

Electrochemical oxidation of phenol in a parallel plate reactor using ruthenium mixed metal oxide electrode

Yusuf Yavuz, A. Savaş Koparal*

Anadolu Üniversitesi, Çevre Sor. Uyg. ve Araş. Merkezi, Eskişehir, Turkey

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Abstract

In this study, electrochemical oxidation of phenol was carried out in a parallel plate reactor using ruthenium mixed metal oxide electrode. The effects of initial pH, temperature, supporting electrolyte concentration, current density, flow rate and initial phenol concentration on the removal efficiency were investigated. Model wastewater prepared with distilled water and phenol, was recirculated to the electrochemical reactor by a peristaltic pump. Sodium sulfate was used as supporting electrolyte. The Microtox[®] bioassay was also used to measure the toxicity of the model wastewater during the study.

As a result of the study, removal efficiency of 99.7% and 88.9% were achieved for the initial phenol concentration of 200 mg/L and chemical oxygen demand (COD) of 480 mg/L, respectively. In the same study, specific energy consumption of 1.88 kWh/g phenol removed and, mass transfer coefficient of 8.62×10^{-6} m/s were reached at the current density of 15 mA/cm². Electrochemical oxygen demand (EOD), which can be defined as the amount of electrochemically formed oxygen used for the oxidation of organic pollutants, was 2.13 g O₂/g phenol.

Electrochemical oxidation of petroleum refinery wastewater was also studied at the optimum experimental conditions obtained. Phenol removal of 94.5% and COD removal of 70.1% were reached at the current density of 20 mA/cm² for the petroleum refinery wastewater.

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Keywords: Electrochemical oxidation; Phenol; Ruthenium mixed metal oxide electrode; Toxicity

1. Introduction

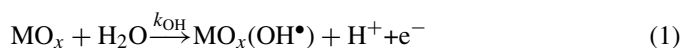
Phenols are aromatic compounds containing one or more hydroxyl group attached to the aromatic ring and produced as wastes in a variety of industries, including oil refineries, dyes, plastics, pharmaceutical, and coke plants.

Phenolic wastes are largely resistant to biological degradation in wastewater treatment plants. Phenols react with chlorine during water treatment and produce chlorophenols, which are carcinogenic [1,2]. Minute concentrations of phenol (2.5 mg/L) cause objectionable tastes in potable water and also may taint the flesh of fish. Larger concentrations not only kill fish, but also completely destroy all life in the stream [3,4]. Phenolic wastes are a health hazard to humans because of their high toxicity. The toxicity and bad smell of phenols warrant further treatment before discharge.

Treatment technologies include activated carbon adsorption, solvent extraction, and biological, chemical, or electrochemical oxidation. Electrochemical methods for water/wastewater treatment have great attention in recent years [1,5–10], and offer many distinctive advantages such as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness [11].

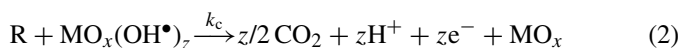
Electrochemical oxidation of phenol has been studied by various workers at platinum [7–9], doped SnO₂ [8,9], PbO₂ [8,12–14], Bi₂O₅–PbO₅ [14], IrO₂ [10], carbon [15] and boron-doped diamond anodes [16]. Among these electrode materials, besides the diamond electrode, metal oxide electrodes, which are cheaper, are also preferred.

It is possible to produce hydroxyl radicals (OH[•]), strong oxidizing agents, by using the oxide anodes (MO_x). The mechanisms of organic matter oxidation and hydroxyl radical formation in an oxide anode are defined as follow [17]:

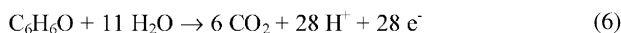
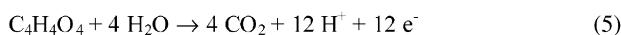
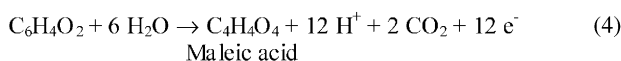
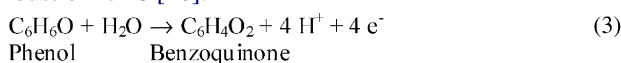


* Corresponding author. Tel.: +90 222 3213550; fax: +90 222 3239501.
E-mail address: askopara@anadolu.edu.tr (A.S. Koparal).

The hydroxide radicals are adsorbed at the electrode surface and degradation of organic matter goes on according to Eq. (2):



Phenol oxidation in a metal oxide electrode has been described in the Sharifian and Kirk [13] study. Reaction sequence obtained by workers includes phenol decomposition, aromatic and aliphatic intermediates and carbon dioxide formation (Eqs. (3)–(5)). Initially, aromatic intermediates such as benzoquinone, catecol and hydroquinone, which are more toxic than phenol, are formed depending on the experimental conditions. Hydroquinone and 1–4 benzoquinone are not detected in electrolysis in alkaline media (benzoquinone itself is unstable in alkaline solution) and the conditions of film formation at the anode are favourable [7]. However, in electrolysis in acidic media hydroquinone and benzoquinone are the principle oxidation intermediates and the formation of the anodic films is inhibited [7]. Further oxidation of these toxic intermediates yields organic acids such as maleic, fumaric, and oxalic acid and/or harmless end-products (CO_2 and H_2O) [7,9,13,14,16]. According to Eq. (6), number of exchanged electrons in phenol combustion is 28 [16].



There are a lot of studies interested in electrochemical oxidation of phenol and metal oxide electrodes, but insufficient data about the phenol removal and toxicity reduction using ruthenium mixed metal oxide electrode. Ruthenium oxide (RuO_2) is an important material in the industry because it is used widely for the Cl_2 and O_2 production [18,19]. RuO_2 has good conductivity, good barrier properties against oxygen diffusion and good stability at room temperature as high as 800°C . Ruthenium and ruthenium oxide have also excellent chemical stability [20].

The term “Electrochemical Oxygen Demand (EOD)” has been proposed and EOD equation has been given by Comninellis and Pulgarin [7]. EOD is the amount of oxygen used for the oxidation of organic compounds, in this case phenol. In the other words, EOD expresses the amount of electrochemically formed oxygen used for the oxidation of organic pollutants.

In this paper, electrochemical oxidation of phenol in a parallel plate reactor using ruthenium mixed metal oxide coated titanium electrode was studied. Toxicity reduction capacity of this electrode material was also investigated.

2. Materials and methods

In this study, electrochemical oxidation of phenol was carried out in a parallel plate reactor which has mainly four compartments of total volume of 270 mL. Each compartment had four anodes and four cathodes made from ruthenium mixed metal oxide electrode in dimensions of $3 \text{ cm} \times 4 \text{ cm}$ (Fig. 1). RuO_2

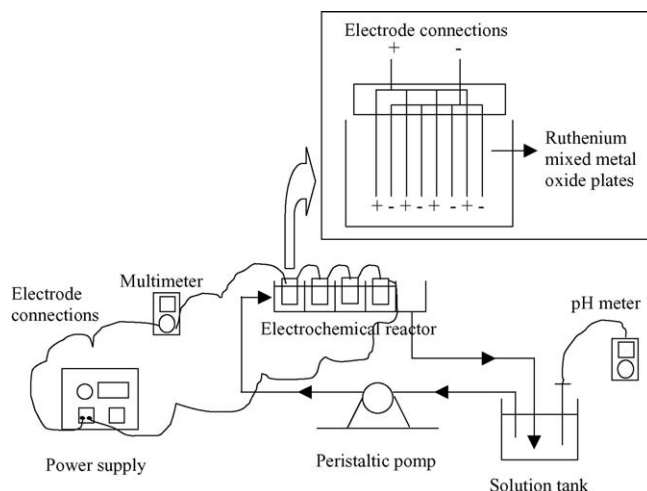


Fig. 1. Experimental set-up used in the studies.

electrodes on a titanium substrate were supplied from Magneto-Chemie B.V. (Schiedam, The Netherlands). Studies were carried out in batch mode, and solution was recirculated to the reactor by means of a peristaltic pump. Model solution was prepared with distilled water and phenol and had an initial phenol concentration of 50, 200 and 500 mg/L. Electrical conductivity of model solution was about $100 \mu\text{S}/\text{cm}$. Experimental set-up used in the study is shown in Fig. 1.

Model solution was recirculated through the electrochemical reactor in the flow rates of 24.83×10^{-3} , 36.3×10^{-3} and $47.8 \times 10^{-3} \text{ L}/\text{min}$ (1.5×10^{-3} , 2.2×10^{-3} and $2.9 \times 10^{-3} \text{ m}^3/\text{h}$). Current densities of 3, 5, 10, 15 and $20 \text{ mA}/\text{cm}^2$ were also studied. The effect of temperature on the phenol removal was investigated at 20, 50°C and laboratory temperature. Studies were done at the pH of 3, 7 (ambient pH or original pH of the phenol solution) and 11 to investigate the initial pH of the solution. In addition, supporting electrolyte concentration was also studied using the solutions of 0.05 and 0.1 M Na_2SO_4 . pH of the working solution was monitored during the studies.

Petroleum refinery wastewater used had a phenol concentration of 192.9 mg/L and COD of 590 mg/L. Electrical conductivity of the wastewater was $15.63 \text{ mS}/\text{cm}$ and pH was 1.97 since the wastewater was preserved with concentrated H_2SO_4 .

2.1. Analysis

Model wastewater studied was prepared with phenol (MERCK). Na_2SO_4 (MERCK) was used as supporting electrolyte, and H_2SO_4 (MERCK) and NaOH (MERCK) were used to adjust the pH of the solution.

Phenol was determined according to the Standard Methods for the Examination of Water and Wastewater (ASTM 5530 D) and COD was measured using COD reactor (HACH) and spectrophotometer.

The Microtox[®] system used was supplied by AZUR Environmental (Carlsbad, CA), and consisted of lyophilized bacterial reagent *Vibrio fischeri*, reconstitution reagents and the Model 500 Toxicity Analyzer (AZUR Environmental). Toxicity of the model solution was determined using Microtox Model 500 Ana-

Table 1
Typical results obtained from the experimental studies ($C_0 = 200$ mg/L, $i = 15$ mA/cm², $V = 500$ mL, $Q = 24.83 \times 10^{-3}$ L/min, $t =$ laboratory temperature)

Time (min)	Applied potential (V)	pH	C_{out} (mg/L)	Current efficiency ϕ (%)	Removal efficiency (%)	Energy consumption (kWh/m ³)	Energy consumption (kWh/g)
0	41.2	7.05	200	–	–	–	–
10	28.2	6.03	33.1	74.1	83.5	50.8	0.304
20	20.0	4.28	24	39	88	72	0.41
30	17.3	4.18	7.3	28.5	96.4	93.42	0.485
40	16.8	4.25	3.03	21.8	98.5	121	0.614
50	16.7	4.61	0	17.7	100	150.3	0.752

COD_{in} = 480 mgO₂/L, COD_{out} = 70 mgO₂/L, COD removal = 85.41%, EOD = 2.05 g O₂/g phenol, Mass transfer coefficient (k_m) = 8.11×10^{-6} m/s.

lyzer. The analyzer utilizes freeze-dried luminescent bacteria (*V. fischeri*, previously named *Photobacterium phosphoreum*) as test organisms. The short-term luminescent bacteria assay was done according to the supplier's protocol for the duplicate basic test [21]. Each test consisted of one control and four serial dilutions of each sample. Toxic effects were monitored as a percent decrease of the light emission of *V. fischeri* after 5 min of incubation at 15 °C with 95% confidence intervals using the Microtox calculation software (version 1.18).

Statron 3234.4 model power supply, OGSM 3900 digital multimeter, Multifix MC 1000 PEC model peristaltic pump, Polyscience 9605 model water bath, Orion 420 A model pH meter, DR Lange CADAS 100 model spectrophotometer were used as auxiliary equipments in the experimental studies.

3. Results and discussion

During the studies, yellow–brown colored polymeric product was detected at the working solutions, especially at basic pH values. However, polymeric product did not adhere on the anode surface, probably because of the circulation of working solution. After the experiment was completed, polymeric product settled down at the bottom of the electrochemical reactor and solution tank itself and was separated from bulk easily. Therefore, a negative effect on the process performance originating from the polymeric product formation was not encountered. Comninellis and Pulgarin [7] also reported that during the anodic oxidation of phenol a polymeric product which may cause inactivation of anode material was formed at the surface of platinum anode. Formation of this polymeric product depends strongly on the experimental conditions. Alkaline media (pH > 9), low current density (<30 mA/cm²), high temperature (≥ 50 °C) and high phenol concentration (50 mmol/L) favour the film formation [7].

In an experimental study, which was realized at laboratory temperature with a current density of 15 mA/cm² and an initial phenol concentration of 200 mg/L, complete phenol removal was achieved after 50 min of electrolysis whereas COD removal efficiency was 85.4% (Table 1). However, COD removal of practically 100% could have been obtained if the electrolysis had been continued after complete phenol removal was reached. Initial pH of 7.05 decreased to the final pH of 4.61 during the study. Decrease in the pH was attributed to the formation of aliphatic oxidation intermediates such as maleic, fumaric and oxalic acids

and side reactions that occurred on the anode and cathode surface.

Current efficiency is defined as the ratio of the electricity consumed by the electrode reaction of interest over the total electricity passed through the circuit. Calculations of current efficiency and [22,23] mass transfer coefficient [22] have been given elsewhere. Current efficiency (ϕ) of 74.1%, which was reached after 10 min of electrolysis, decreased the 17.7% at the end of the study with an energy consumption of 0.752 kWh/g. EOD was calculated as 2.05 g O₂/g phenol. Variation of calculated mass transfer coefficients with the working parameters is summarized in Table 2.

3.1. Effect of temperature and flow rate

To study the influence of temperature on the electrochemical oxidation process, temperature of the solution tank was adjusted to the 20 and 50 °C. The other runs were performed at laboratory temperature. While working at laboratory temperature, initial solution temperature of 20–25 °C increased up to a final temperature of 50 °C in some experiments depending on the composition of solution and study parameters.

Table 2
Variation of mass transfer coefficients with the working parameters

Parameter	Value	Mass transfer coefficient (k_m , 10 ⁻⁶ m/s)
Current density (mA/cm ²)	10	3.81
	15	8.02
	20	13.25
pH	3	0.42
	11	0.337
	Original	2.04
Supporting electrolyte (Na ₂ SO ₄ , M)	Without supporting electrolyte	0.43
	0.05	0.55
Flow rate (10 ⁻³ L/min)	0.1	1.45
	24.83	8.11
	36.3	8.02
	47.8	8.62

When studying at laboratory temperature, temperature of solution was initially about 20–25 °C, and increased up to 50 °C during the electrolysis with increase in electrode temperature.

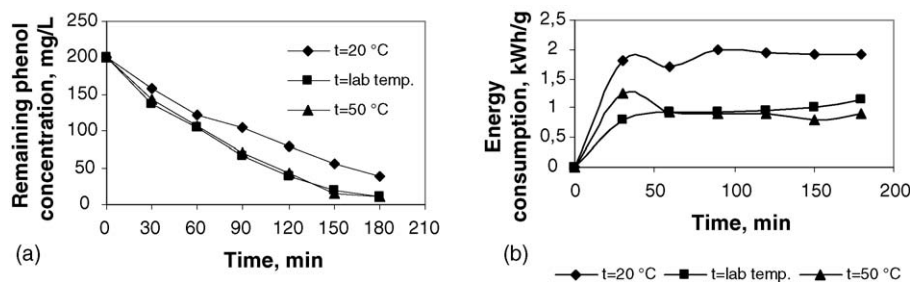


Fig. 2. Variation of remaining phenol concentration (a) and energy consumption (b) with temperature ($C_0 = 200$ mg/L, $V = 500$ mL, $i = 10$ mA/cm², $Q = 36.3 \times 10^{-3}$ L/min, pH = original).

Temperature exhibited an acceleration effect on the electrochemical decomposition of phenol. Variation of remaining phenol concentration with temperature as a function of time is shown in Fig. 2a. Increase in the temperature, resulted also in increase in the removal efficiencies for both phenol and COD. Specific energy consumption decreased with increase in temperature since higher removal efficiency for contaminants were reached (Fig. 2b).

There was no significant effect of flow rate on phenol degradation except for the flow rate of 24.83 L/min (Fig. 3). This was the lowest one among the flow rates studied. Study at this low flow rate led to increased in contact time between the solution and electrodes. Increase in contact time resulted in increase in the solution temperature. Increase in the temperature accelerated the degradation as mentioned above. Since the solution temperature changed with the flow rate, phenol removal has slightly increased. So, there is a combined effect of flow rate and temperature.

3.2. Effect of initial pH

To investigate the effect of initial pH on the removal efficiency, initial pH of the solution was adjusted to 3 and 11 using H₂SO₄ and NaOH. In addition, some studies were carried out at ambient pH (original pH) of the solution (initial pH was ~7). Results show that pH adjustment is not necessary because the most appropriate results are reached when studying with the original sample (Fig. 4). Highest mass transfer coefficient value was also computed when studying with original sample as shown in Table 2.

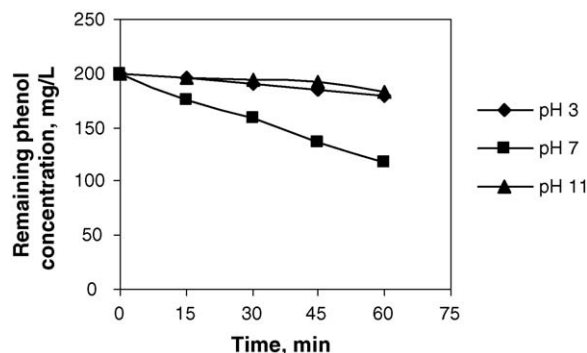


Fig. 4. Variation of remaining phenol concentration with initial pH values ($C_0 = 200$ mg/L, $V = 500$ mL, $i = 5$ mA/cm², $Q = 36.3 \times 10^{-3}$ L/min, $t =$ laboratory temperature).

3.3. Effect of supporting electrolyte

It is well known that supporting electrolyte has an important effect on the electrochemical process. In this work sodium sulfate was used as supporting electrolyte to investigate its influence on the electro-oxidation of phenol. When supporting electrolyte of 0.05 and 0.1 M Na₂SO₄ were used, variation of pH had similar trend and tended to increase up to basic pH values. Variation of pH with time as a function of supporting electrolyte concentration is depicted in Fig. 5.

Phenol removal was directly proportional with supporting electrolyte concentration as shown in Fig. 6a. Because of the low electrical conductivity of solution, higher voltage was required for the electrochemical reactor to reach the desired current

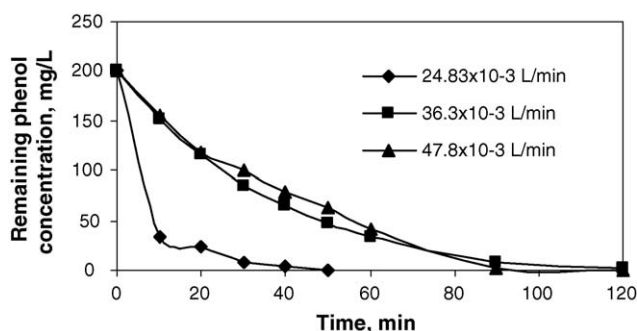


Fig. 3. Variation of remaining phenol concentration with flow rate ($C_0 = 200$ mg/L, $V = 500$ mL, $i = 15$ mA/cm², $t =$ laboratory temperature, pH = original).

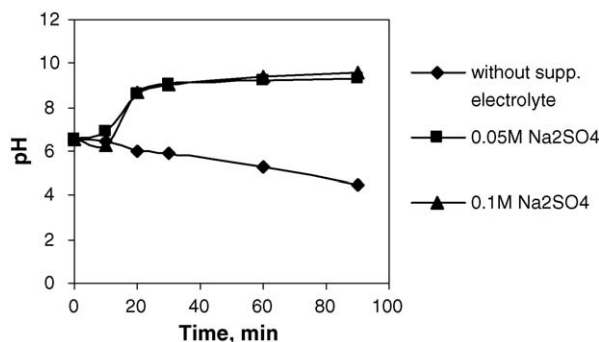


Fig. 5. Variation of pH with time while studying influence of supporting electrolyte concentration on removal efficiency ($C_0 = 50$ mg/L, $V = 500$ mL, $i = 5$ mA/cm², $Q = 36.3 \times 10^{-3}$ L/min, $t = 20$ °C).

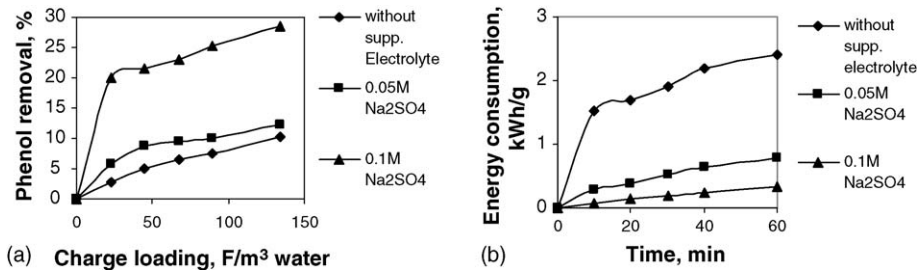


Fig. 6. Variation of remaining phenol concentration (a) and energy consumption (b) with supporting electrolyte concentration ($C_0 = 200$ mg/L, $V = 500$ mL, $i = 15$ mA/cm², $Q = 36.3 \times 10^{-3}$ L/min, $t =$ laboratory temperature).

density. This problem may be overcome by using supporting electrolyte, if the electrical conductivity of the solution is low. According to the results, it can be said that increase in the supporting electrolyte concentration results in increase in mass transfer (Table 2) and decrease in energy consumed. Energy consumption was approximately five times higher in the original samples than that in supporting electrolyte containing samples as shown in Fig. 6b.

3.4. Effect of current density

Current density is related with the applied potential closely. It should be kept in mind that higher potential must be applied to the electrochemical reactor to study at a higher current density.

Mass transfer coefficient was directly proportional with increase in the current density as shown in Table 2. Current density was one of the most important parameters that affected the phenol and COD removal. As the current density was increased, remaining phenol concentration decreased in the study (Fig. 7a). It can be said that increase in the current density greatly accelerated the removal of phenol.

When a charge loading of 269 F/m³ water was applied to the reactor, phenol removals of 47%, 67% and 78% were obtained with the current densities of 10, 15 and 20 mA/cm², respectively (Fig. 7b). These results showed that higher removal efficiencies were obtained at higher current densities when the same charge loading value was applied to the reactor. In addition, 98.2% phenol removal was achieved at the current density of 20 mA/cm² with a charge loading of 626.7 F/m³ water, whereas 99% phenol removal was achieved at the cur-

rent density of 15 mA/cm² with a charge loading of 806 F/m³ water.

3.5. Effect of initial phenol concentration

Experimental conditions when the effect of initial phenol concentration was investigated were as follows; flow rate of 24.83×10^{-3} L/min, current density of 15 mA/cm², laboratory temperature, and the original pH of the solution. Complete removal of phenol was reached for all initial phenol concentrations (Fig. 8a). However time necessary to reach the complete removal increased as initial phenol concentration increased, as expected. Variation of remaining phenol concentration with initial phenol concentration as a function of time is depicted in Fig. 8a. Phenol concentration of 0.151 mg/L was obtained after 30 min of electrolysis with the initial phenol concentration of 50 mg/L, whereas it took 90 min to reach an outlet phenol concentration of 1.51 mg/L with the initial phenol concentration of 500 mg/L. As another result of the study, increase in the initial phenol concentration resulted in decrease in the pH of the solution under same conditions (Fig. 8b).

Variation of current efficiency, as another important parameter, with time is shown in Fig. 8c. Current efficiency had naturally a decreasing trend with time. Current efficiency of as high as 88% was obtained in the study. Phenol removals of over 95% were obtained with a charge loading of 200 F/m³ water for the initial concentrations of 50 and 200 mg/L. Charge loading of 600 F/m³ water is required for almost the complete removal of 500 mg/L phenol (Fig. 8d).

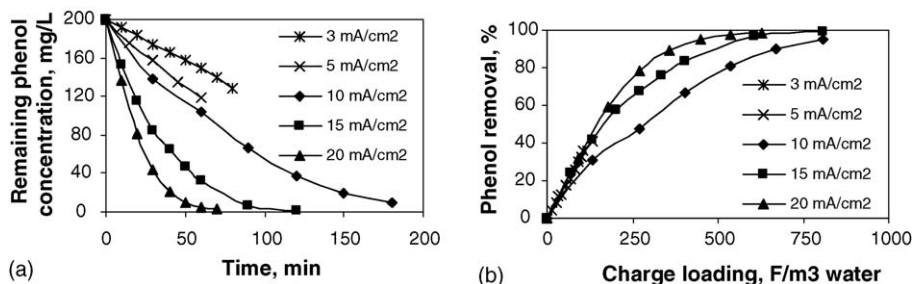


Fig. 7. Variation of remaining phenol concentration as a function of time (a) and phenol removal as a function of charge loading (b) with current density ($C_0 = 200$ mg/L, $V = 500$ mL, $Q = 36.3 \times 10^{-3}$ L/min, $t =$ laboratory temperature, pH = original).

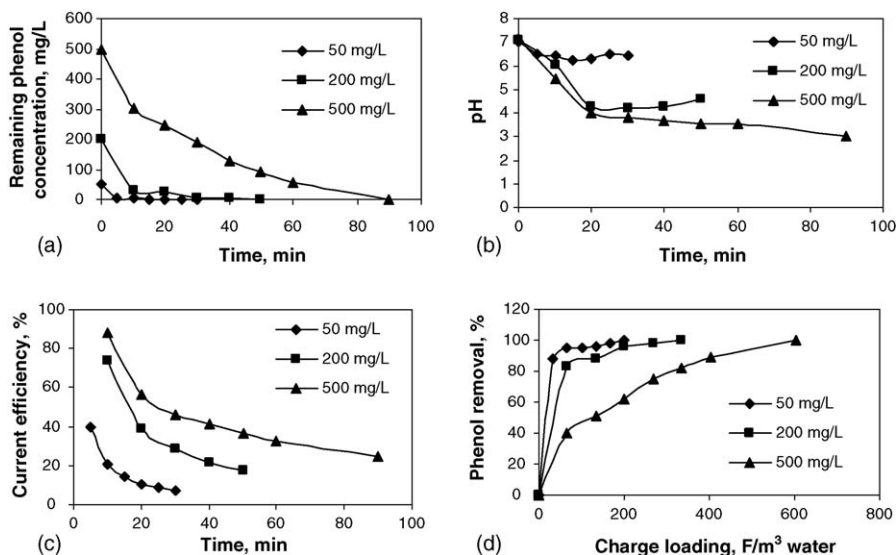


Fig. 8. Variation of remaining phenol concentration (a), pH (b), current efficiency (c) with initial phenol concentration as a function of time and phenol removal (d) with initial phenol concentration as a function of charge loading ($V = 500$ mL, $Q = 24.83 \times 10^{-3}$ L/min, $i = 15$ mA/cm², $t =$ laboratory temperature, pH = original).

According to the results it can be emphasized that higher charge loading is necessary for higher phenol concentration.

3.6. Petroleum refinery wastewater

Petroleum refineries are the main sources of phenolic wastewaters. Under the optimum experimental conditions, a real petroleum refinery wastewater, which was obtained from a national oil refinery, was exposed to electrochemical oxidation using ruthenium mixed metal oxide anodes. Wastewater used in the studies had an initial phenol concentration of 192.9 mg/L and COD of 590 mg/L.

After 210 min of electrolysis, 94.5% phenol removal was reached for the petroleum refinery wastewater. However, since the wastewater generally has a variety of organic and inorganic contaminants, COD removal is more difficult and longer electrolysis time is necessary for COD removal compared to phenol removal. COD removal of up to 70.1% was obtained with ruthenium oxide anode after 300 min of electrolysis (Fig. 9). Since effluent met the discharge standards after 300 min of electrolysis,

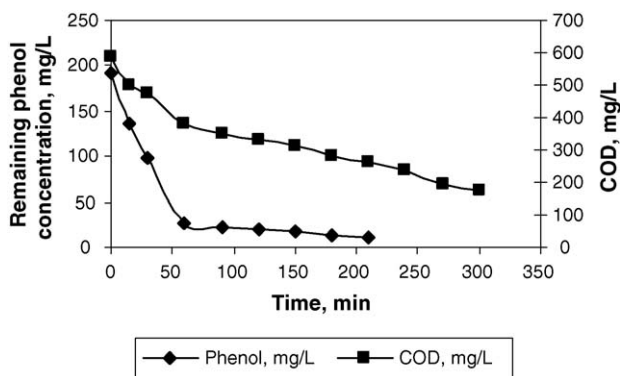


Fig. 9. Variation of remaining phenol concentration and COD as a function of time ($i = 20$ mA/cm², $Q = 24.83 \times 10^{-3}$ L/dak, $t = 20$ °C).

practically 100% COD removal was not taken into consideration.

3.7. Toxicity studies

Microtox[®] bioassay test was performed to have information about the toxic effect of the initial and treated solutions under optimum experimental conditions. Toxicity results were given as relative toxicity index (RTI) [24]:

$$RTI = \frac{\%EC_{50}(t = 0)}{\%EC_{50}(t = t)} \quad (7)$$

where $\%EC_{50}(t = 0)$ and $\%EC_{50}(t = t)$ are the 5 min Microtox toxicity of the sample at times 0 and t .

The results obtained from different initial phenol concentrations are given in Fig. 10 as a function of time. It is clear from this figure that increase in the initial phenol concentration, also increases the time necessary to reach proper toxicity value, because higher concentration means, at the same time, higher toxicity. During the experiment, an increase in the toxicity of the working solution was observed after a given time period because of the formation of more toxic intermediate products such as benzoquinone and/or hydroquinone as mentioned

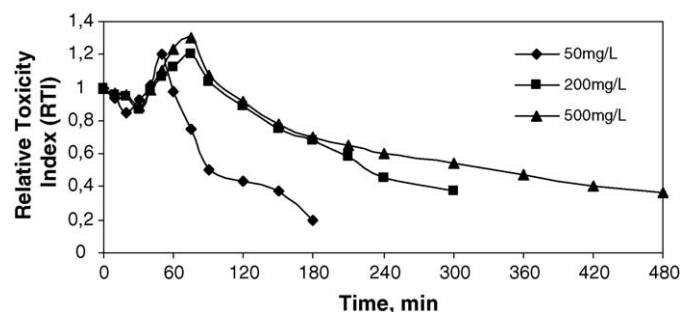


Fig. 10. Variation of toxicity results with time for the different initial phenol concentrations.

before. After the oxidation of these intermediates to the organic acids such as maleic acid, fumaric acid and/or end-products such as CO₂ and H₂O, toxicity value firstly turned to its initial value, then began to decrease gradually as shown in Fig. 10. In the studies, approximately 80% toxicity reduction was accomplished for the 50 mg/L phenol concentration. Significant degree of toxicity reduction was also achieved for the initial phenol concentrations of 200 and 500 mg/L.

4. Conclusion

Electrochemical oxidation of phenol using ruthenium mixed metal oxide anode seems to be a very efficient method for wastewater treatment according to the study results obtained. Some important experimental parameters such as temperature, flow rate, current density, and initial phenol concentration were investigated for phenol and COD removal. Complete phenol removal was obtained for all initial phenol concentrations and high COD removal efficiencies were also reached. High phenol and COD removal from the real wastewater were also achieved.

Increase in the temperature, current density and supporting electrolyte concentration resulted in increase in the phenol and COD removal. Initial pH of the solutions had no significant effect on the process performance. Variation of mass transfer coefficient with studying parameters was also investigated and it was found that increase in the current density and supporting electrolyte concentration resulted in increase in the mass transfer coefficients. Flow rate had no significant effect on the mass transport because of the combined effect of flow rate and temperature.

Microtox[®] bioassay results show that electrochemical oxidation using ruthenium mixed metal oxide anode is a good way of toxicity reduction for the toxic substances like phenol.

Acknowledgement

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