wastewater [3]. The EC treatment technique is among them. A host of very promising techniques based on EC technology are being developed, and existing ones improved that do not require chemical additions [4]. EC can be used to remove irons, silicates, humus, and dissolved oxygen [5], phenol and copper reduction [6,7] and decolorization [8,9]. EC has been also applied successfully to treat potable water, food and protein wastewater, yeast wastewater, urban wastewater, restaurant wastewater, tar sand and oil shale wastewater, nitrate containing wastewater, heavy metals, textile dyes, fluorine, polymeric wastes, organic matter from landfill leachate, suspended particles, chemical and mechanical polishing wastes, aqueous suspensions of ultrafine particles and phenolic waste [10].

Today, EC technologies are more efficient and more compact [5]. Removal mechanisms of the EC process include coagulation, adsorption, precipitation and flotation [11]. Although EC

---

* Corresponding author. Tel.: +90 2122597070; fax: +90 2122619041.
E-mail addresses: avsar@yildiz.edu.tr, yavsar@gmail.com (Y. Avsar).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.02.048

has many advantages for treating different kinds of wastewaters, EC has also some disadvantages. The benefits and drawbacks of the EC technique are described below.

- EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered during treatment operations.
- Wastewater treated by EC yields palatable, clear, colorless and odorless water.
- Sludge formed by EC tends to be readily settable and easy to de-water because it is primarily composed of metallic oxides/hydroxides.
- Flocs formed by EC are similar to chemical flocs, except that EC flocs tend to be much larger, contain less bound water, are acid-resistant and more stable, and therefore, can be separated faster by filtration.
- EC produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
- The EC process has the advantage of removing the smallest colloidal particles because the applied electric field sets them in faster motion, thereby, facilitating the coagulation.
- The EC process avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as during chemical coagulation of wastewater.
- The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
- The electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring less maintenance.
- The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process [3].

Another advantage is that EC is considered to be a low sludge producing technology when compared to CC technology [12]. The flocs formed by EC are relatively large, contain less bound water, and are more stable. Holt et al. [13] also determined that the EC technique yielded better results than the CC technique when removing clay pollutant during a lab scale study.

In addition to these advantages, EC also has some disadvantages. These disadvantages of EC are expressed below.

- The ‘sacrificial electrodes’ are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.
- The use of electricity may be expensive in many places.
- An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit.
- High conductivity of the wastewater suspension is required.
- Gelatinous hydroxide may tend to solubilize in some cases.

The mechanism of EC is highly dependent on the chemistry of the aqueous medium especially conductivity. In addition to this, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the EC process. The mechanisms of removal of ions by EC will be explained using two specific examples involving aluminum and iron because these two metals have been extensively used to clarify wastewater [14].

There is no available information on the treatment of rose processing wastewater in the literature. Thus, treatment plants designed to treat rose processing wastewater have not been established in Isparta. This study will be the first application of treating this kind of wastewater. In addition, a comparison of the EC process to other chemical treatment techniques such as CC treatment and FA treatment techniques was also done in this study.

Wastewater from rose processing is produced only 45 days a year during the spring season in Turkey. Due to the fact that rose plant processing is intermittent, biological wastewater treatment techniques do not give high enough removal efficiency [15].

2. Experimental

During the rose oil process, the amount of water needed is three times the weight of the roses processed. The rose processing wastewater used in this study was obtained from a rose oil industry in Isparta (Turkey). Before starting for the subsequent studies, the wastewater was first filtered using a screen filter to remove large suspended solids. All of the experiments were conducted using the filtered sample.

To treat the wastewater, different alternative treatment techniques were used. Previous studies examined CC coagulation by using $Al_2(SO_4)_3{\cdot}18H_2O$, $FeCl_2{\cdot}6H_2O$ and $Ca(OH)_2$ MERCK quality chemical coagulants using a jar testing technique. Then samples were taken for COD, turbidity analysis. All experiments were conducted at ambient temperature (nominally 24 °C).

Another previously tested treatment method used in rose processing wastewater was FA. FA is an alternative advanced oxidation method which is as efficient and yet less expensive to implement. Therefore, it would be highly desirable. This method employs hydrogen peroxide (H_2O_2 30%) and ferrous sulfate ($FeSO_4{\cdot}7H_2O$) to form a strong oxidizing agent (hydroxyl radicals) during the oxidation process [15]. In that study, different experiment conditions such as optimization of H_2O_2 on constant Fe concentration, optimization of Fe on constant H_2O_2 concentration, and graded Fenton applications (GFA) were used. The main iron source was $FeSO_4{\cdot}7H_2O$ in the study.

The last treatment technique was EC. The experimental setup is shown in Fig. 1. The EC cell was made of glass with the dimensions 85 mm diameter and 150 mm height at constant stirring speed (200 rpm). In the study, iron electrode (99.5%) with dimensions of 60 mm × 150 mm × 1 mm was used. There is a definite amount of metal ions required to remove a given mass of pollutants. Iron is generally used in wastewater treatment technologies because it is relatively cheap [5].

The total effective electrode area was 48 cm^2, and the spacing between electrodes was 65 mm. The electrodes were connected to a digital DC power supply (GW INSTEK, GPS 3030 DD, 30 V, 3 A). All the runs were performed at a constant temperature

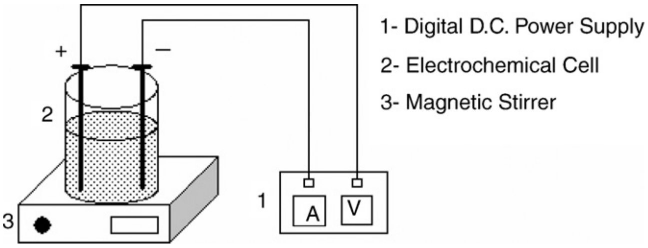

Fig. 1. Schematic diagram of experimental set-up.

of 25 °C. In each run, 400 cm^3 of the wastewater solution was placed into the electrochemical cell. The current density was adjusted to a desired value and then coagulation was started. At the end of the EC application, the solution was filtered and then analyzed.

All the chemical analyses were carried out according to the Standard Methods for Examination of Water and Wastewater [16]. The turbidities (NTU) of samples were analyzed using a MERCK SQ 118 spectrophotometer. The pH was measurement by a pH meter (JENWAY 3040 Ion Analyzer). Conductivity was determined by a conductivity meter (AGB–1001). The pH and conductivity were adjusted to a desirable value by using NaCl (Merck, analytic quality) which is generally added as a supporting electrolyte and a source of chloride reactant for the EC process [17]. Besides its ionic contribution in carrying the electric charge, it was found that chloride ions could significantly reduce the adverse effect of other anions such as HCO_3^-, SO_4^{2-}. It is therefore recommended that among the anions present, there should be 20% Cl^- to ensure a normal operation of EC in water treatment [5]. The addition of NaCl will also lead to the decrease in power consumption because of the increase in conductivity. Moreover, the electrochemically generated chlorine was found to be effective in water disinfections [5].

3. Results and discussion

According to the laboratory protocol, the wastewater was analyzed and the results are given in Table 1. As seen in Table 1, the wastewater includes high COD concentration as 9500 mg/L and also rose processing wastewater are produced only 45 days in a year, so chemical treatability of the wastewater should be considered as an appropriate solution.

3.1. Classical chemical (CC) application

Previous results of Avsar et al. [18] regarding classical chemical treatment and Fenton application (FA) treatment applied to rose processing wastewater are given in Table 2. As seen in Table 2, treatability of rose processing wastewater considered only two parameters such as COD and turbidity during application of the CC technique. The highest COD and turbidity removals in the study reached 29.2% and 43.5%, respectively, with $Al_2(SO_4)_3 \cdot 18H_2O$ application. These removal rates are rather low.

Table 1
Characteristics of rose processing wastewater [18]

Parameter	Value
pH	4.0
Turbidity, NTU	750
Chemical oxygen demand (COD) (mg/L)	9500
Biological oxygen demand (BOD_5) (mg/L)	4950
Total solids (TS) (mg/L)	7960

Table 2
The classical chemical (CC) treatment results of rose processing wastewater [18]

Parameter	Removal efficiencies (%)				
	$Al_2(SO_4)_3 \cdot 18H_2O$	$FeCl_2 \cdot 6H_2O$	$Ca(OH)_2$	CFA	GFA
Turbidity	43.5	33	43.2	67.5	74.2
COD	29.2	26.5	28.5	65.7	72.5

In FA applications, Avsar et al. [18] conducted experiments using both classical Fenton application (CFA) and graded Fenton applications. In the CFA study, the optimum H_2O_2 and Fe^{2+} doses were found to be 8325 mg H_2O_2/L and 200 mg Fe^{2+}/L of wastewater, respectively. Results are summarized in Table 2. At the end of a 3-h retention time, the highest COD and turbidity removal ratios were determined to be 65.7% and 67.5%, respectively. In the GFA study, the experiment was done in two stages. Total doses were 100 mg Fe^{2+} and 840 mg H_2O_2 for 0.5 L wastewater. Half of the total dose was used at the same ratios in every one of the two stages. Reaction time was three hours. At the end of the GFA study, the COD and turbidity removal ratios reached up to 72.5% and 74.2%, respectively.

When it is tought the aim of treatment, reaching low COD removal efficiency at the end of the process is not reasonable. Based on the results of CC treatment tests, we deemed CC treatment to be inefficient for treating the wastewater.

3.2. Electrocoagulation application

The main goal of this study is to compare EC and the results of earlier CC treatment of rose processing wastewater. Before setting up the experimental study, crucial parameters of the EC experimental protocol were evaluated. One of them was selection of electrode materials. Prior to this study, a series of pilot EC tests were performed using a continuous EC reactor to process the wastewater. When an iron electrode is used to treat the wastewater, soluble iron concentration in upper phase of wastewater was determined to be lower than 0.2 mg Fe^{2+}/L. Unlike iron, an aluminium anode generated high soluble aluminium concentration in filtrate. Accordingly, iron was chosen for use in this study because of its low solubility.

The feasibility of the treatment depends strongly on its energy requirement. Energy consumption is controlled by the applied amperage or voltage and the resistance of the electrolyte.

It has been established that pH is an important operating factor influencing the performance of EC process. This change depends on the type of electrode material and on initial pH. For iron, the final pH is always higher than initial pH. The conductivity of a suspension can be adjusted by varying its salinity. The initial pH,

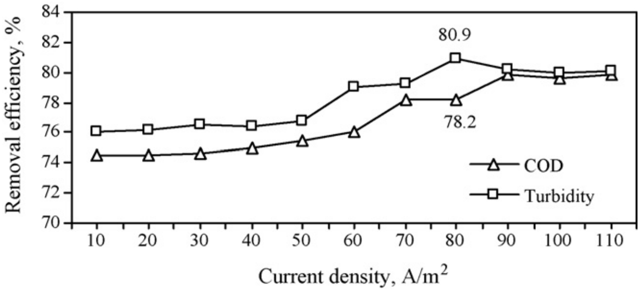

Fig. 2. Effect of current density on COD and turbidity removal efficiency at original pH value of 4.0.

current intensity and voltage of experimental conditions were 4.0, 0.5 A and 15 V, respectively. In the case of iron, 80 A/m^2 current density was sufficient. In this study, optimal values of the current density and application time were between 80–100 A/m^2 and 20 min, respectively.

EC experiments were performed at constant temperature of 25 °C and a-400 cm^3 volume of wastewater. The current intensity was adjusted to 0.5 A and then coagulation was started. One normal “NaCI” solution was used for the duration of the EC experiments to keep this intensity,. The required “NaCI” solution was determined to be 2125 mmol/L for optimum for 400 ml of wastewater. At the end of EC process, the solution was filtered and then analyzed for COD and turbidity.

3.2.1. *Effect of current density*

As the current density can influence the treatment efficiency of the electrochemical process, this parameter was examined to determine an optimum level. An initial pH (4.0) value was used in this study. The current density ranged from 10 to 110 A/m^2 in the experiments, and the results are shown in Fig. 2. When the current density was increased from 10 to 110 A/m^2, it was observed that the retention time of the wastewater in the EC unit shortened from 120 to 20 min. The removal efficiencies of COD and turbidity do not change from 80 to 110 A/m^2. For this reason, the optimal current density and retention time for treatment of rose processing wastewater are considered to be 80 A/m^2 and 20 min. With these experimental conditions, the COD and turbidity removal efficiencies reached up to 78.2% and 80.9%, respectively, as seen in Fig. 2.

3.2.2. *Effect of initial pH*

The performance of EC process is highly dependent on the pH of the solution. As shown in Fig. 3, the original pH value of the wastewater was 4.0. The experiments were carried out at different initial pH values at the range of pH 4.0–7.6. Generally, the pH of the medium tended to increase during the process. The change in pH depends on the type of electrode material and initial pH value. For iron, the final pH was always higher than initial pH as seen from Fig. 3. At low pH, CO_2 is over saturated in wastewater and can be released during H_2 evolution, causing a pH increase. The effect of initial pH on the COD and turbidity removal efficiencies is presented in Fig. 3. As seen in Fig. 3, COD and turbidity removal is 80% and 82.1% as a maximum in accordance with a pH of 6.4 and pH of 7.1 for the initial and final values, respectively. The maximum removal rates were obtained at the end of a 40 min reaction time. After 40 min, efficiencies of COD and turbidity started to drop. The maximum removal efficiency occurred at the final value of pH 7.1 which is nearly neutral. As shown in Fig. 3, the pH of rose processing wastewater changes during the treatment process.

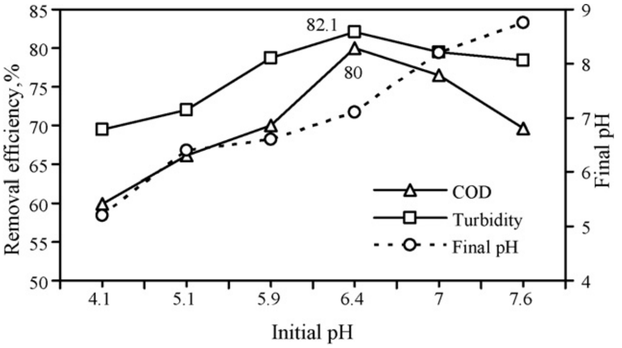

Fig. 3. Effect of initial and final pH on COD and turbidity removal efficiency.

3.2.3. *Effect of conductivity*

The conductivity of the rose processing wastewater was adjusted to the desired levels by adding an appropriate amount of 1N NaCl solution. The experimental conditions were: initial pH of 4.0; current intensity of 0.5 A (current density 80 A/m^2); and EC application time of 40 min. The effect of conductivity on performance of the EC process is shown in Fig. 4. In Fig. 4, COD and turbidity removal efficiencies remain almost unchanged between the conductivity range of 750 and 2750 μS/cm.

According to the experimental results for iron electrodes, the energy consumption decreases with increasing wastewater conductivity because of decreasing the resistance of the wastewater. As shown in Fig. 4, the process performance for removal efficiency is stable in the conductivity range of 750–2750 μS/cm for both COD and turbidity parameters. In This study demonstrates that conductivity does not affect COD and turbidity removal as much as other parameters.

3.2.4. *Effect of operating time*

To explore the effect of operating time, the current intensity was adjusted to 0.5 A and current density was held constant at 80–100 A/m^2. The initial pH was 4.0 and the volume of the

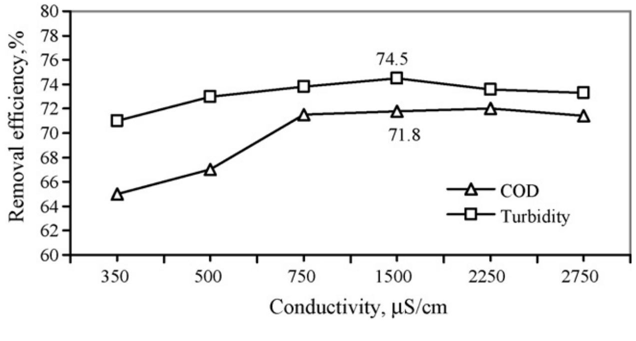

Fig. 4. Effect of conductivity on COD and turbidity removal efficiency.

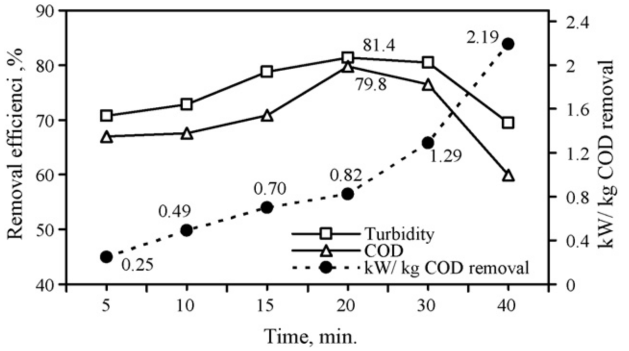

Fig. 5. Effect of EC time on COD and turbidity removal efficiency.

wastewater treated was 0.4 L. As shown in Fig. 5, the optimum operating time was determined to be 20 min for good COD and turbidity removal efficiencies (79.8 and 81.4%, respectively).

As shown in Fig. 3, COD and turbidity removals have maximum removal rates (80% and 82.1% for COD and turbidity, respectively). These values are rather close the another values obtained in Fig. 5. After 20 min, it is clear that removal efficiencies do not change considerably. So, optimum reaction time can be considered to be 20 min with removal efficiencies of 79.8% and 81.4% for COD and turbidity, respectively. The final pH of the process was determined to be 6.8.

3.2.5. *Economy of the electrocoagulation process*

As for the economy of the EC process, the required energy consumption per volume of wastewater can be calculated according to some of the data in the experiments conducted (see Fig. 5). The optimum operational parameters for the experiment such as current density, voltage, and the reaction time were determined to be 0.5 A, 15 V and 20 min, respectively. The required energy is calculated as:

$$\text{Electricity consumption} = 0.5 \times 15 = 7.5\,\text{Wh}/0.4\,\text{L wastewater.}$$

$$= 18.75\,\text{Wh/L}$$

Assuming a 20 min reaction time, the required energy can be calculated to be 6.25 kW/m^3 wastewater.

To determine the required energy for COD removal, the COD removal efficiency was considered to be 79.8% during the optimum operating time. The initial COD value was 9.5 kg COD/m^3 wastewater. Removal COD value can be calculated:

$$= 0.798 \times 9.5 = 7.58\,\text{kg COD/m}^3\ \text{wastewater.}$$

Therefore, 6.25 kW/7.58 kg COD = 0.825 kW/kg COD.

According to the required energy quantity to remove per kg COD unit, Fig. 5 was developed as graph with the removal efficiency%.

4. Conclusions

The study shows comparison of EC and chemical treatment techniques. As a result, maximum COD and turbidity removals were obtained as 29.2% and 43.5%, respectively, during the $Al_2(SO_4)_3{\cdot}18H_2O$ application in CC process. In FA experiments, the process was tested both CFA and GFA processes as two stages. The GFA gave better results than the CFA. COD and turbidity removal efficiencies were 72.5% and 74.2% for the GFA, 65.7% and 67.5% for the CFA process, respectively.

As for the EC process, shorter reaction time and having the highest COD and turbidity removal rates make the EC process the most favorable treatment technique in the study. The highest COD and turbidity removals were 79.8% and 81.4% and the optimum reaction time was 20 min.

When it is compared the all treatment techniques in this study, the sequence of treatment methods is EC > GFA > CFA > CC, respectively, for COD and turbidity removals.

References

[1] M. Kurkcuoglu, Determination of Turkish rose oil production and its features, M.S. Thesis, Anatolian University, Eskisehir, 1988.
[2] O. Ozcan, Rose farming in Isparta city and its contribution to Turkey economy, M.S. Thesis, Marmara University, Social Sciences Institute, Istanbul, 1998.
[3] C. Feng, N. Sugiura, S. Shimada, T. Maekawa, Development of a high performance electrochemical wastewater treatment system, J. Hazard. Mater. B103 (2003) 65–78.
[4] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)-science and applications, J. Hazard. Mater. B84 (2001) 29–41.
[5] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.
[6] C. Comninellis, C. Pulgarin, Electrochemical oxidation of phenol for wastewater treatment using SnO_2, anodes, J. Appl. Electrochem. 23 (2) (1993) 108–112.
[7] T.L. Hatfield, D.T. Pierce, Electrochemical remediation of metal-bearing wastewaters Part II: corrosion-based inhibition of copper removal by iron(iii), J. Appl. Electrochem. 28 (4) (1998) 397–403.
[8] T. Bechtold, C. Mader, J. Mader, Cathodic decolourization of textile dyebaths: tests with full scale plant, J. Appl. Electrochem. 32 (9) (2002) 943–950.
[9] M.Y.A. Mollah, S.R. Pathak, P.K. Patil, M. Vayuvegula, T.S. Agrawal, J.A.G. Gomes, M. Kesmez, D.L. Cocke, Treatment of orange II azo-dye by electrocoagulation (EC) technique in a continuous flow cell using sacrificial iron electrodes, J. Hazard. Mater. B109 (2004) 165–171.
[10] 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.
[11] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, J. Hazard. Mater. B100 (2003) 163–178.
[12] B. Zhu, D.A. Clifford, S. Chellam, Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes, Water Res. 39 (2005) 3098–3108.
[13] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A: Physicochem. Eng. Aspects 211 (2002) 233–248.
[14] A. Bes-Piá, J.A. Mendoza-Roca, M.I. Alcaina-Miranda, A. Iborra-Clar, M.I. Iborra-Clar, Reuse of wastewater of the textile industry after its treatment with a combination of physico-chemical treatment and membrane technologies, Desalination 149 (1–3) (2002) 169–174.

[15] H.L. Sheng, M.L. Chi, G.L. Horng, Research note; operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation, Water Res. 33 (7) (1999) 1735–1741.

[16] Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association (APHA), Washington, DC, 1995.

[17] K. Tak-Hyun, P. Chulhwan, S. Eung-Bai, K. Sangyong, Decolorization of disperse and reactive dyes by continuous electrocoagulation process, Desalination 150 (2002) 165–175.

[18] Y. Avsar, U. Kurt, I. Tosun, A. Gunay, Treatability of rose oil industry wastewater. Research project, Project no: 24-05-02-01, Yildiz Technical University, 2005.