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Treatment of phenol-formaldehyde resin manufacturing wastewater by the electrocoagulation process

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ABSTRACT

The removal of total organic carbon (TOC) from wastewater generated from phenol-formaldehyde resin manufacturing industry using the electrocoagulation process was studied in this paper. Experiments were carried out at current densities of 5.0, 7.5 and 10.0 mA/cm^2 using iron electrodes connected in parallel arrangement in an undivided electrochemical reactor. TOC content was determined during the different stages of electrolysis in order to know the feasibility of the electrocoagulation treatment for highly concentrated bio-refractory organic pollutants present in the industrial wastewater. Different operational conditions such as pH, time, and electrical conductivity were studied for TOC removal. Experimental values indicated that the electrocoagulation process showed high TOC removal efficiencies, 78.7% within 60 min of electrolysis, with an initial concentration of 23.8×10^3 mg/l TOC. Thus, these results showed that the electrocoagulation process is effective for the removal of initially high TOC content and may be used as pretreatment of industrial real effluents.

Keywords: Electrocoagulation; Energy consumption; Iron electrodes; Resin manufacturing; Phenol wastewater; Total organic carbon

1. Introduction

Nowadays the number, variety, and composition of synthetic chemical compounds have increased tremendously and their use has influenced every aspect of modern life. A particularly widespread group of chemical compounds are phenolic resins (phenol-formaldehyde resins or Bakelite) which have been reported to have a high stability and high environmental toxicity with additionally carcinogenic properties and so can damage human health [1]. These phenol-formaldehyde resin producing industries generate wastewater with high concentration of organic matter (40×10^3 mg/l of chemical oxygen demand and between 2×10^4 to 3×10^4 mg/l total organic carbon (TOC). Such wastewaters are difficult to be treated by biological processes when the phenol is present at high concentration because it causes inhibition to the normal function of microbial population [2]. At present, these residues are diluted before been discharged to a biological water treatment or are incinerated [3]. This situation demands clean water and pollutes both water bodies and the atmospheric air which affects strongly the life of the environment. Several methods have been used to

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treat wastewater containing phenol and formaldehyde compounds [1–7]. Amongst these methods, the electrochemical processes are alternative treatment methods for partial or total degradation of toxic organic substances. Rajkumar and Palanivelu treated phenolic compounds by electrochemical method using $Ti/TiO_2–RuO_2–IrO_2$ electrode in an undivided reactor. These authors found that the electrochemical process proved to be effective for the treatment of highly concentrated bio-refractory organic pollutants present in the industrial wastewater [4]. Luenloi et al. studied the kinetics for the photodegradation of phenol catalyzed by TiO_2 coated on acrylic sheets [5]. These authors also reported that several parameters (the number of TiO_2-coated acrylic sheets, initial phenol concentration, hydrogen peroxide concentration and UV light power) affected the apparent reaction rate constant of phenol photodegradation and found that 97.1% efficiency can be attained with three photodegradation stages. Tahar and Savall tested doped bismuth lead dioxide anodes for the oxidation of phenol in aqueous solution and found that the phenol degradation was more efficiently carried out on a PbO_2 anode doped with perchlorate and with bismuth than on the same electrode doped only with perchlorate [6]. Katal and Pahlavanzadeh studied the influence of different combinations of aluminum and iron electrode on the electrocoagulation efficiency on the treatment of paper mill wastewater; they found that an increase in the current the speed of the treatment enhanced significantly, but simultaneous increase of electrode and energy consumption was observed [7]. The electrocoagulation process (EC) is an attractive method for the treatment of various kinds of wastewater, by virtue of various benefits including environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness. EC consists of three successive stages: (a) creation of coagulants by electrolytic oxidation of the 'sacrificial electrode'; (b) destabilization of the pollutants, suspended particulates, and breaking of suspensions; (c) agglomeration of the destabilized phases to form flocks of metallic hydroxides within the effluent to be cleaned, by electrodissolution of soluble anodes. The cell reaction, using an iron anode, is given by Eq. (1):

$$2Fe_{(s)} + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_{2(g)} \quad (1)$$

With $Fe(OH)_3$ formation in which the pollutants (phenol and formaldehyde) may co-precipitate or adsorb:

$$Fe(OH)_{3(solid)} + pollutant_{(aqueous)} \rightarrow [Fe(OH)_3\ \ pollutant -] \atop (solid) \quad (2)$$

Advantages of electrocoagulation technology consist of: removing the smallest colloidal particles, producing relatively low amount of sludge. Requiring the simple equipment and easy to operate, formation readily sludge settable and easy to de-water, producing effluent with less total dissolved solids (TDS) content as comparison with chemical treatments. Generation the gas bubbles during electrolysis that caring the pollutant to the top of the solution where it can be more easily concentrated, collected and removed [8–10]. In recent years, although there has been a lot of works on the wastewater treatment by electrochemical treatment methods, but very few researchers have made an effort to treat real industrial wastewater using these methods [11–13]. The aim of this study was to investigate the removal of TOC from phenol-formaldehyde resin manufacturing wastewater by electrocoagulation using Fe electrodes. In this work the influence of current density, pH and electrical conductivity was studied.

2. Experimental

2.1. Chemicals

All solutions were prepared with distilled water using sulfuric acid, sodium chloride, sodium hydroxide, hydrochloride acid. Chemicals were purchased from Merck and used as received without further purification.

2.2. Collection of wastewater samples

The industrial wastewater was collected and preserved according to standard procedure from a phenol-formaldehyde resin manufacturing industry, Ghazvin, Iran [14]. The sampled wastewater was stored in plastic containers at 4°C.

2.3. Electrocoagulation experiments (EC)

The electrocoagulation treatment for TOC removal from the industrial wastewater was carried out using a reactor made up of an electrolytic cell with a pair of iron anodes and a pair of iron cathodes in parallel arrangement of 1.5 l capacity (Plexiglas rectangular cell, $15 \times 10 \times 15\ cm^3$). The distance between the electrodes was 15 mm and the effective area of each electrode was 150 cm^2. The electrodes were carefully rinsed with HCl solution (15% wt.) for cleaning prior to use, and connected to a DC power supply (0–40 V, 0–3 A). The current density studied was inside the range of 5 to 10 mA/cm^2. The electrodes were replaced each time when more than 20% of the electrode material was missed. The weight of the iron electrodes was recorded (when they were freshly prepared and after each electrolysis) at room temperature after drying them at 70°C and kept in a glass desiccator overnight. For each run one liter of sample was placed into the

EC cell. EC experiments were carried out for 60 min and samples were collected at regular time intervals for pH (4, 7 and 10) and TOC analyses. The pH was adjusted to the desired value with sodium hydroxide. The conductivity values employed were 1.54 and 3.00 mS/cm. The pH and the conductivity measurements were carried out using a Precision pH-Conductivity Meter Metrohm 827 pH lab, Switzerland. TOC analyses were performed (using Shimadzu, V-CSH TOC analyzer) after the samples were filtered (using a 0.45 µm filter) and acidified with 0.1 mol/l HNO_3 solution.

3. Results and discussion

3.1. Characterization of the industrial wastewater

The wastewater from the phenol-formaldehyde resin manufacturing plant has a mildly acidic condition (pH 4) with high content of TOC (23.8×10^3 mg/l). Also, the wastewater exhibits relatively low conductivity (1.54 mS/cm) and low total dissolved solids (TDS = 7.7×10^2 mg/l). The concentration of phenol and formaldehyde present in the wastewater was not determined; however, according to Araña et al. the phenol-formaldehyde resin preparation generates residues containing between 6×10^2 to 2×10^3 mg/l of phenol and between 5×10^2 to 1.3×10^3 mg/l of formaldehyde [3].

3.2. Removal of TOC under different conditions

3.2.1. Current density

The removal of TOC was investigated using different current densities under its natural pH and conductivity. Fig. 1 shows that the rate of TOC removal increases by increasing the current density during the electrolyses carried out under the natural pH and conductivity of the industrial wastewater. TOC abatements of 49, 70 and 76% were achieved at 60 min of electrolysis with current densities of 5.0, 7.5 and 10.0 mA/cm^2 respectively. This behavior is explained by the fact that with increasing the current density, the amount of Fe^{2+} species formed by anode dissolution increases. Higher electrocoagulation efficiency and more significant destabilization of the emulsion result in higher amount of dissolved Fe. Furthermore, higher generation of hydrogen allowed by higher currents helps the flotation of the flocculation matter [15]. The theoretical iron dosing during the electrocoagulation was obtained by using the Faraday's law (Eq. 3) that describes the relationship between current density and the amount of iron that goes into solution:

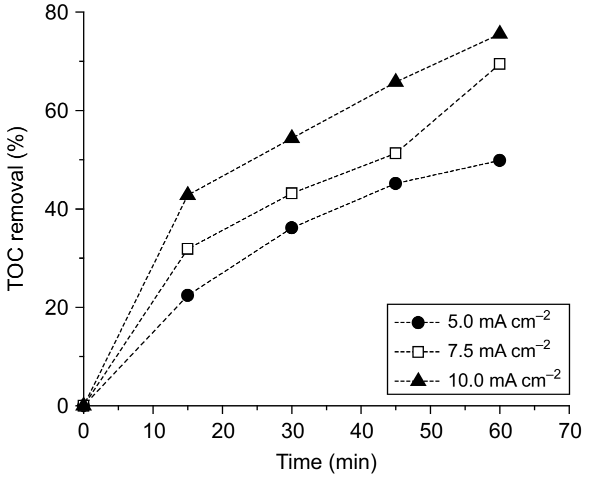

Fig. 1. Effect of current density on TOC removal at initial TOC of 23.8×10^3 mg/l under its natural pH (4), and conductivity (1.54 mS/cm).

$$w = \frac{ItM}{zF} \tag{3}$$

with w = iron dissolved (g Fe cm^{-2}), I = current density (A/cm^2), t = time (s), M = molecular weight of Fe (M = 55.84 g/mol), z = number of electrons involved in the oxidation/reduction reaction (n = 2) and F = Faraday's constant (96487 C/mol). It was calculated that 7.8×10^{-3} and $10.4 \text{x} 10^{-3}$ g Fe/cm^2 are put in solution at 60 min of electrolysis for the removal of 70% and 76% of TOC using 7.5 and 10 mA/cm^2 of current densities, respectively. Thus, it seems that the use of 7.5 mA/cm^2 of current density adds less electrolytic iron in the solution achieving good degree of mineralization and less electrical energy consumption. It is also observed that the TOC removal rate followed a first order kinetics as shown in Table 1.

3.2.2. Different initial pH value

It has been found that initial pH is an important operating factor that influences the performance of the electrocoagulation process [16–18]. The effect of the initial pH values (4, 7 and 10) on the electrocoagulation efficiency of the industrial wastewater was studied employing a constant current density of 7.5 mA/cm^2 at its natural electrical conductivity. Fig. 2 shows the variation

Table 1
Effect of applied current density on TOC abatement rates at 60 min of electrocoagulation

Current density (mA/cm^2)	TOC removal (%)	k_{TOC} (min^{-1})	R^2
5	49	1.15×10^{-2}	0.968
7.5	70	1.80×10^{-2}	0.963
10	76	2.22×10^{-2}	0.976

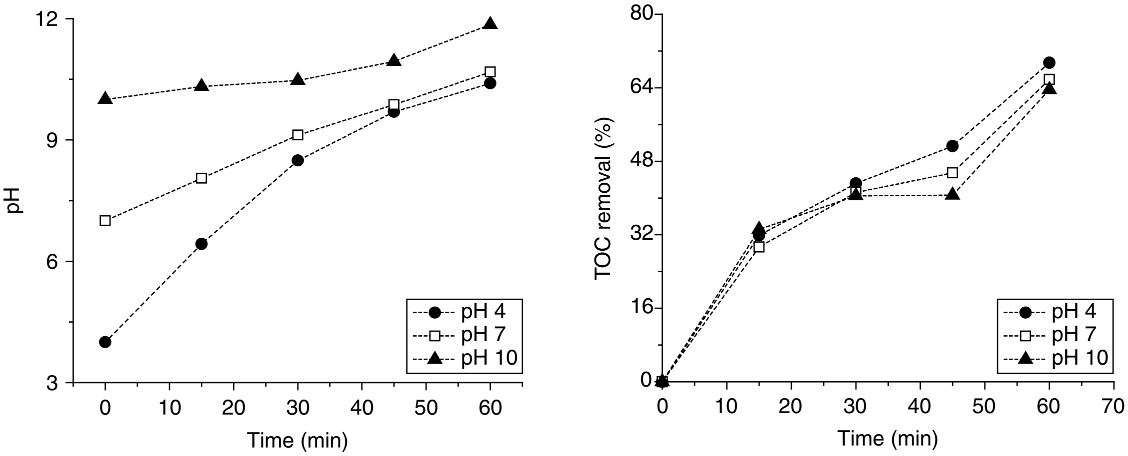

Fig. 2. pH variation and its effect on TOC removal and during treatment. Initial TOC of 23.8×10^3 mg/l, current density of 7.5 mA/cm^2, and conductivity of 1.54 mS/cm.

in the pH and TOC during the electrocoagulation process of the wastewater. The removal of TOC is slightly higher at pH 4 (69.4%) when compared to that obtained at pH 7 (65.8%) and pH 10 (63.6%). It was observed that the efficiency for TOC removal decreased by increasing the pH, in agreement with previous works related to EC using Fe electrodes [19–22]. Regarding the pH variation, during the electrocoagulation process, this figure shows that the initial value of pH 4 rapidly changes during the electrolysis reaching a pH of ~10.4 at 60 min. The increase of pH in the mildly acidic condition, and also in the neutral pH, was attributed to the simultaneous generation of OH^- ions and evolution of hydrogen at the cathode surface due to water reduction [23,24]. While, in the alkaline condition the final pH does not change very much because ionic forms of Fe-hydroxides dominate which decrease the efficiency of TOC removal by electrocoagulation.

3.2.3. Initial electrical conductivity

The effect of the electrical conductivity (1.54 and 3.00 mS/cm) on the electrocoagulation efficiency of the liquid waste was also studied. All runs were conducted with fixed current density of 7.5 mA/cm^2 at initial pH 4. Sodium chloride was added to adjust the conductivity of the solution to 3 mS/cm in order to minimize energy consumption. The chloride ions added to the solution can be oxidized in the anode electrogenerating chlorine (reaction towards the left):

$$Cl_{2(g)} + 2e^- \leftrightarrow 2Cl^-;\ E^\circ = 1.36\ \text{V vs. SHE} \qquad (4)$$

Then the chlorine, in contact with water, can generate HOCl and Cl^- species and, depending on the pH of the solution the hypochlorous acid (HOCl) may dissociate forming hypochlorite ions (OCl^-):

$$\begin{aligned} &Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-; \\ &\quad k = [HOCl][H^+][Cl^-] / P_{Cl_2} \end{aligned} \qquad (5)$$

$$HOCl \leftrightarrow H^+ + OCl^-; \qquad k_a = [H^+][OCl^-]/[HOCl] \quad (6)$$

The HOCl and OCl^- ions are oxidizing agents, k is the equilibrium constant, k_a is the acid dissociation constant and P_{Cl_2} is the pressure of Cl_2 gas. Thus, the pollutants may also be destroyed in the bulk solution by the oxidation reaction with the generated oxidants. According to the *pKa* (= 7.54) of the HOCl / OCl^-, at pH < 7.54, HClO predominates, whereas hypochlorite ions predominate at pH > 7.54. Thus, the results reported here indicate that the indirect oxidation mechanism with the participation of HOCl may also contribute to the TOC removal.

According to Fig. 3, TOC removal was enhanced by increasing the electrical conductivity; for instance, 69.4% TOC was decreased with 1.54 mS/cm while 78.7% TOC removal was achieved using a conductivity of 3 mS/cm at 60 min of the electrolysis. Even though TOC removal is favored at higher conductivity, the employment of the lower and natural conductivity (1.54 mS/cm) of the wastewater will help to reduce the operational costs associated with sodium chloride addition to increase the conductivity of the phenol-formaldehyde resin manufacturing wastewater. Nevertheless, the associated costs of the electrical energy requirement should also be taken into account. The insert of this figure shows that the pH variation is very similar for the two conductivity tested values.

3.3. Energy consumption

The main operating cost for the removal of TOC by electrocoagulation process is related to the consumption of electrical energy. The national discharge permissions and electrical energy consumption (operating costs) required

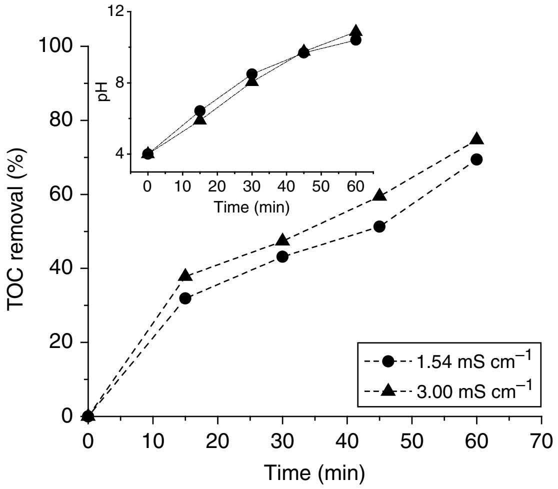

Fig. 3. Effect of electrical conductivity on the TOC removal at initial TOC of 23.8×10^3 mg/l, 7.5 mA cm^{-2} and initial pH 4. The insert shows pH variation during treatment.

to reach the desired degree of treatment will determine the feasibility of a proposed treatment method. Therefore, it is essential to calculate electrical energy requirements per unit volume of treated wastewater to decide whether the electrocoagulation process is feasible for TOC removal of phenol-formaldehyde resin manufacturing wastewater. The electrical energy consumed (*P*, kWh/m^3) during the process was calculated using Eq. (7):

$$P = \frac{Eit}{V} \tag{7}$$

where *E* is the cell voltage (V), *i* is the average cell current (A), *t* is the electrolysis time (h) and V is the treated volume (m^3). Fig. 4 shows the energy consumption as a function of electrical conductivity (1.54 and 3 mS/cm) at current density of 7.5 mA/cm^2 and its natural pH 4. It is observed that 78.7% TOC removal was achieved at an electrical conductivity of 3 mS/cm with 13 kWh/m^3 of energy consumption at 1 h of electrolysis; while 22 kWh/m^3 of energy consumption was required to remove 69.4% of TOC 1.54 mS/cm. These results show that the electrical conductivity of the effluent significantly influence the power consumption. The higher power consumption due to lower electrical conductivity leads to higher operating cost, lower efficiency of the electrocoagulation process for TOC removal and more time of electrolysis. Finally, the cost associated to the addition of NaCl to increase the conductivity to 3 mS/cm is very low (6 US cents).

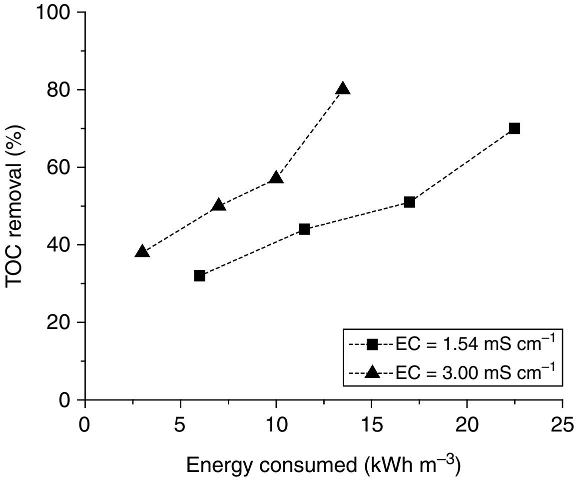

Fig. 4. Energy consumption for TOC removal with different electrical conductivity during EC process using 7.5 mA/cm^2 and initial pH 4.

4. Conclusions

In this study the electrocoagulation process using Fe electrodes was employed to investigate the effectiveness of treatment of phenol-formaldehyde resin manufacturing wastewater. It was observed that the pH, current density and electrical conductivity influenced TOC removal. The optimum conditions to achieve 78.7% of TOC removal in a short time period were a current density of 7.5 mA/cm^2, pH 4 (wastewater natural pH) and an electrical conductivity of 3 mS/cm. Under such conditions, the energy consumption was 13 kWh/m^3 at 60 min of reaction. In spite of significant removal efficiency, the final TOC value (5.8×10^3 mg/l) is still higher than the standard discharge. Nevertheless, the EC process proved to be effective for the removal of initially high TOC content from a real effluent coming from the industry. Thus, the EC process would be useful as pretreatment step to this type of wastewater prior to a treatment process.

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