Desalination and Water Treatment
www.deswater.com

26 (2011) 66–71
February

doi: 10/5004/dwt.2011.2111

Treatment and recycling facilities of highly polluted water-based paint wastewater

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Received 25 November 2009; Accepted 30 March 2010

ABSTRACT

The study presented focuses on treatment and recycling facilities of highly polluted water-based paint wastewater from electronics industry, using coagulation-flocculation, Fenton's oxidation and membrane processes. The treated water is sought after for recycling purposes within the painting unit and the water quality is negligible except suspended solids. The wastewater used in this study was characterized as highly polluted wastewater with high concentrations of COD (55,000–144,000 mg/l) and SS (9500–32,000 mg/l), alkaline and blackish colored. Coagulation-flocculation using alum and $FeSO_4$ was investigated. 67% of COD removal was achieved at 1000 mg/l of alum dosage whereas coagulation with $FeSO_4$ obtained 45% removal efficiency at 750 mg/l dosage. The Fenton's oxidation process gave good results for the removals of COD and color. 81% of COD removal was achieved at a molar ratio of $[H_2O_2]/[Fe^{+2}] = 10$ with 2 m H_2O_2. Waste sludge produced during the Fenton's process was less than that of coagulation, but still required hazardous chemical sludge disposal. This study showed that the total flux decline for the FM UP005 ultrafiltration membrane was 73% and the flux decline due to membrane fouling was 9%. The use of membrane filtration causes no sludge disposal problems since the concentrate can be recycled or reused. Cost analysis involving investment, operation and maintenance, and waste sludge disposal should be made to decide the treatment and/or recycling process.

Keywords: Coagulation; Fenton's reaction; Membrane process; Recycling; Treatment; Water-based paint wastewater

1. Introduction

Water-based paints, sometimes referred to as latex paints, have been evaluated as alternatives to solvent-based paints processes have. The volatile organic compound (VOC) content of water-based paints is significantly lower than conventional solvent-based paints, thereby reducing VOC emissions [1]. Latex paints generally consists of organic and inorganic pigments and dyestuffs, extenders, cellulosic and non-cellulosic thickeners, latexes, emulsifying agents, anti foaming agents, preservatives, solvents and coalescing agents. Due to the varying degree of chemicals used, the waste-water contains appreciable concentrations of BOD, COD, suspended solids, toxic compounds and color [2]. Among the various chemical treatment options applicable to highly polluted, toxic and colored effluents, the most commonly used treatment schemes are coagulation-flocculation [3] and Fenton's oxidation [4–6].

Membrane been widely used in both water supply and wastewater treatment application. The application of membrane processes has an increasing trend to recover both water and rejected water [7,8]. Recovery of valuable substances such as detergent, pigment, solvent

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Presented at the International workshop on urbanisation, land use, land degradation and environment (ULE 2009), 28 September – 1 October 2009, Denizli, Turkey

along with water makes membranes a more attractive process. Other studies focused on use of ultrafiltration for coating materials such as paper coatings, latex and flexographic ink, and showed that the advantages can be directly translated into very short payback times for ultrafiltration systems of typically less than two years [9].

The aim of this study is to investigate the treatment and recycling facilities of highly polluted water-based paint wastewater from the electronics industry by using coagulation-flocculation, Fenton's oxidation and membrane process. The application of membrane process in this study focused on the recovery of both water and pigments to eliminate the waste sludge disposal, therefore the raw wastewater was directly fed to the membranes.

2. Materials and methods

2.1. Wastewater

The water-based paint wastewater was collected from the painting unit of an electronics industry which manufactures a various range of color televisions. The wastewater originates from over sprayed paint in the paint spray operation wherein the over sprayed paint comes into contact with water. The characterization of the water-based wastewater is given in Table 1. The wastewater used in this study was collected three times on different dates and stored at +4 °C. The characterization of the wastewater depends on the painting duration so the COD concentration range varies widely (Table 1). The flow rate of wastewater from the painting unit was 5 m^3/d and discharged everyday. Suitable treatment of the wastewater is sought after for recycling within the painting unit [10].

2.2. Analytical procedures

Analytical procedures were conducted according to Standard Methods (APHA, 1995) [11]: COD (5220 D Closed Reflux, Colorimetric Method), SS (2540 D Total Suspended Solids). A double beam PC Instruments T80 spectrophotometer was used for closed reflux COD. Determination of the color of the wastewater was carried by measuring the absorbance at wavelengths (436, 525 and 620 nm) after sample dilution (1:1000) [12].

Table 1
Characterization of the water-based paint wastewater

Parameter	Average	Standard deviation
pH	7.87	0.8
COD_{tot} (mg/l)	97,300	44,650
COD_{sol} (mg/l)	69,750	31,435
SS (mg/l)	23,000	12,000
Turbidity (NTU)	13,100	11,790
Conductivity (ms/cm)	2.87	0.89
DFZ* (m^{-1})		
436 nm	8113	3277
525 nm	6893	2612
620 nm	6883	2198

*DFZ (Durchsichts Farb Zahl): Indexes of Transparency.

2.3. Coagulation flocculation

Laboratory scale evaluation of chemical coagulation flocculation was performed using a four-place jar test apparatus, Armfield PWT Project Ltd, UK. The jar test procedure included high sheer mixing at 200 rpm for 5 min followed by 15 min flocculation at 20 rpm and settling. The experiments were carried out with 250 ml of liquid at 24 ± 1 °C. Jar-tests were conducted using two inorganic coagulants ($Al_2(S0_4)_3 \cdot 18H_2O$ and $FeSO_4 \cdot 7H_2O$) and commercial anionic polyelectrolyte (13050 Rielli). 2 ml of polyelectrolyte was added to the sample as a prepared 0.1% (w/v). In order to determine the optimum coagulant dosages and the pH condition, jar-tests were carried out at various reaction conditions (concentration of alum 600–4000 mg alum/l, concentration of $FeSO_4$ 500–4000 mg/l, and pH 6–10) [13]. First, the optimum coagulant dosage at pH 9 was determined. Following this, the optimum pH at the determined optimum coagulant dosage was then obtained. $Ca(OH)_2$ and NaOH were used to adjust pH. Performance of the coagulation was determined by COD removal efficiency and turbidity. All chemicals used were Merck analytical grade.

2.4. Fenton's oxidation

Fenton's oxidation was conducted in a batch test using a sample volume of 250 ml and a sample temperature at 24 ± 1 °C. After dosing the reagents, the pH was adjusted to 3 if the pH was over 3. The high concentrations of reagents used in the experiments decreased the pH to around 2.3–3 so pH adjustment was not necessary. The solution was initially stirred for 5 min at 200 rpm and subsequently for 45 min at 20 rpm. After the first settling period, the supernatant was withdrawn to another beaker and the pH was adjusted to 8.5–9 by using $Ca(OH)_2$ [14]. The studies on Fenton's oxidation kinetics was carried out in a temperature controlled water bath and allowed to attain the preset experimental temperature. The aqueous solution of Fenton's reagent and wastewater was magnetically stirred during the reaction period. Samples were withdrawn at every 10 min for the first 1 h, every 30 min from 1 to 4 h, and the last one on the 24th hour [4]. After 50 ml of sample was withdrawn the oxidation reaction was immediately stopped by adding $Ca(OH)_2$ (pH 9). COD and residual H_2O_2 were analyzed. Residual H_2O_2 was determined by titration with 0.1N $KMnO_4$.

The positive interferences of H_2O_2 on COD analysis were eliminated by adding 3.7 mg Na_2SO_3/mg H_2O_2. Performance of the oxidation process was followed by the analysis of COD at various concentrations and different time intervals, up to 1 d. All chemical treatment experiments were undertaken in triplicates.

2.5. Membrane process

The membrane studies were carried out in a lab-scale plant with a plate and frame module, which was purchased from Osmo, Germany. The membranes used in this study were FM UP020, FM UP005 and FM NP010 (Microdyn-Nadir GmbH, Germany). Permeate of the membrane FM UP005 was fed to the membrane FM NP010 to eliminate additional COD. The flow rate was kept at 2.0 l/min during the experiments. The experimental runs were carried out with a feed volume of 4 l for FM UP020, FM UP05, and 2.55 l for FM NP010 at the beginning of each run. The membrane pressure was kept constant at 8 bar for the membranes FMUP020 and FMUP005 and at 12 bar for FM NP010. The temperature of the feed solution was adjusted to 25 ± 1°C by using the cooling water. All experiments were conducted in concentration mode of filtration (CMF). Permeates were collected in a beaker and the stream of concentrate was circulated to the feed vessel. The permeate flow rate was measured by an electronic balance (Precisa 320 XB-1200C) and recorded by a computer [8]. The volume reduction factor (VRF), calculated as the initial volume of the feed divided by the final volume of the concentrate, was 2.75 for FM UP020 and FM UP005. 2.55 l of permeate from the membrane FM UP005 was fed to the membrane FM NP010 and the VRF value of 2.98.

3. Results and discussion

3.1. Coagulation-flocculation

Numerous jar-tests were carried out in order to establish a practical understanding of the coagulation performance for the extremely polluted water-based paint wastewater. Figs. 1(a) and 1(b) show the optimum alum dosage at pH 9 and the optimum pH at optimum alum dosage, respectively. The optimum alum dosage was obtained at 1000 mg/l with 67% of COD removal efficiency and 4 NTU of turbidity. The optimum pH at optimum alum dosage was determined as 7.

The coagulation performance with $FeSO_4$ is given in Fig. 2(a). The best treatment efficiency at 750 mg/l of $FeSO_4$ dosage was achieved with 45% of COD removal and 5.2 NTU of turbidity. Fig. 2(b) shows the optimum pH at 750 mg/l of $FeSO_4$ dosage. The optimum pH was determined as 9.

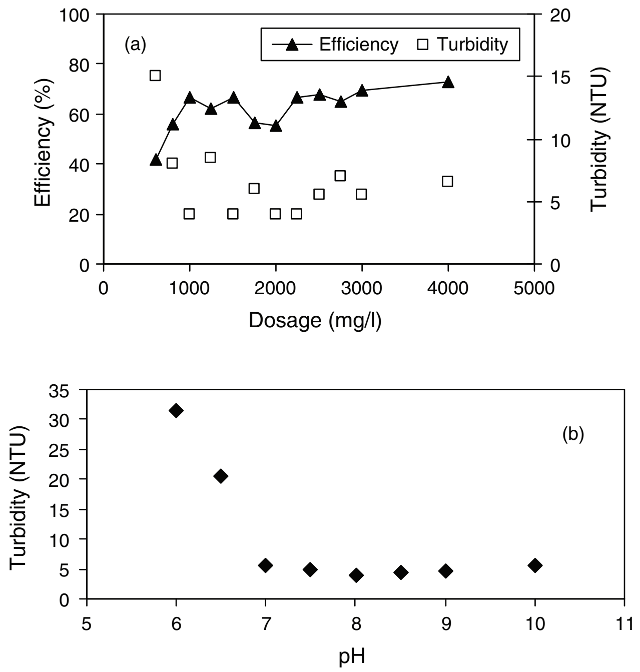

Fig. 1. Coagulation performance with alum (a) optimum alum dosage at pH 9 and (b) optimum pH at 1000 mg/l of alum dosage.

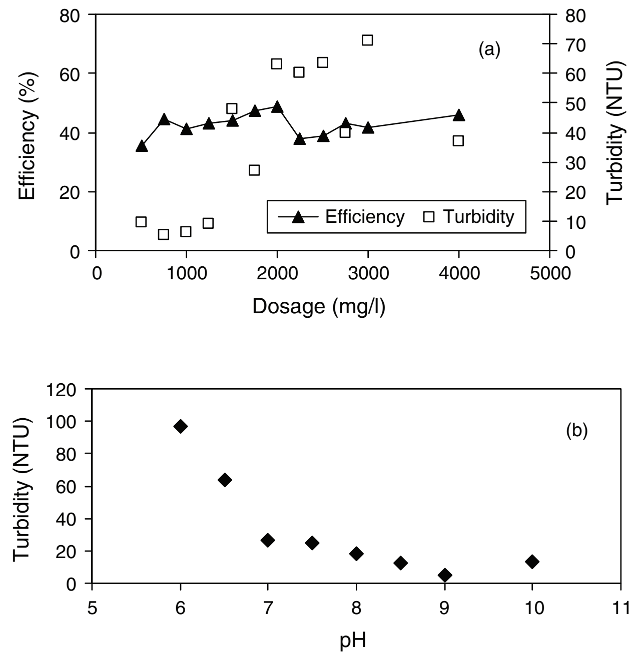

Fig. 2. Coagulation performance with $FeSO_4$ (a) optimum $FeSO_4$ dosage at pH 9 and (b) optimum pH at 750 mg/l of $FeSO_4$ dosage.

3.2. Fenton's oxidation

Limited COD removal with coagulation-flocculation was obtained whereas color and turbidity were removed to acceptable values. The reasoning was thought to be due to high soluble COD concentration of the water-based wastewater used in this study. To increase COD removal efficiency several experiments were carried out at varied concentrations of Fenton's reagent and different oxidation time.

To investigate the effect of $[Fe^{+2}]$ on Fenton's oxidation, the different molar concentrations of $[Fe^{+2}]$ were studied with the constant $[Fe^{+2}]$ = 0.02 m giving the different ratios of $[H_2O_2]/[Fe^{+2}]$ and the constant ratio of $[H_2O_2]/[Fe^{+2}]$ = 10 (Fig. 3). In this experiment the molar concentrations of $[H_2O_2]$ were selected as 0.2, 0.5, 1.0 and 2.0 M. As shown in Fig. 3, the efficiency of Fenton's oxidation sharply increased when the constant ratio of $[H_2O_2]/ [Fe^{+2}]$ was applied. 81% of COD removal was achieved with $[H_2O_2]/[Fe^{+2}]$ = 10 at 2 m of $[H_2O_2]$ whereas the COD removal was only 60% with the constant $[Fe^{+2}]$ at the same $[H_2O_2]$ concentration. The ratio of COD (mg/l):$[Fe^{+2}]$:$[H_2O_2]$ was found as 40:0.1:1 for water-based paint wastewater. It was reported that the dye can be most effectively oxidized in an aqueous solution with a molar ratio of 1:1.15:14.1 (dye: Fe^{+2}: H_2O_2) [15].

The Fenton's oxidation of waster-based paint wastewater followed by coagulation was investigated since the wastewater contained the high concentration of SS together with COD. After the coagulation with alum, the effluent was subjected to Fenton's oxidation at the molar concentration of $[H_2O_2]$ between 0.2 and 1 m at the constant $[H_2O_2]/[Fe^{+2}]$ = 10 ratio (Fig. 4). The efficiency of COD removal was increased from 25% to 59%, while the COD removal efficiency of raw wastewater was increased from 49% to 65% at the same conditions. The effluent of coagulation with alum contained mostly some solutes because the suspended solids were removed by coagulation. Known paints contain some additives such as TiO_2, which is a catalyst in oxidation processes. It was thought that the highest removal efficiencies with the raw wastewater could be explained by the effect of TiO_2 on Fenton's oxidation. The total removal efficiency of alum and Fenton's was 81% at 1 M of $[H_2O_2]$ concentration. The color and turbidity were completely removed in all Fenton's experiments.

3.3. Fenton's oxidation kinetic

The other important parameter of Fenton's oxidation is the process time. To optimize the reaction time Fenton's oxidation was observed by sampling every 10 min for the first 1 h, every 30 min from 1 to 4 h, and the last one on the 24th h. Fig. 5 shows the effect of Fenton's oxidation time on COD removal. COD removal occurred very fast first 10 min and slowed after 10 min. The COD profile reached a plateau starting at 150th min. It can be said that 60% of total COD removal was achieved in the first 10 min of reaction. During the Fenton's oxidation, the easily oxidisable substances were readily removed in the first 10 min. It was reported that faster reaction times with extremely high polluted pharmaceutical wastewater achieved 90% of COD removal in the first 10 min [5]. As seen in Fig. 6 the removal of COD was accomplished at two

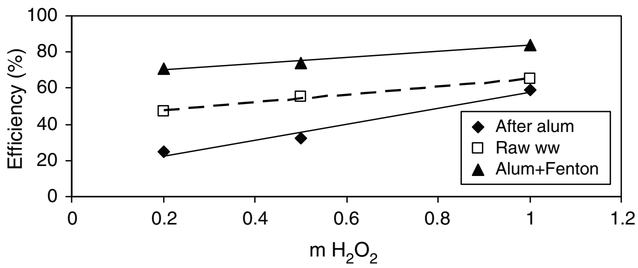

Fig. 4. Fenton's oxidation of the effluent from coagulation with alum.

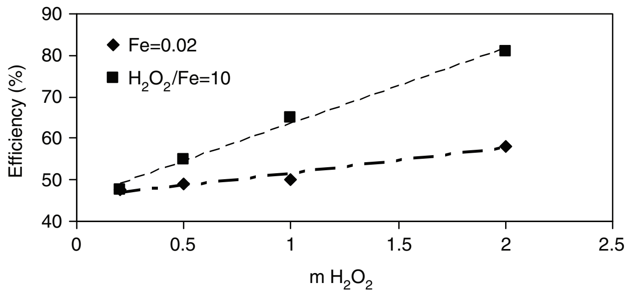

Fig. 3. Effect of $[Fe^{+2}]$ concentration on Fenton's oxidation for water-based paint wastewater.

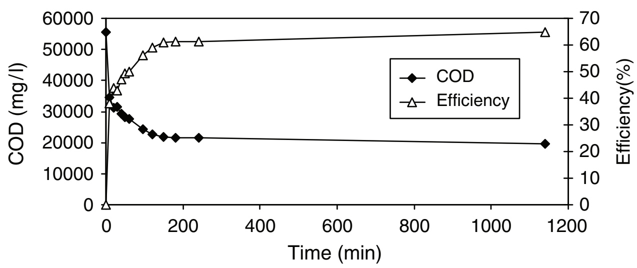

Fig. 5. Effect of Fenton's oxidation time on COD removal: $[H_2O_2]$ = 1 m, $[Fe^{+2}]$ = 0.1 m, temperature = 25 °C.

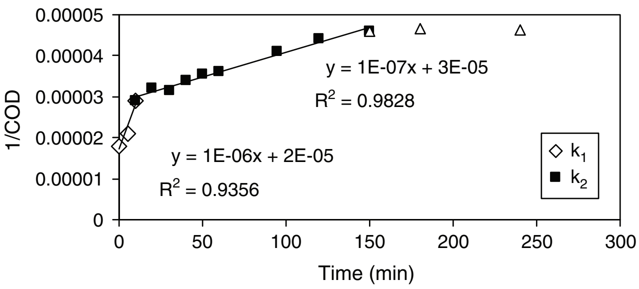

Fig. 6. Kinetics of COD oxidation during Fenton's oxidation: $k_1 = 1\times10^{-6}$ l/mg min, $k_2 = 1\times10^{-7}$ l/mg min.

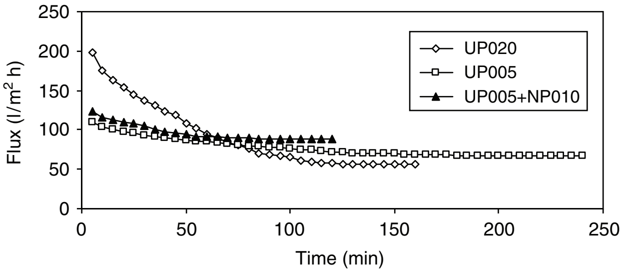

Fig. 7. Flux declines as a function of time for all membranes.

different rates according to the second-order reaction model. The second order rate constant, k was determined for both of the reaction rates. The results showed that the first rate in 10 min was 10 times faster than the second one.

3.4. Membrane studies

Several experiments with the raw water-based paint wastewater were conducted to examine the effectiveness of membrane filtration to remove COD and to investigate the recycling and reuse facilities of both water and pigments. The flux decline caused by concentration polarization and fouling was calculated by given [8]. The flux declines as a function of time are given in Fig. 7, and the flux declines calculated are presented in Table 2. The flux decline caused by fouling is irreversible although the flux decline caused by concentration polarization is reversible. As seen in Table 2, the total flux declines for the ultrafiltration membranes FM UP020 and FM UP005 were 88 and 73%, respectively. The extremely polluted raw wastewater led to the fouling of the ultrafiltration membranes which were only 7 and 9%. It can be said that the pollution occurred on the surface of the ultra filtration membranes, not in the membrane pore size. The flux recoveries of the membranes FM UP020 and FM UP005 were 93 and 91%, respectively. Table 3 gives the COD removal of all membranes used. The COD removal efficiencies for the membranes FM UP020 and FM UP005 were reached to 53 and 66%, respectively. The color was completely eliminated by both of the membranes, but limited COD removal was achieved since certain solutes in the feed water permeated through the membrane. Permeate of the membrane FM UP005 was subjected to the membrane FM NP010 to accomplish additional COD removal. The flux decline by fouling for the membrane FM NP010 was 15% which was almost half of the total flux decline although the total flux decline was only 36%. The nanofiltration membrane has a pore size of 1000 Da, the pollution therefore occurred both on the surface and in the pore of the membrane. COD removal efficiency of the membrane FM NP010 was negligible, at only 4%.

Table 3
Process performances of all membranes used in this study

Membrane	Influent COD (mg/l)	Permeate COD (mg/l)	Removal efficiency (%)
FM UP020	144,000	67,460	53
FM UP005	144,000	48,680	66
FM NP010 after UP005	48,680	44,700	4

Table 2
The flux decline results of FM UP020, FM UP005 and FM NP010 after FM UP005 and VRF values for the water-based paint wastewater

Membrane	Flux (l/m² h)			Flux decline (%)			V_f (l)	V_c (l)	VRF (V_f/V_c)
	J_w	J_s	J_f	Total	Conc. Pola.	Fouling			
FM UP020	458	56	425	88	81	7	4	1.45	2.75
FM UP005	244	67.2	222	73	64	9	4	1.45	2.75
FM NP010 after UP005	137	88	117	36	21	15	2.55	0.855	2.98

4. Conclusion

The treatment and recycling facilities of highly polluted water-based paint wastewater from the electronics industry were studied by using coagulation flocculation, Fenton's oxidation and membrane processes. Based on the experimental findings, the following conclusions can be drawn:

- All alternatives applied in this study produced colorless effluent. Therefore the effluents from the all alternatives can be used in the painting unit for the recycling purpose. On the other hand, the amount of waste sludge produced by the treatment facilities should be taken into account because the waste sludge needs hazardous disposal.
- Coagulation-flocculation using alum and $FeSO_4$ was investigated. 67% of COD removal was achieved at 1000 mg/l of alum dosage whereas coagulation with $FeSO_4$ obtained 45% of removal efficiency at 750 mg/l dosage. The color and turbidity were removed to acceptable values. Waste sludge produced by coagulation flocculation should consider the disposal of hazardous waste.
- Fenton's oxidation gave good results for the removals of COD and color. 81% of COD removal was achieved at a H_2O_2:Fe^{+2} molar ratio of 10:1 in the presence of 2 m H_2O_2. The oxidation time reached a plateau at 150th min whereas 60% of total COD removal was achieved in the first 10 min of reaction. The color and turbidity were completely removed in all Fenton's experiments and waste sludge produced during the Fenton's process was less than that of coagulation, but still requires hazardous disposal.
- Membrane process presented a more environmentally friendly solution to recover both water and pigments. Membrane filtration does not require sludge disposal since the concentrate can be recycled or reused. This study showed that the total flux decline for the ultrafiltration FM UP005 membrane was 73% and the flux decline by fouling for the membrane was 9%.
- Cost analysis involving investment, operation and maintenance, and waste sludge disposal should be made to decide the treatment and/or recycling process.

Acknowledgement

Authors thank Dr. Yasemin Kaya and Dr. Beril Gonder for their contributions to membrane studies.

References

[1] Hazardous and Medical Waste Management Program. Fact Sheets and Information Papers, (2005), (chppm-www.apgea.army.mil/hmwp/Factsheets/waterbased.pdf), (accessed 2009-08-26).
[2] B.K. Dey, M.A. Hashim, S. Hasan and B. Sen Gupta, Adv. Environ. Res., 8 (2004) 455–466.
[3] G. Eremektar, S. Goksen, F.G. Babuna and S. Dogruel, J. Environ. Sci. Heal. A., 41 (2006) 1843–1852.
[4] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, Water Res., 35 (2001) 2129–2136.
[5] N.S.S. Martinez, J.F. Fernandez, X.F. Segura and A.S. Ferrer, J. Hazard. Mater., B101 (2003) 315–322.
[6] U. Kurt, Y. Avsar and M. Gonullu, Chemosphere, 64 (2006) 1536–1540.
[7] K. Uenoyama, T. Kajino, T. Okai and T. Koike, J. Cleaner Prod., 4 (1996) 79.
[8] Y. Kaya,. H. Barlas and S. Arayici, Sep. Purif. Technol., 65 (2009) 117–129.
[9] F. Lipnizki, Desalination, 224 (2008) 98–104.
[10] M. Mamadiev; Treatability of Electronics industry effluents, Istanbul University, MSc Thesis (2009) (in Turkish).
[11] APHA, Standard Methods for the Examination of Water and Wastewaters, APHA-AWWA-WPCF, Washington, DC (1995).
[12] Europäische Norm, ISO 7887: Water Quality Examination and Determination of Color, Brussels (1994).
[13] M. Guida, M. Mattei, C.D. Rocca, G. Melluso and S. Meriç, Desalination, 221 (2007) 113–127.
[14] E. Cokay and F. Sengul, DEU Fen ve Muhendislik Dergisi, 8(2) (2006) 1–9 (in Turkish).
[15] K. Dutta, S. Mukhopadhyay, S. Bhattacharjee and B. Chaudhuri, J. Hazard. Mater., B84 (2001) 57–71.