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Effect of operational parameters on the removal of phenol from aqueous solutions by electrocoagulation using Fe and Al electrodes

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ABSTRACT

The removal of phenol from aqueous solutions in a batch electrocoagulation (EC) process using Fe and Al electrodes was investigated. Experiments were carried out to remove phenol by the EC covering a wide range of operating conditions such as initial pH (4–9), current density (20–80 A/m^2), initial phenol concentration (20–80 mg/L), conductivity (500–1,500 µS/cm), and operating time (0–100 min). The optimum operating conditions were determined as initial pH 7.0, initial concentration of 50 mg/L, current density of 40 A/m^2, operating time of 100 min, and conductivity of 1,200 µS/cm for both electrodes, respectively. The removal efficiencies of phenol at the optimum operating conditions were 98.6% for Fe electrode and 99.2% for Al electrode. The operating cost and consumptions of electrode and energy in the EC process were calculated as 7.4 €/m^3, 3.85 kg/m^3, and 43.27 kWh/m^3 for Fe electrode and 6.1 €/m^3, 1.28 kg/m^3, and 42.18 kWh/m^3 for Al electrode, respectively. The EC process with Al electrode was found to be more efficient than the EC process with Fe electrode in terms of the removal efficiency and operating cost.

Keywords: Electrocoagulation; Phenol removal; Operating cost; Iron electrode; Aluminum electrode

1. Introduction

Phenols are aromatic compounds containing one or more hydroxyl group(s) attached to the aromatic ring. The global phenol production reached 7.8 million tons in 2001 because of increasing industrial activities [1]. Many industries are characteristic sources of phenolic pollutants, including petroleum refining, coke manufacturing, pulp and paper mills, plywood manufacturing, iron and steel manufacturing, synthetic resin manufacturing, leather tanning and finishing, aircraft maintenance, pharmaceuticals, paints, foundry operations, explosives manufacture, fiberglass manufacturing, chemical plants, textile mills operations, plastic, rubber reclamation plants, and mine discharge [2,3]. Phenol compounds are considered as priority pollutants since they are toxic to aquatic life and human beings at low concentrations (5–25 mg/L) and many of them have been classified as hazardous pollutants due to their potential to harm human health [4]. Chronic toxic effects due to phenols reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting, and other mental disturbances [5,6]. Phenol is highly toxic and difficult to degrade biologically which has led to the setting up of rigid limits on the acceptable level of phenol in the environment. Therefore, Environmental Protection Agency (EPA) has set a limit of 0.1 mg/L of phenol in

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wastewater and the World Health Organisation (WHO) recommends the permissible phenolic concentration of 0.001 mg/L in potable waters [7]. In Turkey, the limit for phenols in potable and mineral waters is 0.5 μg/L, which is in agreement with the recommendations of the European Union, while the limits for wastewater emissions are 0.5 mg/L for surface waters and 1 mg/L for the sewerage system [6,8]. Therefore, wastewater containing phenol may not be conducted into open water without treatment because of the toxicity of phenol.

A number of treatment methods such as chemical oxidation with hydrogen peroxide, ozone, etc. [9–11], biological degradation [12], membrane process [13,14], reverse osmosis [15], ion exchange [16], adsorption [17], electrochemical oxidation [18,19], microwave catalytic oxidation [20], and photocatalytic degradation [21,22] have been used for the removal of phenol. The use of biological methods is not suitable because of the refractory chemical nature of phenol [2]. Industrial wastewaters may contain an extremely wide range of phenolic materials. Therefore, the wastewater containing phenol in the range of >500, 5–500, and <5 mg/L may be considered of high, intermediate strength, and dilute wastes, respectively. Activated carbon adsorption treatment yielded an effluent phenol level below 0.1 mg/L. However, a rapid phenol breakthrough in the carbon columns was of concern, relative to process economics such as carbon incinerator and regeneration costs. Phenol concentrations up to 500 mg/L are generally considered suitable for treatment (95–99%) by various biological processes such as activated sludge, trickling filter, lagoons, and oxidation ditches [3].

Electrochemical methods for water/wastewater treatment have attracted great attention in recent years, and offer many distinctive advantages such as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost-effectiveness [23–25]. Toxic organics can be oxidized by the EC with unique features such as simplicity, environmental compatibility, and cost-effectiveness where the flocculating agent is generated by electrooxidation of sacrificial anode, generally made up of iron and aluminum. Compared with traditional chemical coagulation, the EC has 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 in motion and also the advantages of producing a relatively low amount and toxicity of sludge [26,27]. The mechanism of the EC process is as follows:

$$\text{At the anode}: \quad M \rightarrow M^{n+} + ne^- \tag{1}$$

$$\text{At the cathode}: \quad nH_2O + ne^- \rightarrow \frac{n}{2}H_2 + nOH^- \tag{2}$$

where M is the anode material (A1 and Fe) and n is the number of electrons involved in the oxidation/reduction reaction. The soluble metal ions are generated at the anode and react with the hydroxide ions formed at the cathode, and the metal hydroxides are produced shown in Eq. (3). These insoluble metal hydroxides react with the suspended and/or colloidal solids and precipitate.

$$M^{n+} + nOH^- \rightarrow M(OH)_{n(s)} \tag{3}$$

M^{n+} and OH^- ions generated by electrode reactions (1) and (2) react to form various hydroxo monomeric and polymeric species, depending on the pH range, which transform finally into $M(OH)_{n(s)}$ according to complex precipitation kinetics. Freshly formed amorphous $M(OH)_{n(s)}$ "sweep flocs" have large surface areas, which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. These flocs polymerize further as $M(OH)_{n(s)}$ and are easily removed from aqueous medium by sedimentation and flotation. Ferric ions generated by the electrochemical oxidation of iron electrode may form monomeric species, $Fe(OH)_3$, and polymeric hydroxyl complexes namely, $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $Fe(OH)_4^-$, $Fe(H_2O)_2^+$, $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe_2(H_2O)_8(OH)_2^{4+}$, and $Fe_2(H_2O)_6(OH)_4^{2+}$, depending on the pH of the aqueous medium. These hydroxides/polyhydroxides/polyhydroxyoxide metallic compounds have strong affinity for dispersed particles as well as counterions to cause coagulation [28]. Al^{3+} and hydroxyl ions generated by electrode reactions form various monomeric–polymeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, $Al_2(OH)_2^{4+}$, $Al_6(OH)_{15}^{9+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$ transformed initially into $Al(OH)_{3(s)}$ and finally polymerized to $Al(OH)_3$ in the solution [29]. The metal cathode may be chemically attacked by OH^- ions especially at high pH values:

$$2M + 6H_2O + 2OH^- \rightarrow 2M(OH)_4^- + 3H_2 \tag{4}$$

If the anode potential is sufficiently high, the electrochemical discharge of chlorine at the anode as secondary electrochemical reactions may also occur such as direct oxidation of organic compounds and Cl^- ions present in wastewater [28]

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad \text{(oxidation)} \tag{5}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^- + Cl^- \quad \text{(bulk of solution)} \tag{6}$$

During electrocoagulation in the presence of NaCl, the formation of hypochlorite (OCl^-) and hypochlorous acid (HOCl) is possible at around neutral pH.

Several works relating to the removal of phenol from water/wastewater by the EC process have been reported in the literature. The possibility of EC was applied to remove the phenol from oil refinery waste effluent by horizontally oriented Al electrodes and obtained a removal efficiency of 94.5% at 23.6 A/m^2, 2,000 mg/L NaCl, 120 min, and pH 7 [30]. The removal of polyphenols from black liquor by EC using Al electrodes was obtained for a removal efficiency of 92% at pH 7, 14 A/m^2, and 50 min [31]. The phenol removal from paper mill effluents with EC was 98% for Al and 93% for Fe electrodes at 4.8 A/m^2 and 7.5 min [32]. The phenol removal from aqueous solutions by EC using combinations of anode/cathode electrodes (steel 310/steel 304, steel 310/Al, Fe/steel 304, Fe/Al, steel 310/graphite, and Fe/graphite) was >95% at 100 A/m^2, 10 min, 300 mg/L NaCl, and pH 9 [33]. An olive mill wastewater was treated by the EC process using Al electrodes and obtained a polyphenol removal efficiency of 91% at pH 4–6, 75 A/m^2 and 25 min [34]. The phenolic compound catechin from aqueous solutions by EC using Al electrodes was evaluated and obtained a removal efficiency above 90% at pH 8, 3.825 A/m^2, 60 min, and 200 mmol/L NaCl [35].

In the present work, the removal of phenol from aqueous solutions was investigated using vertically oriented parallel plate, Fe and Al electrodes. The effects of operating parameters such as initial pH, current density, operating time, initial phenol concentration, and conductivity of solution on the removal efficiency were investigated to determine the optimum operating conditions. The operating costs for the EC process were also calculated.

2. Materials and methods

2.1. Materials

Phenol (C_6H_5OH) of analytical reagent grade (Merck, 99.99%) was used for the preparation of the synthetic phenol solutions of various initial concentrations (C_0) in the range of 20–80 mg/L. The required quantity of phenol was accurately weighed and dissolved in distilled water. Fresh stock solution as required was prepared every day and was stored in a brown-colored glass reservoir. The C_0 was ascertained before the start of each experimental run.

2.2. Experimental setup and procedure

The experimental setup for the EC reactor was reported elsewhere [28,29]. The EC experiments were carried out in a batch mode using a 350 mL plexiglass reactor (100 mm × 70 mm × 50 mm) using vertically positioned Fe/Al electrodes spaced by 11 mm and dipped in a phenol solution. Two anodes and two cathodes with dimensions of 50 mm × 50 mm × 2 mm made of iron (Fe: 99.5% purity) and aluminum (Al: 99.3% purity) plates were connected to a digital DC power supply (Agilent, 6675A model) in monopolar parallel connection mode. The total effective electrode area was 150 cm^2. The phenol solution in the reactor was mixed at 300 rpm with a magnetic stirrer (Heidolp, 3600D model) to reduce the mass transport over potential of the EC reactor.

The phenol solutions were prepared using distilled water. The pH and conductivity of solutions before and after the EC process were measured by a pH meter (Mettler Toledo 2050e) and a conductivity meter (Mettler Toledo 7100e). The pH of the solutions was adjusted by adding either 0.10 N NaOH or 0.10 N HCl. The conductivity of the solutions was adjusted with NaCl to a desired value. In each run, 275 mL of phenol solution was dropped into the EC reactor and then the current density was adjusted to a desired value by a digital DC power supply and the experimental operation was started. In order to determine the phenol removal efficiencies, the samples were periodically taken from the reactor during the EC process and filtered through 0.45 µm membrane filters before analysis. After each experimental run, the electrodes were dipped into solutions of HCl (35%) and hexamethylenetetramine (2.8%) to remove the oxide and/or passivation layers from the electrodes [28]. The electrode surfaces were rinsed several times with deionized water, dried, and weighted before and after each experiment. All experiments were performed at 25°C.

2.3. Analytical measurements

The concentration of phenol by the 4-aminoantipyrene method was determined using a double-beam UV–vis spectrophotometer (PerkinElmer, Lamda 35) at $\lambda_{max} = 500$ nm [36]. All experiments were conducted in triplicate, and the averages of the results were submitted for data analysis. The removal efficiency (R_e) of phenol in the EC process was calculated with the following equation:

$$R_e(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{7}$$

where C_0 (mg/L) and C_t (mg/L) are the concentrations of phenol in aqueous solution at initial stage and at time, t_{EC} (min), respectively.

The operating cost for the EC process includes materials, mainly electrodes and electrical energy costs, as well as labor, maintenance, sludge dewatering and disposal, and fixed costs. The latter cost items are largely independent of the type of the electrode material [37]. In this study, energy and electrode material costs were taken into account as major cost items in the calculation of the operating cost for the EC process as €/m^3:

$$\text{Operating cost (OC)} = aC_{\text{energy}} + bC_{\text{electrode}} + cC_{\text{chemical}} \tag{8}$$

where C_{energy} (kWh/m^3) and $C_{\text{electrode}}$ (kg/m^3) are the consumption quantities for phenol removal, obtained experimentally. *"a"* and *"b"* given for the Turkish market in December 2011 are as follows: *"a"* is the electrical energy price (0.095 €/kWh), *"b"* is the electrode material price (0.85 €/kg for Fe and 1.65 €/kg for Al), and *"c"* denotes the chemical consumption (C_{chemical}) prices of compounds such as NaOH (0.73 €/kg), H_2SO_4 (0.29 €/kg), and NaCl (0.10 €/kg), respectively. The electrical energy and electrode consumptions are calculated using Eqs. (9) and (10)

$$C_{\text{energy}}\ (\text{kWh/m}^3) = \frac{U \cdot I \cdot t_{EC}}{v} \tag{9}$$

$$C_{\text{electrode}}\ (\text{kg/m}^3) = \frac{I \cdot t_{EC} \cdot M_w}{z \cdot F \cdot v} \tag{10}$$

where U is the cell voltage (V), I is the current (A), t_{EC} is the operating time (s) and v is the volume (m^3) of the wastewater, M_w is the molecular mass: iron (55.85 g/mol) and aluminum (26.98 g/mol), z is the number of electrons transferred ($z_{Fe} = 2$, $z_{Al} = 3$), and F is Faraday's constant (96,487 C/mol).

3. Results and discussion

3.1. *Influence of initial pH*

The initial pH is an important parameter in determining the performance of the EC process. The effect of the initial pH 4–9 on phenol removal using iron and aluminum electrodes was investigated under constant operating conditions (40 A/m^2, 50 mg/L, and 1,200 μS/cm). Fig. 1a shows that the maximum removal of phenol for Fe and Al electrodes took place in the pH range of 6–8. As seen in Fig. 1a, the maximum phenol removal efficiencies were 98.6% for Fe electrode and 99.2% for Al electrode at pH 7, but significant reductions in removal efficiencies were observed at pH < 6 and >8. This reduction can be explained by the chemical species associated with the aqueous pH as presented in Fig. 1. At pH values below 4.5, the M^{n+} ion (Fe^{2+} or Al^{3+}) is the predominant species. However, at pH values of 4.5–9.5, the predominant metal chemical species is $M(OH)_{n(s)}$ such as $Fe(OH)_{3(s)}$ and $Al(OH)_{3(s)}$ in Eq. (3). In fact, at initial pH 6–8 of solution for both electrodes, the polymeric-metal complexes generated during the EC process were capable of attracting the charge of organic polluting species such as phenol and remove them from solution by destabilization and adsorption

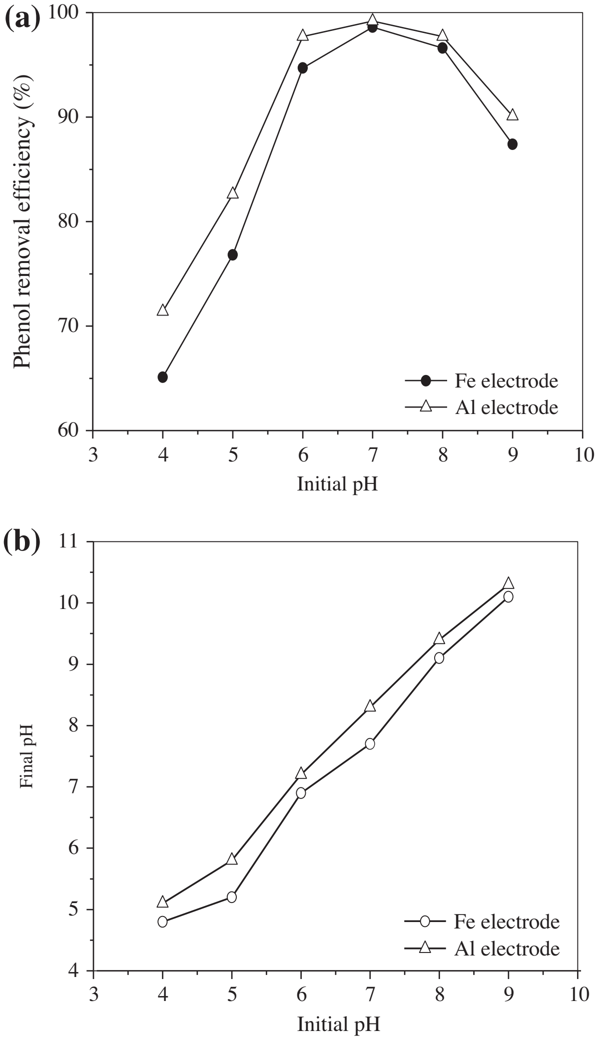

Fig. 1. (a) Effect of initial pH on the removal of phenol from aqueous solutions and (b) changes in initial pHs (conditions: Current density of 40 A/m^2, initial phenol concentration of 50 mg/L, and conductivity of 1,200 μS/cm).

on the surface of metallic hydroxides such as $Fe(OH)_{3(s)}$ and $Al(OH)_{3(s)}$. Monomeric/polymeric-metal species and $M(OH)_{3(s}$ between pH 4 and 9 and $M(OH)_4^-$ in pH > 9.5 were formed during the EC process. The formed $M(OH)_{3(s)}$ (sweep flocs) flocs had a large specific surface area that can absorb some soluble organic compounds (OCs) onto its surface [28]. Monomeric and polymeric-metal species are explained in Eqs. (11)–(15) with respect to change in pH values:
Charge neutralization and precipitation:

$$\mathrm{OCs} + \mathrm{Monomoric} - \mathrm{M} \rightarrow (\mathrm{OCs}\ - \mathrm{Monomoric} - \mathrm{M})_{(s)} \quad (\mathrm{pH}\ 4\text{–}6) \tag{11}$$

$$\mathrm{OCs} + \mathrm{Polymeric} - \mathrm{M} \rightarrow (\mathrm{OCs} - \mathrm{Polymeric} - \mathrm{M})_{(s)} \quad (\mathrm{pH}\ 6\text{–}7.5) \tag{12}$$

Adsorption and sweep coagulation (pH > 6.5–7.5):

$$\mathrm{OCs} + \mathrm{M(OH)}_{3(s)} \rightarrow (\mathrm{OCs} - \mathrm{M(OH)}_{3(S)}) + \mathrm{M(OH)}_{3(S)} \tag{13}$$

$$\mathrm{OCs} + \mathrm{M(OH)}_{3(S)} \rightarrow (\mathrm{OCs} - \mathrm{Polymeric} - \mathrm{M})_{(S)} + \mathrm{M(OH)}_{3(S)} \tag{14}$$

$$\mathrm{OCs} + \mathrm{M(OH)}_{3(S)} \rightarrow \mathrm{OCs} - \mathrm{Polymeric} - \mathrm{M} - (\mathrm{M(OH)}_{3(s)} + \mathrm{M(OH)}_{3(s)} \tag{15}$$

Hence, the removal efficiencies of phenol were maximal at a pH interval of 6–8. Several authors have reported that during EC, the organic pollutants could be removed by surface complexation or electrostatic attraction. However, it is interesting to note that, at pH values $\geqslant 9.5$, $M(OH)_4^-$ was formed. Fig. 1(b) shows the variation of the final pH with the initial pH. There was an increase in the final pH value after the phenol removal. This effect was important once the experimental pH increased during the EC mainly due to the production of hydroxide ions at the cathode (Eq. (2)). When the initial pH value was 7, the final pH values for Fe and Al electrodes were 7.7 and 8.3, respectively. As the initial pH values increased to 6–8, the final pH values were changed to 6.9–9.1 for Fe electrode and 7.2–9.4 for Al electrode in the EC reactor. The results revealed that the phenol removal was more efficient for the final pH between 6 and 8. This aspect could be primarily attributed to the formation of metal hydroxides in these final pH values. In addition, a higher phenol removal was reported in the literature at pH close to neutral [33–35]. Therefore, the phenol removal efficiency was maximal at final pH interval 7.7–8.3 for both electrodes and pH 7 was taken as the optimum initial pH for all subsequent EC experiments.

3.2. Effect of current density

It is well known that the current density determines the production rate of coagulant (amount of Al^{3+} or Fe^{2+} ions released by the anode), also adjusts bubble production, its size and distribution, and hence affects the growth of flocs ($Al(OH)_{3(s)}$, $Fe(OH)_{2(s)}$, or $Fe(OH)_{3(s)}$ coagulate particles) in the EC process [38]. Batch EC experiments were carried out for different current densities at constant operating conditions (initial pH 7, 50 mg/L, and 1,200 μS/cm).and the results are shown in the Fig. 2 for both electrodes.

Fig. 2 shows that the phenol concentration in the solution decreased with increase in operating time. It was found that the maximum removal efficiencies of phenol at operating time of 100 min for current densities of 20, 40, 60, and 80 A/m^2 or as charge loadings of 67.84, 135.68, 203.51, and 271.35 Faradays/m^3 were obtained as 90.6, 98.6, 98.8, and 99.1% for Fe electrode and 92.4, 99.2, 99.3, and 99.9% for Al electrode, respectively. The residual phenol concentrations at 40 A/m^2 (135.68 Faradays/m^3), 100 min of operating time, and initial phenol concentrations of 50 mg/L were 0.7 mg/L for Fe electrode and 0.4 mg/L for Al electrode, respectively. It is seen from the figure that the removal efficiencies of phenol for both electrodes slightly increased from about 90 to 98% by increasing the charge loading from 67.84 Faradays/m^3 (20 A/m^2) to 271.35 Faradays/m^3 (80 A/m^2). The optimum charge loading should be 135.68 Faradays/m^3 (40 A/m^2) for both electrodes. Over the optimum values there was a slight improvement in the removal of phenol with increment of charge loading, which resulted from electrochemical oxidation. Current density or charge loading is the most important parameter for controlling the reaction rate in most electrochemical processes, because it determines the coagulant dosage within the EC process [39]. The charge loading is defined as the charges transferred in electrochemical reactions for a given amount of water treated. According to Faraday's law, the amount of iron and aluminum dissolved electrochemically from anode electrodes is proportional to the charge loading. The quality of the EC effluent depends on the amount of coagulant produced (mg) or the applied charge loading. When 1 Faraday of charge passes through the circuit, 9.0 g of aluminum or 28 g of iron is dissolved at each anode in the EC process. When the charge loading was low, iron or aluminum

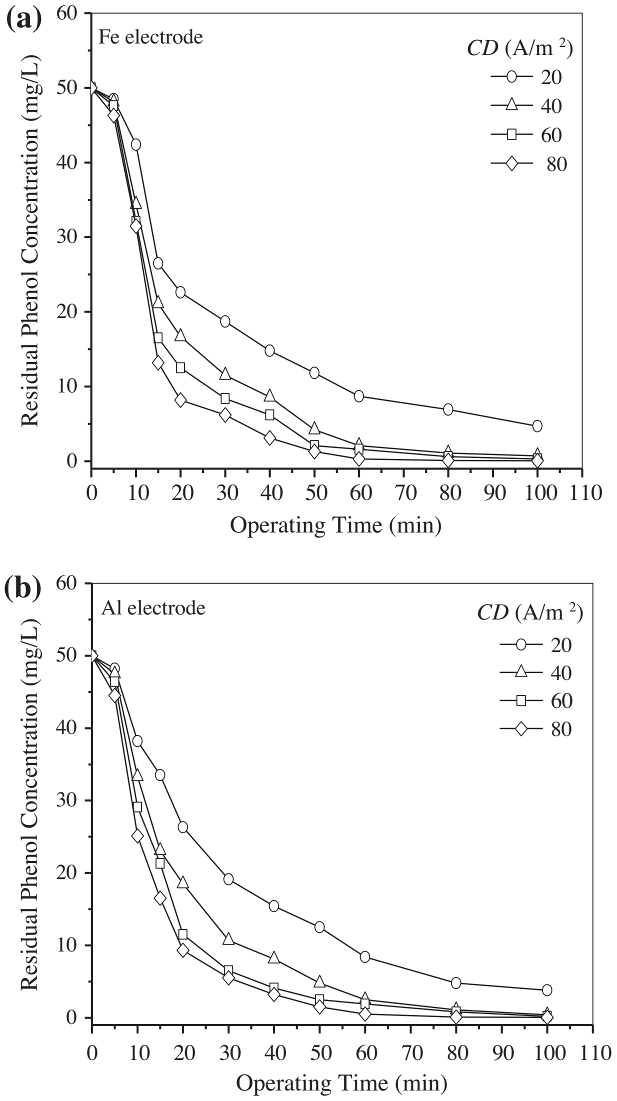

Fig. 2. Effect of current density on the removal of phenol from aqueous solutions (conditions: initial phenol concentration of 50 mg/L, initial pH 7, and conductivity of 1,200 μS/cm).

dose (Al^{3+} or Fe^{2+}) was not sufficient. In that case, only a small amount of $Fe(OH)_3$ or $Al(OH)_3$ flocs was formed, which could not adsorb the phenol effectively. As the charge loading increased, iron or aluminum dose increased accordingly. In such a case, more $Me(OH)_3$ flocs were formed, which could adsorb more phenol. As a result, the effluent phenol concentration in the EC process decreased.

In any EC process, current density and operating time are important operational parameters setting for the ultimate removal and defining the electrical energy and power consumption. The energy consumptions were found to be 21.82–87.33 kWh/m^3 for Fe electrode and 20.80–86.25 kWh/m^3 for Al electrode when the current density was in the range of 20–80 A/m^2. The electrode consumptions were calculated as 1.91–7.60 kg/m^3 for Fe electrode and 0.62–2.45 kg/m^3 for Al electrode, respectively. The operating cost values and amount of sludge produced at 20–80 A/m^2 were 3.7–10.6 €/m^3 and 1.17–1.76 kg/m^3 for Fe electrode and 5.1–8.1 €/m^3 and 1.29–1.88 kg/m^3 for Al electrode, respectively.

3.3. Effect of initial phenol concentration

Phenol solutions with different initial concentrations in 20, 50 and 80 mg/L were treated by the EC process using Fe and Al electrodes at constant operating conditions (40 A/m^2, initial pH 7, and 1,200 μS/cm). As shown in Fig. 3, the phenol removal efficiency gradually decreased with an increase in the initial phenol concentration for both electrodes. At 100 min of operating time, the residual phenol concentrations in the solution were 0.10 mg/L (99.5%), 0.70 mg/L (98.6%), and 2.5 mg/L (96.9%) for Fe electrode and 0.50 mg/L (98.1%), 0.4 mg/L (99.2%), and 6.9 mg/L (91.4%) mg/L for Al electrodes at initial phenol concentrations of 20, 50, and 80 mg/L, respectively. The experiments performed at lower C_0 showed a higher initial removal efficiency compared to experiments performed at higher C_0. It is quite clear that under the present experimental conditions, the lower phenol concentrations resulted in better phenol removal efficiencies.

Therefore, the amount of iron or aluminum hydroxide produced at higher C_0 was not enough to remove all the phenol molecules causing a slight decrease in the phenol removal efficiency. The phenol from aqueous solutions onto these metallic hydroxide flocs was adsorbed and the adsorption capacity of flocs was limited at higher phenol concentrations. In addition, at higher C_0, $Al(OH)_3$ or $Fe(OH)_3$ that formed near the surface fouls the electrodes and intermediate products formed in the solution, which blocked the electrode active sites. Both of these factors decreased the phenol removal efficiency. According to these results, Fe electrode was found to be slightly more effective than Al electrode.

The electrode consumptions at 100 min of operating time were increased from 3.82 to 3.87 kg/m^3 for Fe electrode and from 1.24 to 1.31 kg/m^3 for Al electrode at initial phenol concentration of 20–80 mg/L, respectively, and the electrode consumptions were not much affected by the changes in C_0. On the other hand, the energy consumptions per m^3 of treated phenol solution were calculated as 40.15, 43.27, and

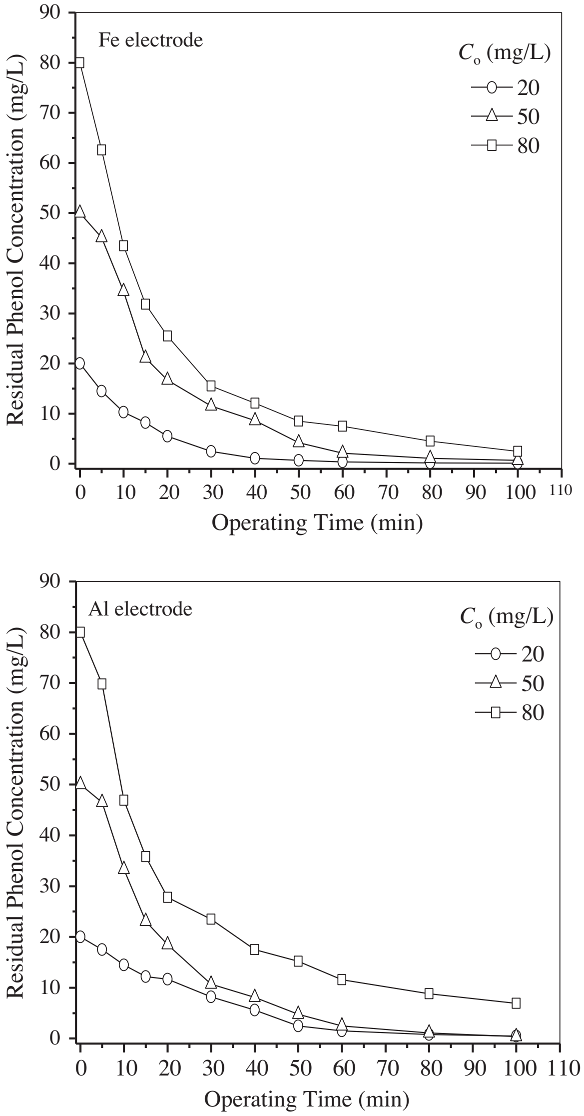

Fig. 3. Effect of initial phenol concentration on the removal of phenol from aqueous solutions (conditions: Current density of 40 A/m^2, initial pH 7, and conductivity of 1,200 μS/cm).

44.53 kWh/m^3 for Fe electrode and 41.20, 42.18, and 43.85 kWh/m^3 for Al electrode at 20, 50, and 80 mg/L of initial phenol concentrations, respectively. The operating cost values and amount of sludge produced in the EC process at 20–80 mg/L were changed from 7.1 to 7.5 €/m^3 and from 1.22 to 1.72 kg/m^3 for Fe electrode and from 6.0 to 6.3 €/m^3 and from 1.19 to 1.65 kg/m^3 for Al electrode.

3.4. *Effect of conductivity on removal of phenol*

Solution conductivity affects current efficiency, cell voltage, and consumption of electrical energy in electrolytic cells since the current passing through the circuit is a function of the conductivity under a certain applied voltage [40]. The most common method used to overcome this problem is to add a small amount of electrolyte, which increases the electric conductivity of the solution and thus reduces the energy consumption during the EC process [41]. In this study, NaCl was used as a supporting electrolyte for increasing the conductivity in aqueous solutions. In addition, increasing solution conductivity with NaCl has some advantages; chloride ions could significantly reduce the adverse effects of other anions such as bicarbonate and sulphate [42]. These steps taken will increase the ohmic resistance of the electrochemical cell. Meanwhile, if the anode potential is sufficiently high, other reactions may take place at the anode such as direct oxidation of organic compounds or H_2O. The effect of conductivity of aqueous phenol solutions was studied in the range of 500–1,500 μS/cm at 40 A/m^2, initial pH 7.0, and 50 mg/L. The experimental results in Fig. 4 showed that the phenol removal efficiency at an operating time of 100 min was ascertained to increase from 90.4 to 99.8% for Fe electrode and from 86.2 to 99.4% for Al electrode as the conductivity varied between 500 and 1,500 μS/cm.

At a given current density of 40 A/m^2, the average potentials at 500, 800, 1,200, and 1,500 μS/cm were 21.8, 16.3, 11.9, and 11.8 V for Fe electrode and 20.3, 14.8, 11.6, and 11.4 for Al electrodes, respectively. Thus, the energy and electrode consumptions at conductivity 500–1,500 μS/cm were calculated as 79.30–42.90 kWh/m^3 and 3.92–3.78 kg/m^3 for Fe electrode and 73.82–41.45 kWh/m^3 and 1.31–1.24 kg/m^3 for Al electrode. The amount of sludge produced at 500–1,500 μS/cm increased from 1.24 to 1.60 kg/m^3 for Fe electrode and from 1.32 to 1.65 kg/m^3 for Al electrode. This showed the economic importance of the presence of NaCl. Therefore, the EC process in the presence of NaCl improved the removal efficiency of phenol by increasing the available metal coagulant in the solution due to reduction of the oxide layer and enhancement of anodic dissolution of the electrode materials. In addition, the problem of electrode passivation was partially solved when NaCl was used as the supporting electrolyte. According to the results, high phenol removal efficiency with low cell voltages and low energy consumption can be obtained in phenol solutions with a conductivity of around 1,200 μS/cm. The increased solution conductivity resulted in the reduction of cell voltages that caused a decrease in electrical energy consumption. As a result, operating cost for both electrode materials decreased with increasing conductivity. In this study, the optimum conductivity was selected as 1,200 μS/cm value.

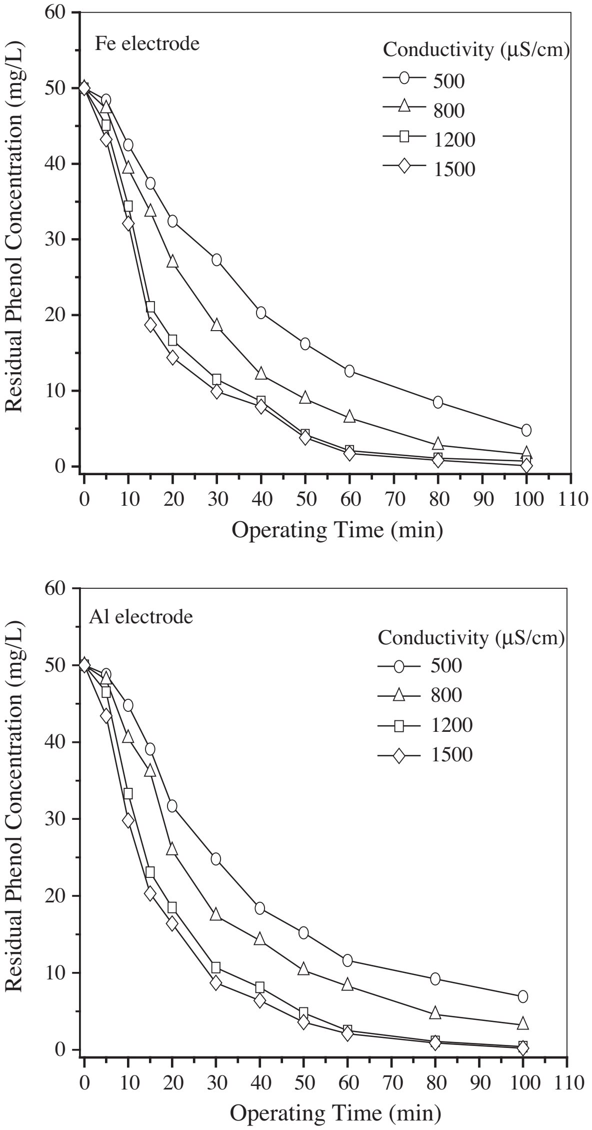

Fig. 4. Effect of conductivity on the removal of phenol from aqueous solutions (conditions: Current density of 40 A/m^2, initial pH 7, and initial phenol concentration of 50 mg/L).

4. Conclusions

Batch EC studies were performed to evaluate the influence of various experimental parameters such as initial pH, current density, electrolysis time, initial phenol concentration, and conductivity on the removal of phenol in aqueous solutions. The experimental results showed that the removal efficiencies of 98.6% for Fe and 99.2% for Al electrodes were achieved at an operating time of 100 min, initial pH 7, current density of 40 A/m^2 (135.68 Faradays/m^3), initial concentration of 50 mg/L, and conductivity of 1,200 μS/cm. The EC process was able to decrease the residual phenol concentration to <10 μg/L. The operating costs at the optimum operating conditions were calculated as 7.4 €/m^3 for Fe and 6.1 €/m^3 for Al electrodes. The experimental results indicated that Al electrodes were more effective than Fe electrodes in terms of phenol removal efficiency and operating cost. In comparison to conventional treatment processes, the present method was more effective and showed a faster removal of phenol. It can be concluded that the EC is an effective alternative process for the removal of phenol.

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