

Treatment of Petrochemical Wastewater Containing Phenolic Compounds by Electrocoagulation Using a Fixed Bed Electrochemical Reactor

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This work explores the possibility of using electrocoagulation to remove phenolic compounds from oil refinery waste effluent using an electrochemical reactor with a fixed bed anode made of randomly oriented Al raschig rings packed in a perforated plastic basket located above the horizontal cathode. The removal of phenolic compounds was investigated in terms of various parameters in batch mode namely: pH, operating time, current density, initial phenol concentration, addition of NaCl, temperature and the effect of phenol structure (effect of functional groups). The chemical oxygen demand (COD) was also measured. In order to throw some light on the economics of the process, energy consumption as well as Al consumption were calculated under different conditions. The study revealed that the optimum conditions for the removal of phenolic compounds were achieved at current density = 8.59 mA/cm², pH = 7, NaCl concentration = 1 g/L and temperature of 25°C. Remarkable removal of 100% of phenol compound after 2 hrs can be achieved for 3 mg/L phenol concentration of real refinery wastewater. The new anode design of electrocoagulation cell permits high efficiencies with lower energy consumption in comparison with other cell design used in previous studies.

Keywords: Electrocoagulation; Phenolic compounds; Energy consumption; Wastewater.

1. INTRODUCTION

Phenols are important industrial chemicals of environmental concern since they are involved in many industries such as coke, refineries, manufacturers of resin, pharmaceuticals, pesticides, dyes, plastics, explosives and herbicides, and can also occur in their wastewaters. Phenols are produced in very large quantities for use as solvents, and starting materials for chemical synthesis [1]. Phenolic

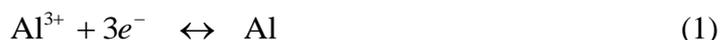
compounds are some of the major hazardous compounds in industrial wastewater due to their poor biodegradability, high toxicity and ecological aspects. For instance phenols are released into water from industrial effluent discharges such as petroleum refinery wastewater. It has also been detected in groundwater as a result of leaching through soil after a spill of phenol from landfill sites. Typical wastewaters from oil refineries contain phenol in concentrations ranging from 500 to 1500 mg/L, and those from coking plants in concentrations ranging from 200 to 1200 mg/L [2]. The presence of phenol in drinking water and irrigation water represents a serious health hazard to humans, animals, plants and microorganisms [3]. Due to the high toxicity of phenols, they are subjected to specific regulations. The Environmental Protection Agency (EPA) calls for lowering phenol content in potable and mineral waters to 0.5 ppb, while the limits for wastewater discharge are 0.5 ppm for surface waters and 1 ppm for the sewerage system [4].

There are different methods for the separation of phenols such as steam distillation [5,6], Separation by extraction [7-11], Separation by adsorption [12-19], Separation by membrane [20-24], Destruction of Phenol by wet-air oxidation [25-28], Electrochemical oxidation [29-37], Biochemical abatement [38-44]. Many problems associated with the above mentioned methods have been reported in the literature such as high cost, low efficiency and generation of toxicity products [45]. Electrocoagulation is the process utilizing "sacrificed" anodes to form active coagulant which is used to remove pollutant by precipitation and flotation in situ. Compared with traditional chemical coagulation, electrocoagulation has, in theory, the advantage of removing the smallest colloidal particles; the smallest charged particles have a greater probability of being coagulated because of the electric field that sets them in motion. It has also the advantage of producing a relatively low amount of sludge [46]. Electrocoagulation is an ideal technology to upgrade water quality. A diversity of opinions exists in the literature for explaining both the key mechanisms and the best reactor configurations [47, 48]. These empirical studies invariably prove the viability of the technology, but singularly fail to fully capitalize on its potential. This is due to a lack of fundamental understanding of the system and hence the inability to accurately predict performance. In addition to this gap we believe that there is a room for improvement of the process of electrocoagulation via the development of more efficient electrochemical reactors.

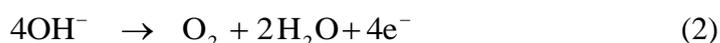
In the present work, the performance of a fixed bed reactor with horizontal cathode made of an aluminum sheet insulated with epoxy from its back placed below a fixed bed anode. The anode consists of a single layer of randomly oriented raschig rings connected together tightly with a thin wire of aluminum to ensure current feed to different rings of the fixed bed during electrolysis. Previous studies on electrocoagulation have mostly emphasized on the use of the traditional parallel plate cell. The effect of phenol structure on the degree of phenol separation was investigated. The use of fixed bed anode is thought to have the following advantages: (i) the high area of the bed reduces the operating current density with a consequent decrease in activation polarization and passivation. (ii) the large amount of Al stored in the bed makes it possible to conduct electrocoagulation for a long time without the need to disrupt the process in order to make up for the dissolved Al anode every short while. (iii) the narrow interstices between the bed particles increase the velocity of the rising H_2 -solution dispersion inside the anode with a consequent decrease in concentration polarization at the anode.

2. EC THEORY

All electrocoagulation reactors are electrochemical cells that consist of an electrode arrangement in contact with the polluted water, with coagulant production *in situ* being their distinguishing feature. To release the coagulant, an applied potential difference across the electrodes is required. Potential requirements for the electrodes can be deduced from the electrochemical half-cell reactions occurring at each electrode, which will vary according to the operational pH and the species present in the system. Aluminum, the most commonly used anode material; go through anodic dissolution as shown in equation (1):



Oxygen evolution is also possible at the anode (equation 2):



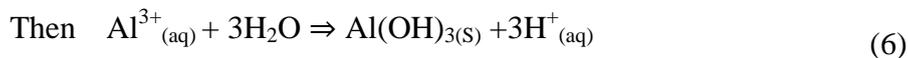
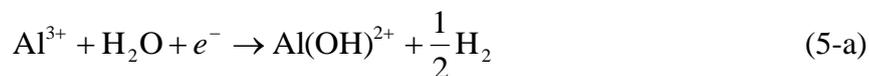
Simultaneously, an associated cathodic reaction, usually the evolution of hydrogen, occurs. The reaction occurring at the cathode is dependent on pH. At neutral or alkaline pH, hydrogen is produced via Equation (3):



While under acidic conditions, Equation (4) best describes hydrogen evolution at the cathode.



Al^{3+} and OH^{-} ions generated by electrode reactions react to form different monomeric and polymeric species, which transform finally into $\text{Al}(\text{OH})_3(\text{S})$ depend upon total metal concentration and pH.



both “Al” cathode and anode may be chemically attacked by OH^{-} ions in view of the amphoteric nature of “Al” [49].



Accordingly, two major interaction mechanisms are being proposed namely: precipitation and adsorption, each one being suggested for a separate pH range. Flocculation in the low pH range is explained as precipitation while the higher pH range (> 6.5) as adsorption [50, 51].

3. EXPERIMENTAL PART

3.1. Chemicals and analytical

A stock solution of each phenolic compound was prepared by using an analytical grade of chemicals and dissolving them in distilled water. Experimental solutions of the desired concentrations were obtained by successive dilution with distilled water.

The pH of the solution was adjusted by means of HCl and /or NaOH solution. A digitally calibrated pH-meter (Hanna, Model pH 211) and a conductivity – meter were used to measure the pH and the conductivity of waste solutions.

The analytical determination of phenol and other phenolic compounds was carried out with the standard spectrophotometric procedure [52] using U.V spectrophotometer (UNICO, Model U.V 2100). At the end of each experiment, the treated solutions were filtered by using Whitman No. 40 filter paper, before analysis. COD of the solution before and after EC was determined by the standard procedure described elsewhere [52].

Oil refinery wastewater was obtained from (El-Amreya Petroleum Company, Alexandria, Egypt).

3.2. The Experimental Set-up

The experimental set-up used in the present work is schematically shown in Fig.1. The EC cell consists mainly of a rectangular vessel made of plexi-glass with the dimensions 10 cm \times 10 cm square base and a height of 20 cm. An aluminum 10 cm \times 10 cm sheet was insulated with epoxy from its back and then placed on the bottom of the cell as the cathode. The anode consists of a single layer of raschig rings connected together with a thin wire of aluminum to make sure that all rings were fed with electrical current. The rings were placed in a perforated plastic basket. The rings were arranged randomly within the bed. The anode-cathode distance was kept at 0.5 cm. the fixed bed anode was fixed in position inside the cell by an outside anode holder which consisted of a ring clamp connected to a vertical stand. The electrical circuit consists of power supply (40V, 20A) with a voltage regulator and multi-range ammeter, all connected in series with the cell, a voltmeter was connected in parallel with the cell to measure its voltage.

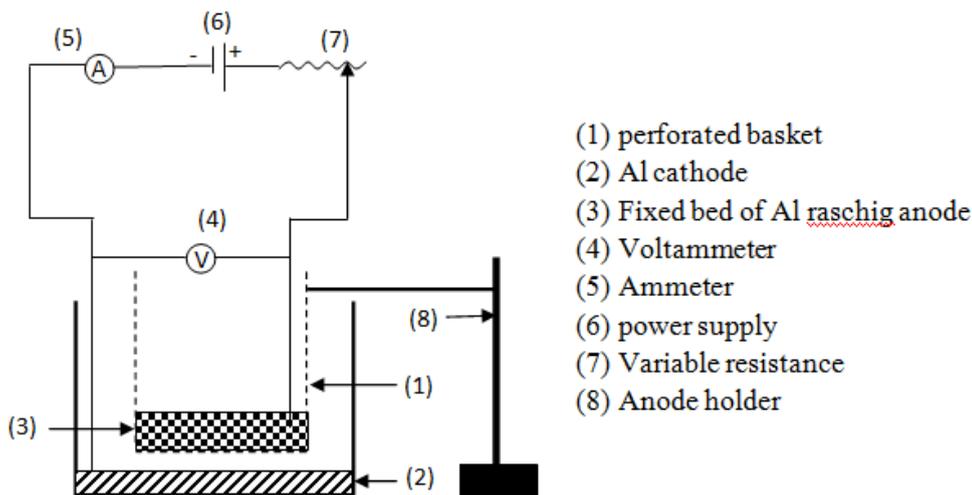


Figure 1. Schematic view of the experimental set-up.

3.3. Electrocoagulation Procedures

For each run a 1.5 L of the synthetic waste solution was mixed with the appropriate amount of sodium chloride which was employed as a conductor. The solutions were placed into the electrolytic rectangular cell. The pH was adjusted by the addition of NaOH and/or HCl solutions. Direct current from the D.C power supply was passed through the solution via the two electrodes during the 180 minutes of electrolysis run. 10 mL of the solution was withdrawn at every 5 minutes interval for the first half hour and 30 minutes interval for the remaining time of the run. The location of sample withdrawal was kept constant for all runs. Samples were filtered, and then taken for absorbance measurements at an appropriate wave length of the maximum absorption for each of the phenolic compounds. The measured absorbance was then converted to the residual concentration of the compound using a calibration curve obtained from a plot between the absorbance versus the known concentration for each compound.

The electrodes were washed with HCl solution (15% w/v) before each run in order to remove any adhering scales or oxides. Following each run, the electrodes were washed with distilled water, dried until the second use. The efficiency of phenol removal, % Removal, was calculated as:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \tag{8}$$

where C_i is initial phenol concentration (mg/L) and C_f is final phenol concentration (mg/L).

4. RESULTS AND DISCUSSION

4.1. Effect of current density

Fig.2 shows that an increase in current density from 1.2 to 9.82 mA/cm² increases the percentage removal of phenol from 40 to 88 .This is ascribed to the fact that at higher current densities

the dissolution of anode to Al^{3+} ions increases according to Faraday's law. Al^{3+} ions undergo hydrolysis and the resulting aluminum hydroxides produce more sludge with a consequent significant removal of phenol due to phenol adsorption on $Al(OH)_3$ and its polymeric compounds [53]. Furthermore, more hydrogen bubbles are generated at the cathode with increasing current density, these bubbles improve the degree of mixing of aluminum hydroxides and phenol and enhance the flotation ability of the cell with a consequent increase in the percentage removal [54]. Also, it was found that the number of H_2 bubbles increases and their size decreases with increasing current density, resulting in a faster removal of phenol and sludge flotation [55]. Apart from phenol adsorption on $Al(OH)_3$ and its polymeric compounds, aluminum ions liberated from the anode may also interact directly with phenol, which then precipitates out of the solution in the form of an insoluble salt, e.g. aluminum triphenolate ($\leq 8\%$ precipitation) [56].

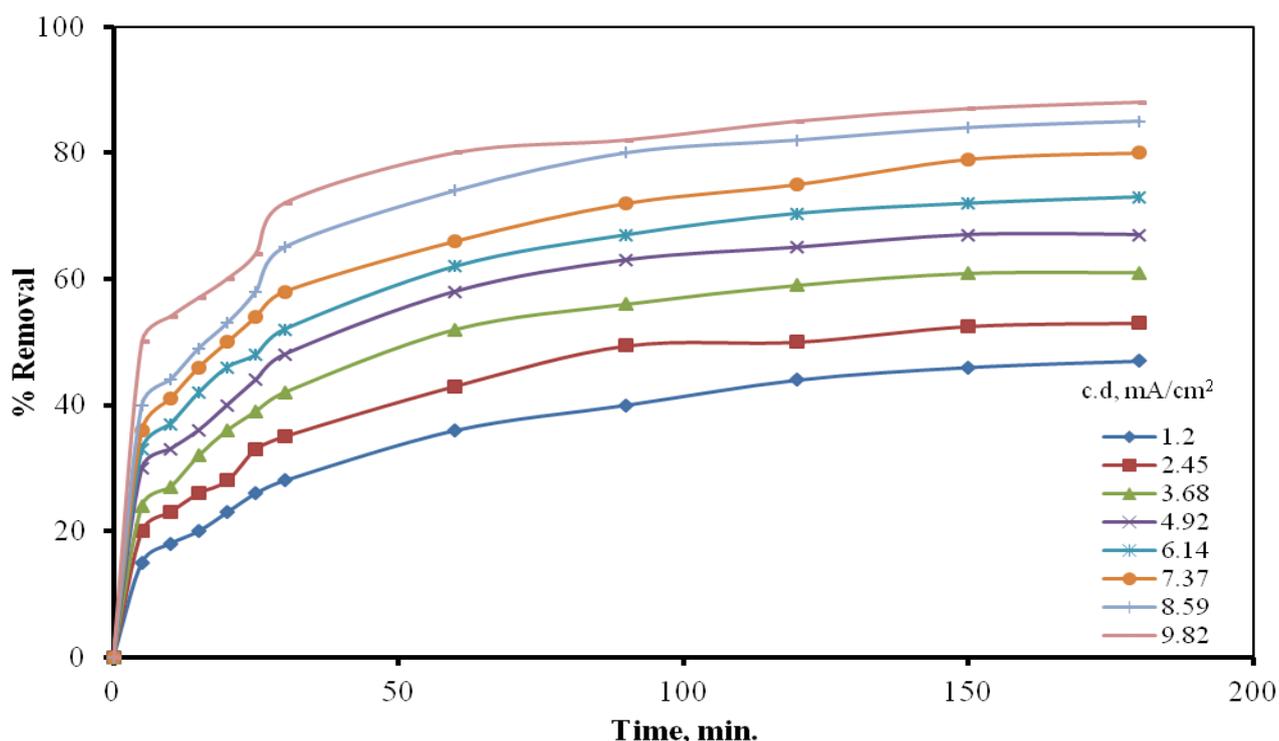


Figure 2. Effect of current density on the percentage removal of phenol ($C_o = 40$ mg/L, NaCl = 1 g/L, pH = 7, Temperature = 25°C)

4.2. Effect of sodium chloride concentration

Fig.3 shows the effect of sodium chloride concentration on the percentage removal of phenol. It was found that, as sodium chloride concentration increases from 0.5 to 7 g/L, the percentage removal of phenol increases from 60 to 85. This may be explained by the fact that the higher chloride ion concentration, the higher the ability of chloride ions to destroy any passive oxide film which tends to form on the anode and limit anode dissolution, hence it increases the availability of aluminum hydroxide in the solution and improve the efficiency of phenol removal [56]. Also, as the concentration of sodium chloride increase, the activity of the dissolved Al^{3+} in the anode vicinity decreases by virtue

of interionic attraction [57] between sodium chloride and the dissolved Al^{3+} , accordingly the potential required to dissolve the aluminum anode (e) decreases according to Nernst equation:

$$e = e_o - \frac{RT}{ZF} \ln a_{Al^{3+}} \tag{9}$$

where e is the electrode potential, e_o is the standard electrode potential, F is Faraday’s constant [$F = 96500$ coulomb], Z is the number of electron involved in the reaction and R is the gas constant ($R = 8.13$ J/mol.K), $a_{Al^{3+}}$ is the activity of Al^{3+} .

The decrease in the potential required to dissolve the anode reduce the tendency of aluminum to passivate and reduce the tendency of chlorine and oxygen evolution at the expense of aluminum dissolution. Meanwhile, Fig.3 shows that beyond 1 g/l sodium chloride concentration, the salt has a little effect on the percentage phenol removal. According to the results, high percentage removal of phenol can be obtained in phenol solution with sodium chloride of about 1 g/L. Hence, 1 g/L sodium chloride was used in the subsequent experiments.

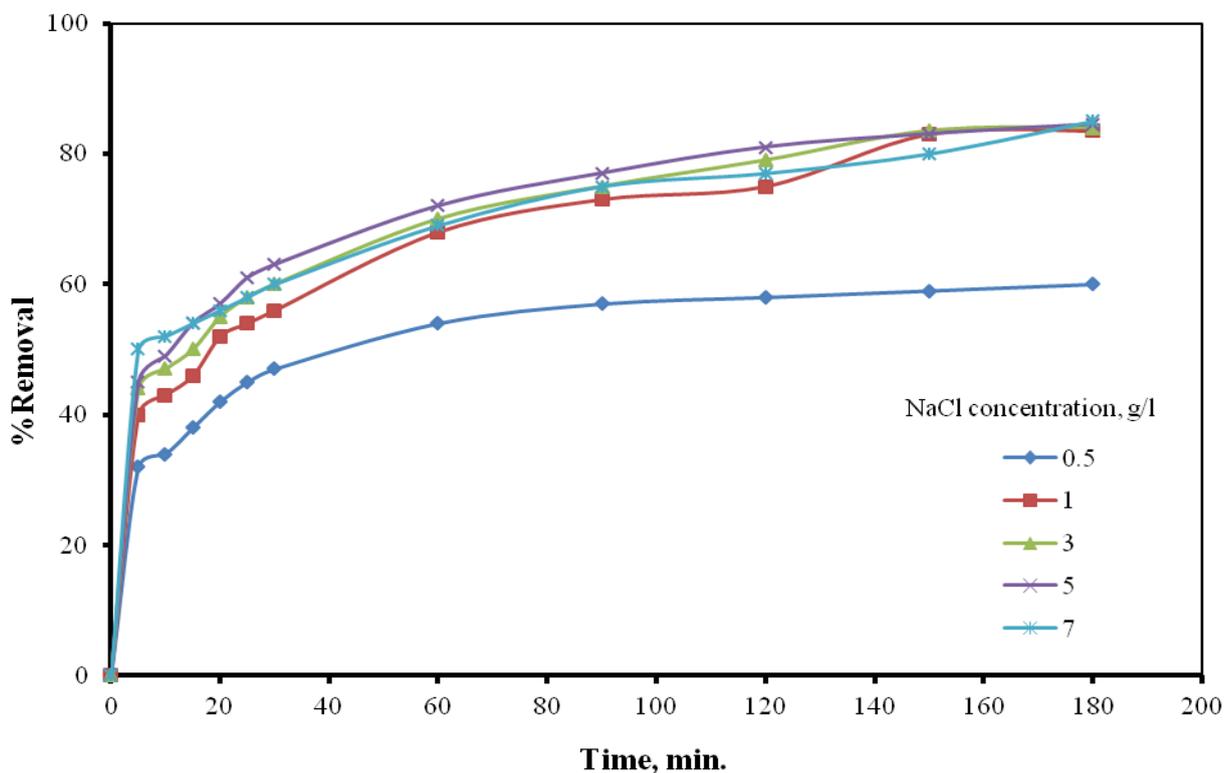


Figure 3. Effect of NaCl concentration on the percentage removal of phenol (Co = 40 mg/L, pH = 7, c.d = 8.59 mA/cm², Temperature = 25°C)

4.3. Effect of the initial pH value

To examine the effect of pH, the sample was adjusted to the desired pH using sodium hydroxide or hydrochloric acid solutions. Fig.4 shows the effect of pH on percentage removal of

phenol. The data show that the percentage removal of phenol increased from 18 to 88 as the pH increases from 1 to 7. Beyond pH 7, the percentage removal decreases. This is attributed to the amphoteric character of aluminum hydroxide which does not precipitate at very low pH [58], while high pH leads to the formation of $Al(OH)_4^-$ which is soluble and useless for adsorption of phenol [59].

The results show that the optimal pH is 7 (initial pH of the solution).

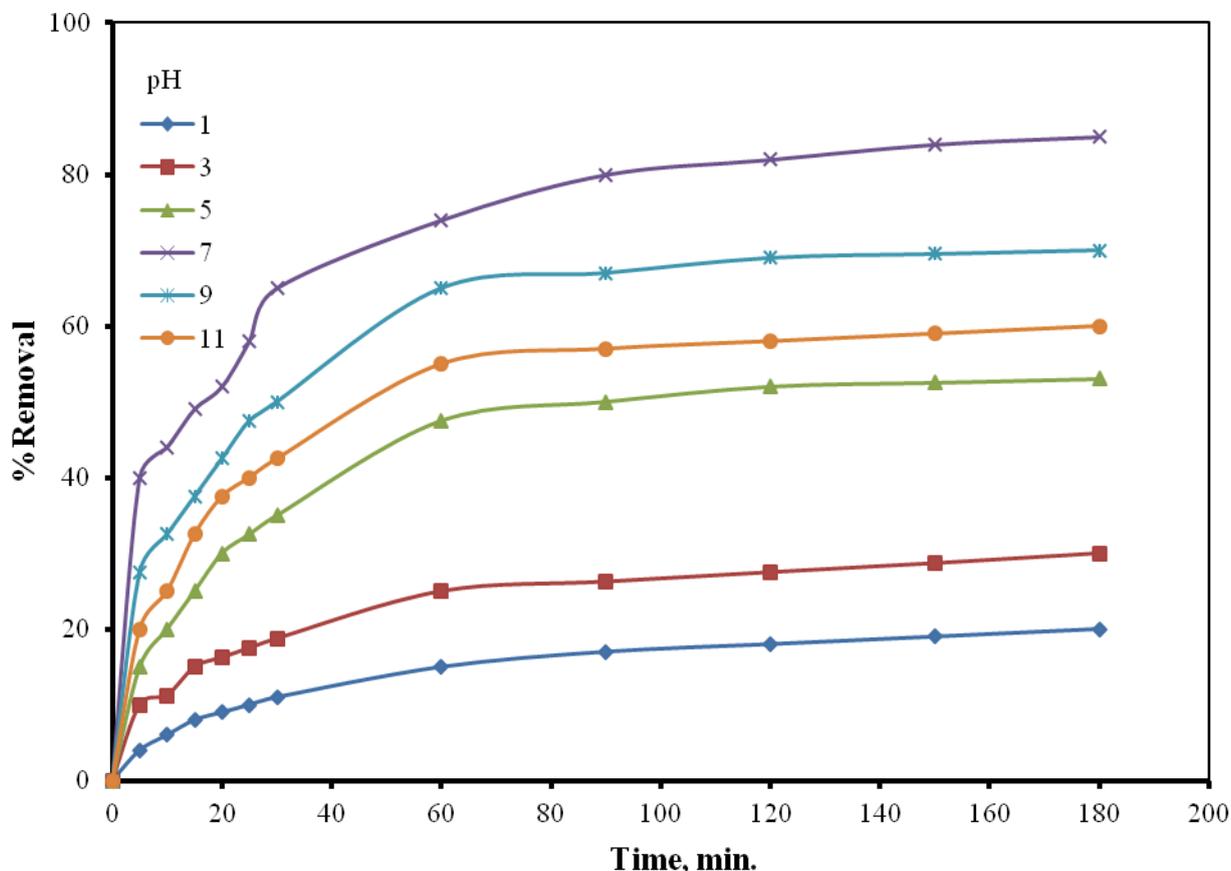


Figure 4. Effect of pH on the percentage removal of phenol ($C_o = 40 \text{ mg/L}$, $pH = 7.3$, $c.d = 8.59 \text{ mA/cm}^2$, Temperature = 25°C)

4.4. Effect of initial phenol concentration

Fig.5 shows the effect of initial concentration on percentage removal of phenol. The percentage removal gradually decreases from 100 to 75 as the phenol concentration increases from 5 to 50 mg/l. This is ascribed to the fact that at a constant current density, the same amount of aluminum ions passes to the solution at different phenol concentration. Consequently, the formed amount of complex aluminum hydroxides was insufficient to coagulate the greater number of phenol molecules at higher phenol concentrations, which is consistent with previous studies [60,61].

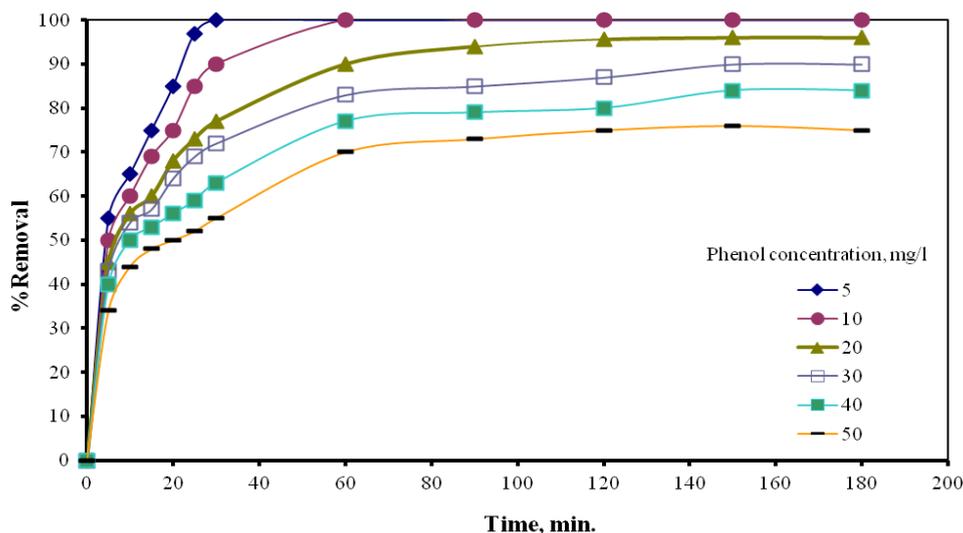


Figure 5. Effect of initial concentration on the percentage removal of phenol (pH = 7, c.d = 8.59 mA/cm², NaCl = 1 g/L, Temperature = 25°C)

4.5. Effect of temperature

The effect of temperature on the percentage removal of phenol is shown in Fig.6. The percentage removal increases from 88 to 95 as the temperature increases from 25 to 45°C, beyond this temperature, there is a little effect on removal efficiency. Temperature influences the rate of phenol removal via the following effects: (i) increase of temperature increases the rate of Al³⁺ hydrolysis to Al(OH)₃ [62]. (ii) increase the temperature increases the diffusivity of Al³⁺ according to the Stokes-Einstein’s equation with a consequent increase in the rate of mass transfer of Al³⁺ from the anode surface to the solution bulk. Beyond 40°C, the solubility of Al(OH)₃ in the solution increases with a consequent loss of the coagulant [63]. Under the present range of conditions it seems that the enhancing effects outweigh the adverse effect.

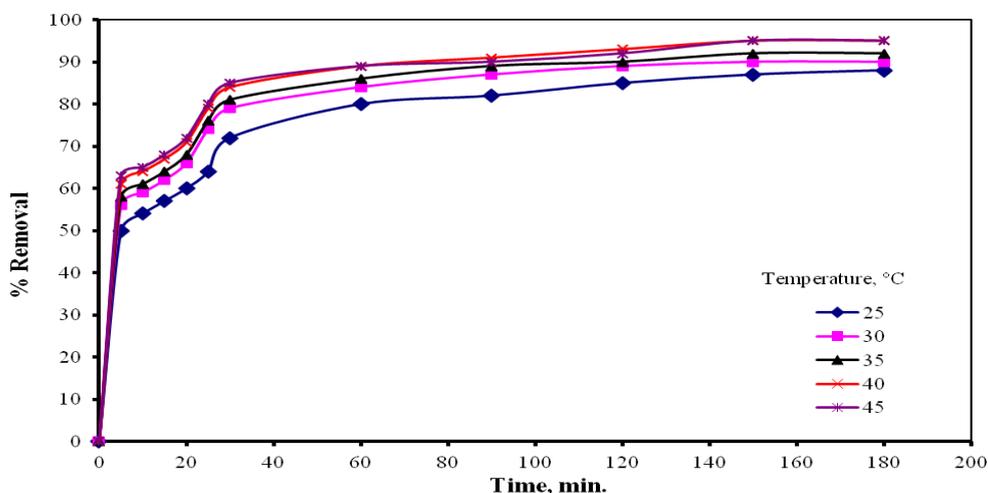


Figure 6. Effect of temperature on the percentage removal of phenol (Co = 40 mg/L, pH = 7, c.d = 8.59 mA/cm², NaCl = 1 g/L, Temperature = 25°C)

4.6. Effect of functional groups of different phenolic compounds (phenol structure)

Physico-chemical properties of the different phenolic compounds influence its interaction within the EC system and eventual removal mechanism. For example, ions are most likely electro-precipitated whilst charged suspended solids are absorbed onto charged coagulant [64]. In order to study the effect of the side group of different phenolic compounds, the percentage removal of each phenolic compound was investigated with time for concentration 40 mg/L using optimum experimental conditions of the batch mode apparatus (current density = 8.59 mA/cm², pH = 7, NaCl concentration = 1 g/L). Fig.7 shows the percentage removal versus time for phenol, m-cresol, orthonitrophenol (O.N.P) and hydroquinone.

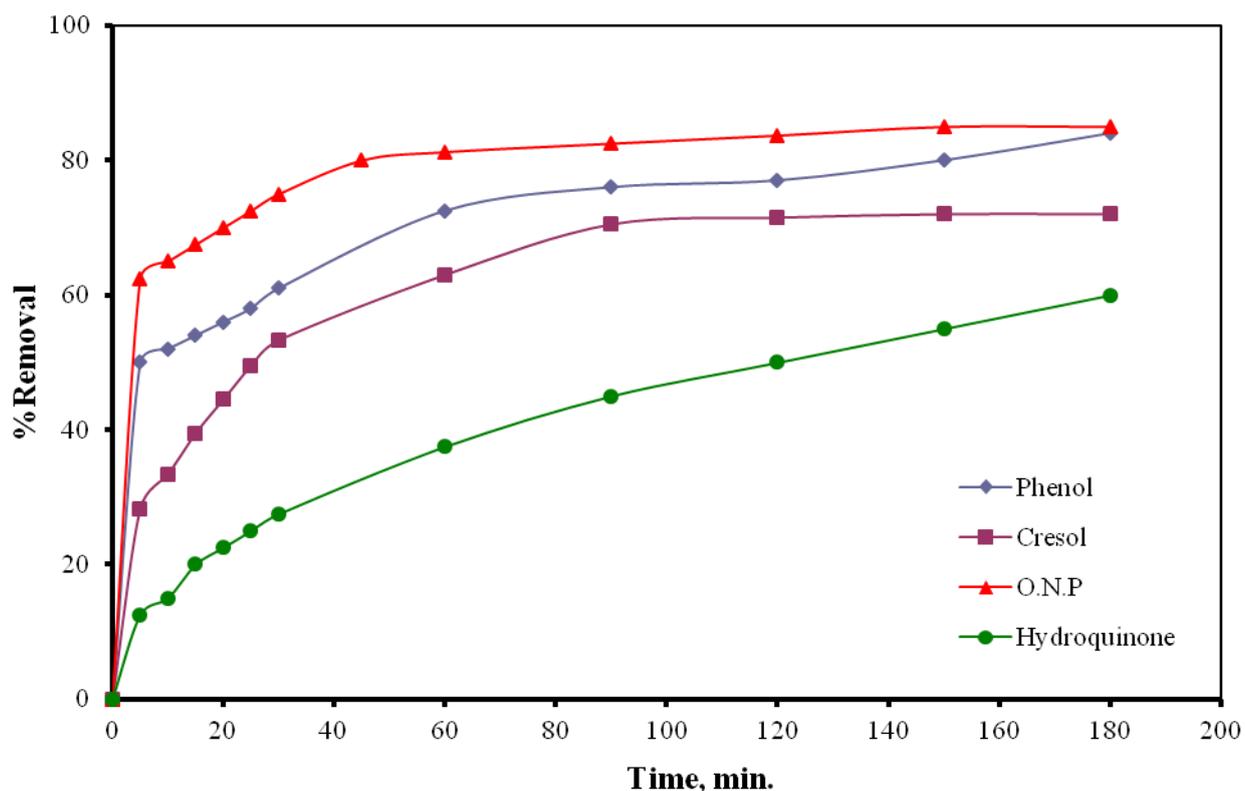


Figure 7. Effect of variation of side groups on the percentage removal of phenolic compounds (Co = 40 mg/L, pH = 7, NaCl = 1 g/L, c.d. = 8.59 mA/cm², Temperature = 25°C)

It was found that O.N.P has the highest efficiency of removal than phenol, and m-cresol. The lowest efficiency of removal was that of hydroquinone. This order of removal efficiencies may be attributed to the acid strength of each phenolic compound. Acid strength depends on the nature of side group present in the benzene ring. Electron withdrawing groups like -NO₂ when present in ortho or para positions increase the acidity of compound by dispersal of negative charge. While, electron releasing groups like -OH, when present in the ortho or para positions decrease the acid strength of the compound by stressing the negative charge (by +R effect). However groups like -CH₃ when present in

m-position increase the acidity of the compound [65]. This theory was further verified by the dissociation constant of phenolic compounds under investigation (Table 1 [65]). The order of dissociation constant is O.N.P > phenol > m-cresol > hydroquinone. Increasing the dissociation constant leads to increase concentration of phenolate ions, the negatively charged phenolate ions migrate towards the positively charged Al anode where it most probably form a complex compound with the anodically dissolved Al^{3+} ions[66]. The complex Al compound along with the undissociated phenol adsorb on $Al(OH)_3$ leading to a higher removal rates [67].

Table 1. Dissociation constant of Some Phenolic Compounds at 25°C.

Name	Formula	Dissociation constant
Phenol	C_6H_5OH	1.3×10^{-10}
m- Cresol	$CH_3C_6H_4OH$	9.8×10^{-11}
o-Nitrophenol	$NO_2C_6H_4OH$	5.9×10^{-8}
Hydroquinone	$C_6H_4(OH)_2$	1.2×10^{-12}

4.7. Energy consumption and Al consumption:

To assist in assessing the economic feasibility of electrocoagulation in comparison with other techniques, the energy consumption and Al metal consumption were calculated as follows [68]:

$$\text{Energy consumption (kWh/g removed)} = \frac{VIt}{(C_o - C_t) \times \text{treated volume (L)}} \quad (10)$$

Where: V is the cell voltage (V), I is the current (A), t is the electrolysis time (h), C_o and C_t are the initial compound concentration and concentration at time t (in mg/L) respectively.

The amount of Al metal consumed in electrocoagulation was calculated from Faraday's law:

$$\text{Al consumption (g Al/g compound removed)} = \frac{ItM}{ZFm} \quad (11)$$

Where : F is the Faraday's constant (96,500 Columb /mol), M the molecular weight of aluminum (27 g/mol) and z is the number of electron transfer ($z_{Al} = 3$).

Figs. (8-10) show that the energy consumption ranges from 0.066 to 16.32 kWh/g phenol removed depending on the operating conditions.

The figures also show that Al consumption ranges from 0.011 to 0.04 g Al/ g phenol removed depending on the operating conditions. It is clear from these figures that energy consumption decreases with increasing initial phenol concentration and NaCl concentration, and increases with increasing current density.

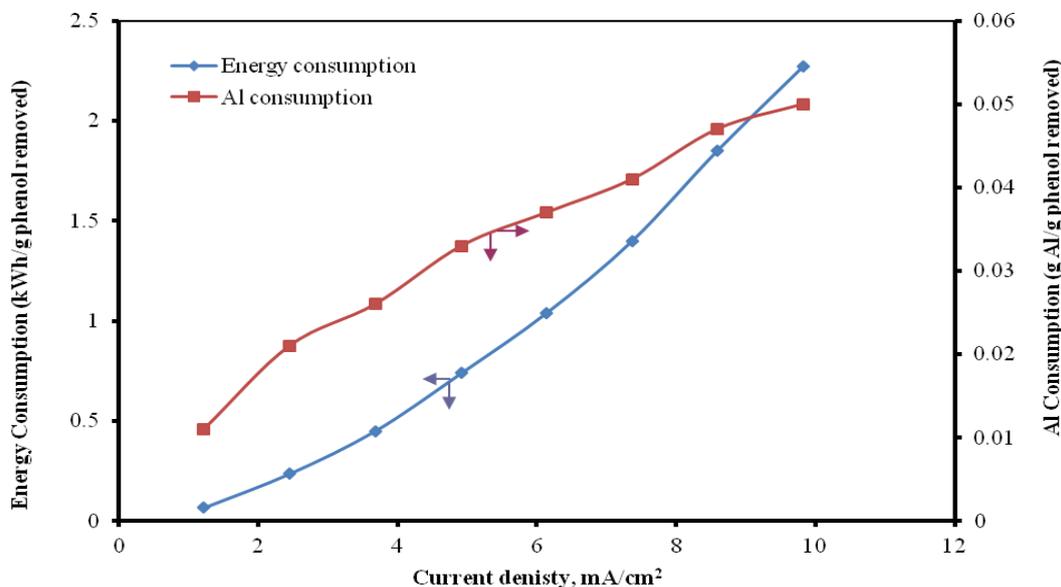


Figure 8. Effect of current density on the Energy Consumption and Al Consumption of phenol (Co = 40 mg/L, pH = 7, NaCl = 1 g/L, Temperature = 25°C)

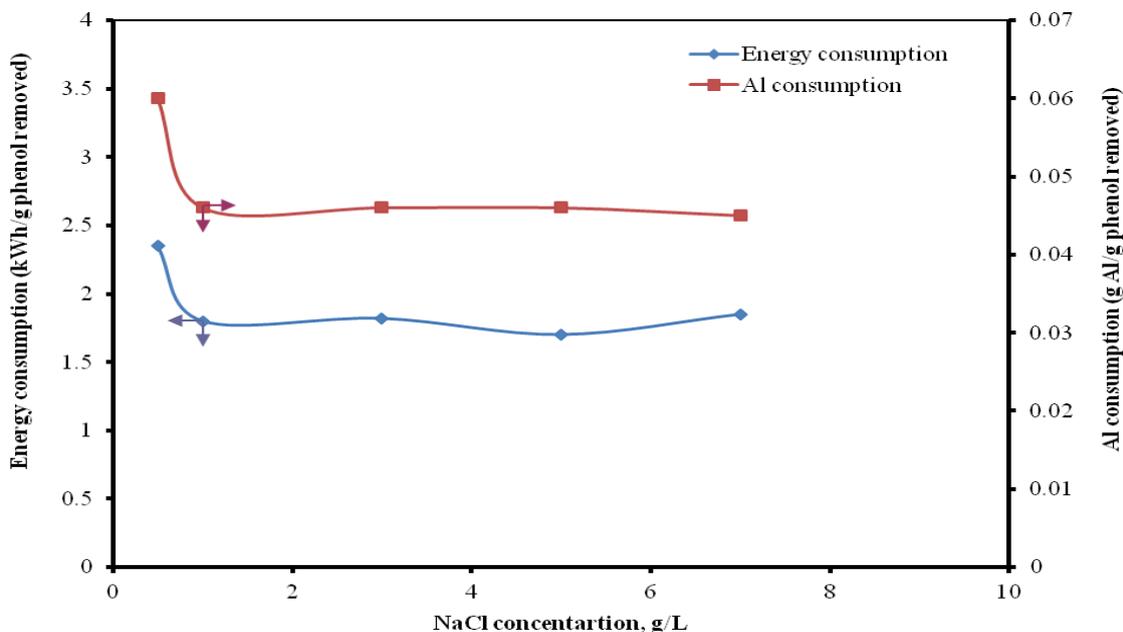


Figure 9. Effect of NaCl Concentration on the Energy Consumption and Al Consumption of phenol (Co = 40 mg/L, pH = 7, c.d. = 8.59 mA/cm², Temperature = 25°C)

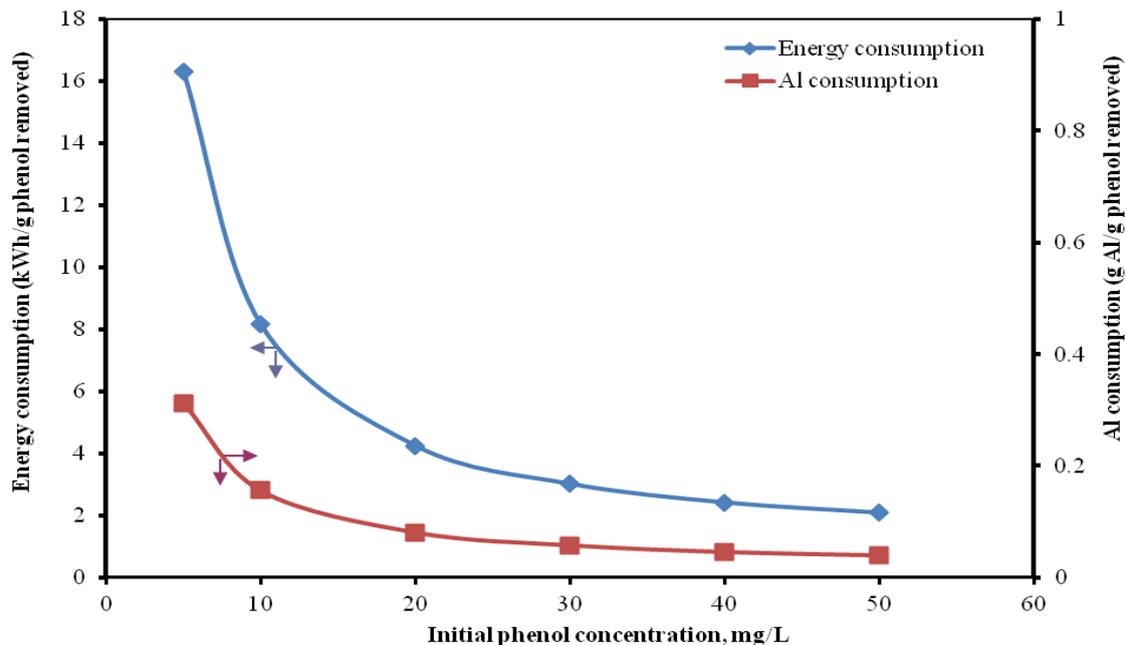


Figure 10. Effect of the Initial concentration on the Energy Consumption and Al Consumption of phenol (NaCl = 1 g/L, pH = 7, c.d. = 8.59 mA/cm², Temperature = 25°C)

4.8. COD Measurements

Table 2. COD Measurements.

Compound	Concentration, mg/L	% COD reduction
Phenol	5	100
	10	71.42
	20	63.63
	30	54.66
	40	52.94
	50	52.38
m-cresol	5	80
	10	56
	20	50
	30	50
	40	44
	50	41.6
o-Nitrophenol	5	100
	10	100
	20	100
	30	77.7
	40	72.7
	50	74
Hydroquinone	5	66.6
	10	66.6
	20	48.5
	30	52.9
	40	50
	50	50

COD values are related to the total concentration of organics in the solution. Mineralization of different phenolic compounds solutions were monitored by COD measurements before electrocoagulation and at the end of the run. It was found that the percentage COD reduction decreases with the increase in phenolic compound concentration. Table (2) shows that the percentage COD decreased from 100 to 52.38 and from 100 to 74, 80 to 41.6, and from 66.6 to 50 as the concentration was increased from 5 to 50 mg/L for each of phenol, O.N.P, m-cresol and hydroquinone, respectively. The percentage reduction in COD of phenol and phenolic compounds by electrocoagulation can be attributed to the removal of suspended solids and to precipitation of dissolved organic molecules as organometallic compounds. Detailed studies on the mechanism of percentage COD reduction was established by Murugan[69] .

4.9. Treatment of industrial petroleum refinery waste water:

Petroleum refineries are the main sources of phenolic wastewaters. A real oil refinery wastewater, was collected from the effluent of El-Amreya Petroleum Company, located in Alexandria, Egypt), and exposed to EC using the experimental apparatus at 8.59 mA/cm² current density and pH 7 for 1.5h and temperature of 25°C. The characteristics of wastewater used in this study before and after treatment is presented in Table (3). After EC period, 100% of initial phenol concentration was removed from the petroleum refinery wastewater. Compared to phenol removal, the removal of other contaminants in wastewater was not excessively changed. Practically, the effluent met the discharged standards after 1.5 h. EC time with energy consumption of 1.75 kWh/g phenol removed and electrode consumption 0.041 g Al/g phenol removed. Table (3) shows that electrocoagulation has resulted in the decrease of COD from 100 to 25 and had completely removed the phenol from the industrial waste. The concentration of phenol in the waste provided by the company was 3 ppm and after electrocoagulation it becomes zero. These results suggest that electrocoagulation can be used as polishing step in the treatment of liquid wastes containing phenol or phenol derivative.

Also from Table (3), the electrical conductivity had decreased. Since the electrical conductivity reflects the amount of dissolved solid in the sample, it follows that the formed aluminum hydroxides remove some of the salts that are adsorbed on its surface. The above mentioned effects show that electrocoagulation is a promising technique for industrial waste water treatment.

A few studies reported the removal of phenol from wastewater by EC. Table (4) presents a comparison of percentage phenol removal obtained from different studies on real wastewater effluents.

Table 3. Physical characteristics of wastewater before and after electrocoagulation treatment.

Parameter Analysis	Before treatment	After treatment
pH	7	9
COD (mgO ₂ /L)	100	25
Conductivity(mS/cm)	3.5	1.77
Phenol content(mg/L)	3	0
Turbidity (NTU)	8.2	3.5

Table 4. Comparison of the % Phenol removal obtained from different wastewater effluents.

Source of effluent	Phenol concentration, mg/L	% Removal	Reference
Petrochemical wastewater	2.5	60	[70]
Paper mill effluent	0.535	99	[71]
Present work	3	100	

5. CONCLUSIONS

EC of phenolic compounds using Al raschig rings connected together in the form of fixed bed sacrificial anode seems to be a very efficient method for petrochemical wastewater treatment as revealed by the present study. Experimental parameters such as pH, time, current density, electrolyte concentration, initial phenolic compound concentration and temperature were investigated for phenolic compounds removal in batch reactor. Maximum removal of phenolic compounds was attained at pH = 7, NaCl concentration = 1 g/L, current density = 8.59 mA/cm², temperature = 25°C. Increase in the current density and NaCl concentration resulted in an increase in the phenolic compound removal and decrease in COD of the treated solution. Meanwhile, removal efficiency of phenolic compounds decreases and COD of the solution increases with the increase in initial phenolic compound concentration and temperature. It was found that O.N.P has the highest efficiency of removal than phenol and m-cresol while the lowest efficiency of removal was that of hydroquinone. Economy of the process in terms of both energy and electrode consumption, is affected by the operating conditions. Energy consumption and electrode consumption of electrochemical coagulation was found to increase with the increase in current density and NaCl concentration for all phenolic compounds. Energy consumption ranged from 0.066 to 16.32 kWh/g of removed phenol. Comparison of the presented data with the data obtained using other cell designs[72] for phenol removal by EC shows that the present cell design is superior to other designs in every respect especially in the higher separation efficiency, the lower energy consumption and the lower COD. Remarkable removal of 100% of phenol compound after 2 hrs can be achieved for 3 mg/l phenol concentration of real refinery wastewater at the optimum operating conditions.

References

1. P. Kumaran and Y. L. Paruchuri, *Wat. Res.* 31 (1997) 11.
2. R. E. Kirk and D. F. Othmer, *Encyclopedia of chemical toxicology*, 3rd Ed., NY, 1980.
3. G. Buscaa, S. Berardinelli, C. Resini and L. Arrighi, *J.Hazard.Mater.* 160 (2008) 265.
4. K. Shailubhai, *Trends Biotechnol.* 4 (1986) 202.
5. V. Janda and K. Krijt, *Chromatography*, 283 (1984) 309.
6. H.G. Franck and J.W. Stadelhofer, *Industrial aromatic chemistry*, Springer Verlag, Berlin, 1989.
7. D.C. Greminger, G.P. Burns, S. Lynn, D.N. Hanson and C. J. King, *Ind. Eng. Chem. Process Des.* 21(1982) 51.
8. R.S. Juang, H.C. Kao and K.J. Tseng, *Sep. Purif. Techhnol.* 71 (2010) 285.

9. O. Koprivnjak, V. Majetić, M.M. Staver, A. Lovrić and B. Blagović, *Food Chemistry*, 119 (2010) 698.
10. F. Ferri, L. Bertin, A. Scoma, L. Marchetti and F. Fava, *Chem. Eng. J.* 166 (2011) 994.
11. N. Deng, M. Li, L. Zhao, C. Lu, S. L. de Rooy and I. M. Warner, *J. Hazard. Mater.* 192 (2011) 1350.
12. A. Dabrowski, P. Podkoscielny, Z. Hubicki and M. Barczak, *Chemosphere*, 58 (2005) 1049.
13. A. Kumar, S. Kumar, S. Kumar and D. V. Gupta, *J. Hazard. Mater.* 147 (2007) 155.
14. V. Fierro, V. Torne-Fernandez, D. Montane and A. Celzard, *Micropor. Mesopor. Mater.* 111 (2008) 276.
15. Q.S. Liu, T. Zheng, P. Wang, J.P. Jiang and N. Li, *Chem. Eng. J.* 157 (2010) 348.
16. M. H. El-Naas, S. Al-Zuhair and M. Abu Alhaija, *Chem. Eng. J.* 162 (2010) 997.
17. S. Kumar, M. Zafar, J. K. Prajapati, S. Kumar and S. Kannepalli, *J. Hazard. Mater.* 185 (2011) 287.
18. R. I. Yousef, B. El-Eswed and A. H. Al-Muhtaseb, *Chem. Eng. J.* 171 (2011) 1143.
19. J.C. Lazo-Cannata, A. Nieto-Márquez, A. Jacoby, A. L. Paredes-Doig, A. Romero, M. R. Sun-Kou and J. L. Valverde, *Sep. Purif. Technol.* 80 (2011) 217.
20. M. Xiao, J. Zhou, Y. Tan, A. Zhang, Y. Xia and L. Ji, *Desalination*, 195 (2006) 281.
21. M. T. A. Reis, O. M. F. De Freitas, M. R. C. Ismael and J. M. R. Carvalho, *J. Membr. Sci.* 305 (2007) 313.
22. Y.S. Ng, N.S. Jayakumar and M.A. Hashim, *J. Hazard. Mater.* 184 (2010) 255.
23. M. T. A. Reis, O. M.F. Freitas, S. Agarwal, L. M. Ferreira, M. R. C. Ismael, R. Machado and J. M.R. Carvalho, *J. Hazard. Mater.* 192 (2011) 986.
24. C. Zidi, R. Tayeb and M. Dhahbi, *J. Hazard. Mater.* 194 (2011) 62.
25. J. Levec and A. Pintar, *Catal. Today*, 124 (2007) 172.
26. S. Zhao, X. Wang and M. Huo, *Appl. Catal. B: Environ.* 97 (2010) 127.
27. R.R.N. Marques, F. Stüber, K.M. Smith, A. Fabregat, C. Bengoa, J. Font, A. Fortuny, S. Pullket and G.D. Fowler, *Appl. Catal. B: Environ.* 101 (2011) 306.
28. S. Lefèvre, O. Boutin, J-H. Ferrasse, L. Malleret, R. Faucherand and A. Viand, *Chemosphere*, 84 (2011) 1208.
29. G. Chen, *Sep. Purif. Technol.* 38 (2004) 11.
30. D. Rajkumar and K. Palanivelu, *J. Hazard. Mater.* B113 (2004) 123.
31. M. Panizza and G. Cerisola, *Electrochim. Acta*, 51 (2005) 191.
32. M. J. Pacheco, A. Morao, A. Lopes, L. Ciriaco and I. Goncalves, *Electrochim. Acta*, 53 (2007) 629.
33. S. Song, L. Zhan, Z. He, L. Lin, J. Tu, Z. Zhang, J. Chen and L. Xu, *J. Hazard. Mater.* 175 (2010) 614.
34. Y. Yavuz, A. S. Kopalal and Ü. B. Ögütveren, *Desalination*, 258 (2010) 201.
35. J. L. Chen, G. C. Chiou and C. C. Wu, *Desalination*, 264 (2010) 92.
36. X. Zhu, J. Ni, J. Wei, X. Xing, H. Li and Y. Jiang, *J. Hazard. Mater.* 184 (2010) 493.
37. P. Jiang, J. Zhou, A. Zhang and Y. Zhong, *J. Environ. Sci.* 22 (2010) 500.
38. P. Saravanan, K. Pakshirajan and P. Saha, *Bioresour. Technol.* 99 (2008) 205.
39. G. Bayramoğlu and M. Y. Arica, *J. Hazard. Mater.* 156 (2008) 148.
40. M. Shourian, K. A. Noghabi, H. S. Zahiri, T. Bagheri, G. Karballaei, M. Mollaei, I. Rad, S. Ahadi, J. Raheb and H. Abbasi, *Desalination*, 246 (2009) 577.
41. X. Jia, X. Wang, J. Wen, W. Feng and Y. Jiang, *Chem. Eng. J.* 157 (2010) 451.
42. C. R. Ispas, M. T. Ravalli, A. Steere and S. Andreescu, *Water Res.* 44 (2010) 1961.
43. H. Uzun, E. Yildiz and A. Nuhoglu, *Bioresour. Technol.* 101 (2010) 2965.
44. L. Pramparo, F. Stüber, J. Font, A. Fortuny, A. Fabregat and C. Bengoa, *J. Hazard. Mater.* 177 (2010) 990.

45. K. Nazari, N. Esmaili, A. Mahmoudi, H. Rahimi and A.A. Moosavi-Movahedi, *Enzyme Microb. Technol.* 41(2007) 226.
46. M.F. Pouet and A. Grasmick, *Water Sci. Technol.* 31 (1995) 275.
47. J. Zhu, H. Zhao and J. Ni, *Sep. Purif. Technol.* 56 (2007) 184.
48. M. Kobya, E. Demirbas, O.T. Can and M. Bayramoglu, *J. Hazard. Mater.* B132 (2006) 183.
49. A.E. Yilmaz, R. Boncukcuoglu, M.M. Kocakerim and B. Keskinler, *J. Hazard. Mater.* B125 (2005) 160.
50. M. Kobya, E. Demirbas, O.T. Can and M. Bayramoglu, *J. Hazard. Mater.* B132 (2006) 183.
51. M. Bayramoglu, O.T. Can, M. Kobya and M. Sozbir, *Sep. Purif. Technol.* 37 (2004) 117.
52. L. S. Clesceri, A. E. Greenberg and R. R. Trussell, Standard methods for the examination of water and wastewater, 17th Ed., American Public Health Association, American Water Works Association, Water Environment Federation, 1989.
53. N. Adhoum and L. Monser, *Chem. Eng. Process.* 43 (2004) 1281.
54. Z. R. Guo, G. Zhang, J. Fang and X. Dou, *J. Clean. Prod.* 14 (2006) 75.
55. A. K. Golder, A. N. Samanta and S. Ray, *Sep. Purif. Technol.* 53 (2007) 33.
56. W. Phutdhawong, S. Chowwanapoonpohn and D. Buddhasukh, *Anal.Sci.* 16 (2000) 1083.
57. P. Atkins, Physical chemistry, 8th edition, Oxford University Press, 2006.
58. F. Shen, X. Chen, P. Gao and G. Chen, *Chem. Eng. Sci.* 58 (2003) 987.
59. J. Zhu, H. Zhao and J. Ni, *Sep. Purif. Technol.* 56 (2007) 184.
60. X. Chen, G. Chen and P. L. Yue, *Sep. Purif. Technol.* 19 (2000) 65.
61. S. H. Lin, C. T. Shyu and M. C. Sun, *Water Res.* 329 (1998) 1059.
62. K. J. Laidler and J. H. Meister, Physical Chemistry, 3rd edition, Boston, 1999.
63. A. I. Vogel, A textbook of quantitative inorganic analysis, 3rd edition, London, 1961.
64. B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, Textbook of practical organic chemistry, 5th Ed., McGraw Hill, Inc. 1991.
65. K. S. Tewari and N. K. Vishnoi, A text book of organic chemistry, 13th Ed, London, Bailliere, Tinnall, Ltd., 1989.
66. B. S. Bahl, Elementary organic chemistry – A modern approach, S. Chand & Co Ltd., NY, 1983.
67. A. N. Nesmeyanov, Fundamentals of organic chemistry, MIR Publisher, Mosco, 1977.
68. K. Kestioglu, T. Yonar and N. Azbar, *Process Biochem.* 40 (2005) 2409.
69. M. Muruganan, G. Raju and B. Prabhakar, *Sep. Purif. Technol.* 40 (2007) 69.
70. A. Dimoglo, H. Y. Akbulut, F. Cihan and M. Karpuzou, *Clean Techn. Environ. Policy*, 6 (2004) 288.
71. M. Uğurlu, A. Gürses, C. Doğar and M. Yalçın, *J Environ Manag.* 87 (2008) 420.
72. O. Abdelwahab, N. K. Amin and E-S. Z. El-Ashtouky, *J. Hazard. Mater.* 163 (2009) 711.