

DEGRADATION OF PHENOL IN WASTEWATER USING ANOLYTE PRODUCED FROM ELECTROCHEMICAL GENERATION OF BRINE SOLUTION

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ABSTRACT

This paper presents the degradation of phenol in wastewater using anolyte, which is generated from electrochemical activation process. Anolyte consists of reactive ions and free radicals, which contribute to its oxidizing behavior. The optimum conditions, which facilitate a complete degradation of phenol, were found using variation of dosage of anolyte and reaction time. It was found that about 20% of anolyte was the optimal dosage which corresponded to 98% degradation of phenol after a reaction time of 60 minutes. The main products during degradation of phenol by anolyte were found to be benzoquinone, hydroquinone, catechol, maleic acid, fumaric acid and oxalic acid.

KEYWORDS: anolyte, electrochemical activation process, phenol degradation, phenol oxidation.

INTRODUCTION

Widespread contamination of water by phenol has been recognized as an issue of growing importance in recent years. Phenol is potential or known human carcinogen and is of considerable health concern, even at low concentration. For instance, Malaysian guidelines limit phenol concentration to 0.001 mg l⁻¹ in wastewater (DOE, 1974). Hence, the treatment of wastewater containing phenol is a necessity.

Many technologies have been investigated for removing and degradation of phenolic compounds in wastewater. They included, adsorption

(Rengaraj *et al.*, 2002), biodegradation (Miland *et al.*, 1996), UV/Fe⁺³ (Zhou *et al.*, 2001), extraction by liquid membrane (Lin *et al.*, 1999) and oxidation (Comminellis and Pulgarin, 1991; Tahar and Savall, 1998; Polcaro *et al.*, 1999; Tahar and Savall, 1999, Awad and Abuzaid, 2000).

Among them, oxidation technology has shown their potential to destroy phenol completely in wastewater. In oxidation process, in the first step, the phenol oxidizes to hydroquinone then into benzoquinone and catechol. Subsequent oxidation of these products, after opening of the aromatic ring, leads to the formation of aliphatic carboxylic acids

such as maleic acid and fumaric acid. When phenol is degraded to aliphatic carboxylic acids the wastewater will become more biodegradable (Wu and Zhou, 2001) and less toxic (Pulgarin *et al.*, 1994). The oxidation of phenol by several oxidizing agents such as ozone, UV and hydrogen peroxide has been extensively studied (Gurol and Vastizas, 1987; Esplugas *et al.*, 1994; Shen *et al.*, 1995; Miland *et al.*, 1996; Benitez *et al.*, 2001, Canton *et al.*, 2002).

Apart from those, in recent years there has been increasing interest in the use of catalytic wet oxidation (Maugans and Akgerman, 1997; Larachi, 2001) and wet oxidation (Prakash *et al.*, 2002) for phenol removal. However those methods have some disadvantages and limitations. Sustainability of catalytic wet oxidation technology depends on kinetic regime in which the catalyst life would compromise to its cost. Masende *et al.* (2002) have reported that total conversion of phenol to CO_2 and H_2O was achieved when the platinum surface was almost oxidized in which it resulted into catalyst deactivation. Wet air oxidation also provides slow and incomplete oxidation, causing the effluent to require further treatment. Supercritical water oxidation has also a very high capital and operating costs due to the extremely harsh operating conditions and the extremely corrosive nature of supercritical water. In other oxidation method such as Horseradish Peroxidase (HRP), in order to achieve a high degree of phenolic removal, large amounts of enzyme are required to counteract the effects of enzyme inactivation, thus limiting its industrial applicability (Klibanov *et al.*, 1980). The anodic oxidation has also been proposed as an alternative method for phenol degradation, in which the type of anode electrode has been the subject of studies concerning oxidation of phenol, in recent years. Anodic oxidation of phenol on graphite electrode (Awad and Abuzaid, 2000), bismuth doped lead dioxide electrode (Tahar and Savall, 1999), platinum electrode (Cominellis and Pulgarin, 1991), b-lead dioxide electrode (Wu and Zhou, 2001) and tantalum/lead dioxide (Tahar and Salvall, 1998) have been documented. In all previous anodic oxidation methods mentioned above, wastewater containing phenol was pumped into the reactor (cell), while in the present study the aim is to examine the effectiveness of anolyte for degradation of phenol in wastewater outside the reactor. To the authors' knowledge, the use of anolyte as oxidizing agent for phenol

destruction has not been investigated to date.

The use of STEL ECA system is gaining popularity as it provides alternative to the use of chlorine gas, ozone and UV-radiation for the treatment of wastewater. The system operates totally without chemical or artificial additives. Only water, regular salt and electrical energy are required to operate the STEL ECA system. As such, there is no detrimental effect on the environment or the ecology and absolutely no pollution or contamination is caused in the purification process. This method eliminates the transportation, storage, and handling of hazardous chemicals and reduces the costs associated with safety procedures, discharge liabilities and environmental exposure.

MATERIAL AND METHODS

Characteristic of the STEL ECA system

Electrochemical activation (ECA) process concept involves the passage of high voltage current through a brine solution with a membrane interposed between the anode and cathode. As a result, this process will produce a substantial electrical potential difference, leading to the generation of two types of water namely anolyte and catholyte.

The STEL system comprises an electrolytic cell made of three components: 1) the anode: an outer titanium tube coated internally with a ruthenium oxide, iridium and platinum; 2) the cathode: a central platinum rod coated with pyrocarbon; 3) an acid and alkali resistant ceramic diaphragm coated with oxides of zirconium, yttrium and aluminum fixed between the electrodes to prevent the inter mixing of solutions in the anode and the cathode chambers of the reactor, whilst not obstructing the movement of ions in the electric field. This produces both anolyte and catholyte solutions.

The schematic of the STEL ECA system are shown in Figure 1. The water was supplied at flow rate of 1 l min^{-1} . A constant electric current (18 volts) is passed through the solution of NaCl (10%). The electron arrival in salt water at the cathode, as well as the discharge of electron from the salt water at anode are accompanied by a series of electrochemical reactions on the cathode and anode surfaces, resulting to the generation of anolyte and catholyte. After about 30 seconds, anolyte and catholyte were collected in two separate beakers. The objective of this work was to investigate the breakdown of phenol in water after they have been treated with anolyte.

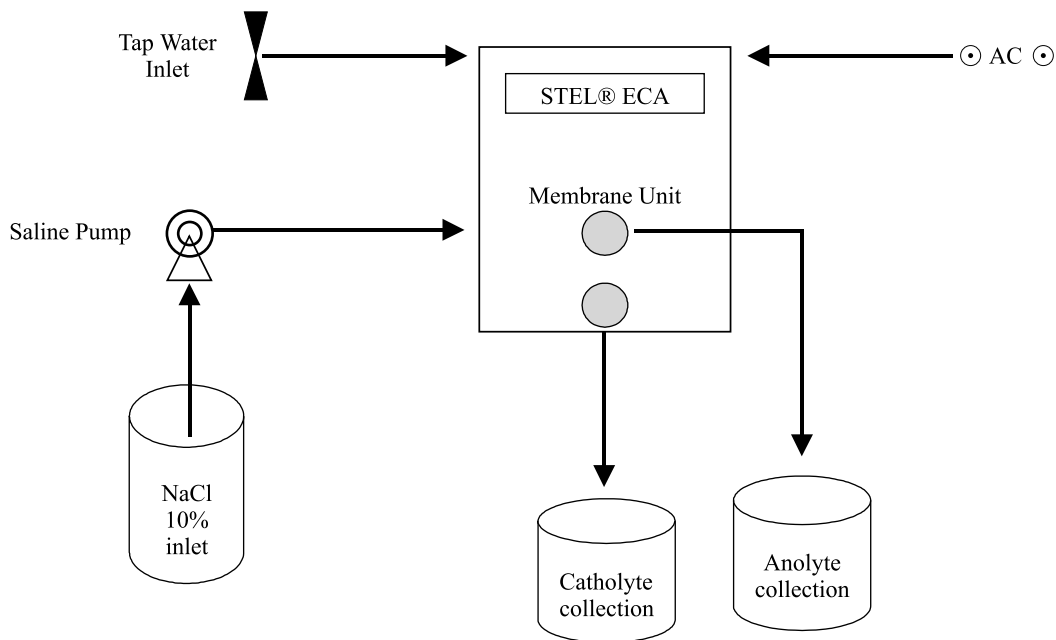


Figure 1. Schematic of ECA process used for producing anolyte

Characteristic of anolyte

The produced anolyte was colourless liquid with pH value of 2-3. As shown in Table 1, anolyte contains reactive ions and free radicals, which contribute to the powerful oxidizing properties. Despite its powerful properties, anolyte is non-toxic and harmless to human (Leonov, 1999).

Experimental Set Up

Experiments were conducted in 500 ml conical flask, each containing 300 ml of phenol solution. Phenol solutions ($C_i = 5, 10, 20, 50, 100 \text{ mg l}^{-1}$) were prepared from stock detached crystal phenol (Fisher, UK). Nano pure water (Barnstead, USA) was used for preparation of all solutions. Anolyte generated from

ECA system, was added to the phenol solutions in the range of 10 to 100 ml. To study the optimal reaction time between anolyte and phenol solutions, the optimal amount of anolyte for the removal of all phenol were added and allowed to remain in contact with the phenol solutions within 10 to 240 min.

Chemical Analysis

The quantitative analyses of the phenol and its oxidation products were determined using high-performance liquid chromatography (HPLC) and UV detector (254 nm). The samples were taken at appropriate time intervals and immediately analysed. The separation was performed using a reversed phase column (C18-ODS) at 25° C and

Table 1. Reactive ions and free radicals formed in the anolyte solution by electrochemical activation (Vlyssides et al., 1999; 2000)

Reactive Molecules	Reactive Ions	Reactive Free Radicals
O ₃	H ⁺	HO
O ₂	H ₃ O ⁺	OH ₂
H ₂ O ₂	OH ⁻	O ₂
ClO ₂	ClO ⁻	O
HClO	Cl ⁻	ClO
Cl ₂		Cl
HCl		
HClO ₃		

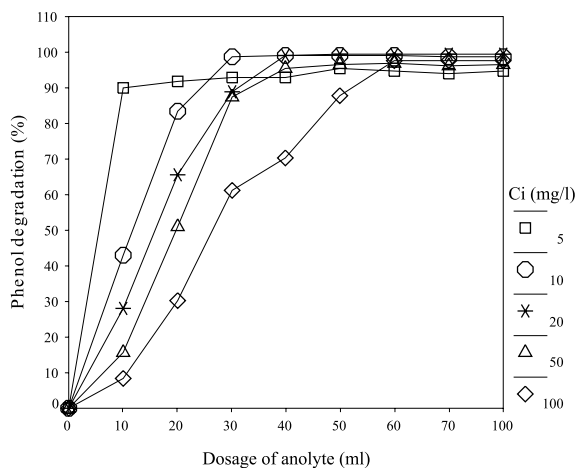


Figure 2. Effect of anolyte dosage on phenol degradation efficiency (reaction time: 60 min).

flow rate of $1.7 \text{ cm}^3 \text{ min}^{-1}$, running with mobile phase of acetonitril/water (v/v) at 60/40 + 0.1% H_3PO_4 . The organic acids were determined by ion chromatography with mobile phase of sodium carbonate (0.85 mmol l^{-1}) and sodium bicarbonate (0.90 mmol l^{-1}) with flow rate of $1.7 \text{ cm}^3 \text{ min}^{-1}$ at 35°C (Wu and Zhou, 2001).

Data Analysis

The term phenol degradation (%) is used to quantify the degree of water purification from phenol and is defined as the percentage of phenol removed from solution under the given experimental conditions. Phenol degradation (%) was calculated as

$$\text{Phenol degradation (\%)} = \left\{ \frac{C_o - C}{C_o} \times 100 \right\},$$

where C_o and C are initial and final phenol concentrations, respectively.

RESULTS AND DISCUSSION

Effect of anolyte dosage on phenol degradation

The phenol degradation at different dosage of anolyte is illustrated in Figure 2. As shown in Figure 2, increasing the dosage of anolyte up to 60 ml, produced very good removal of phenol (92-98%). However, the phenol degradation rate did not improve when the anolyte was increased from 60 ml to 100 ml. Therefore, 60 ml (20%) of anolyte was found to be the optimum dose for complete phenol degradation.

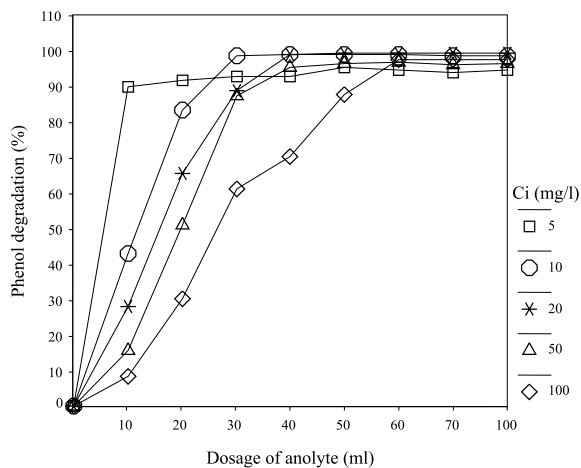


Figure 3. Effect of reaction time on phenol degradation efficiency (anolyte dosage: 60 mL)

Effect of reaction time on phenol degradation

Experiments were carried out to determine the reaction time of phenol with anolyte. Figure 3 shows the effect of reaction time on phenol degradation. As shown in Figure 3, degradation of phenol solutions using low concentration ($C_i=5, 10 \text{ mg l}^{-1}$), reached 98% within 10 minutes of reaction. While, in the case of higher phenol concentrations ($C_i=20, 50, 100 \text{ mg l}^{-1}$), 98% phenol degradation was achieved within 60 min of reaction time.

A comparison of phenol degradation using anolyte and other oxidizing agents revealed anolyte to be superior. For instance, Gurol *et al.* (1987) reported only 20 to 60% phenol degradation within 60 min using ozone and UV process. Others such as Miland *et al.* (1996) found that 98% phenol degradation could be achieved after 24 h upon addition of horseradish peroxidase (1 U cm^{-3}) and H_2O_2 (1 mmol dm^{-3}) to a solution of 94 mg dm^{-3} phenol. While our results showed that 60 min of reaction time was sufficient to achieve the 98% of phenol degradation.

Oxidation products

Chromatography results showed that the main products formed during the reaction of phenol with anolyte were benzoquinone (BQ), hydroquinone (HQ), catechol (CT), maleic acid, fumaric acid and oxalic acid. According to the results presented in Figure 4, the concentration of benzoquinone, hydroquinone and catechol in solution increased within the first 20 min and then rapidly

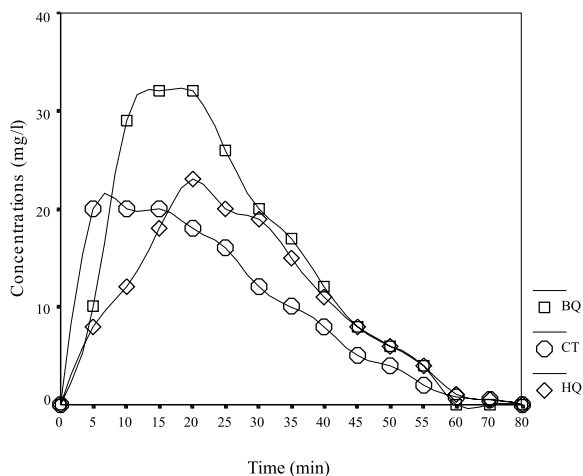


Figure 4. Cyclic products resulted from oxidation of phenol ($C_i=100 \text{ mg l}^{-1}$) using anolyte.

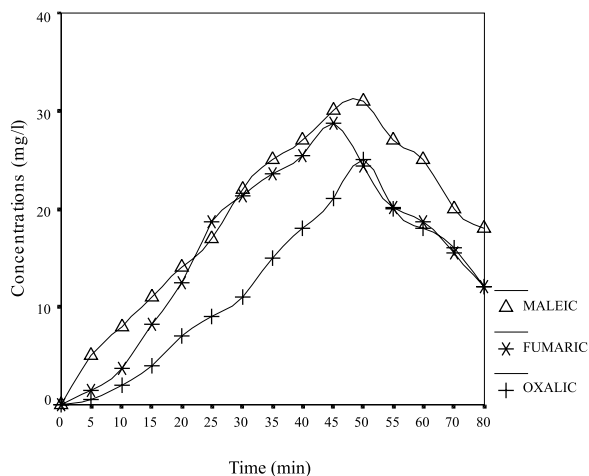


Figure 5. Aliphatic carboxylic acid products resulted from oxidation of phenol ($C_i = 100 \text{ mg l}^{-1}$) using anolyte.

decrease. It can be also seen that benzoquinone, hydroquinone and catechol are almost disappeared at 60 min (Figure 4).

This behavior could be due to the attack of free radicals on these compounds and resulting in ring opening reaction to form aliphatic organic acids. In Figure 5, it can be seen that, the concentration of aliphatic organic acids (maleic acid, fumaric acid and oxalic acid) rapidly increases during the first 45 min and then begins to decrease. Decrease of aliphatic organic acids could be due to mineralisation to CO_2 and H_2O (Fleszar and Ploszynska, 1985; Tahar and Salvall, 1998, 1999; Awad and Abuzaid, 2000; Wu and Zhou, 2001). A comparison of reaction products formed by phenol oxidation using anolyte in this study and other oxidation agents showed that the reaction products are almost the same (Gurol and

Vatistas, 1987; Esplugas *et al.*, 1994; Shen *et al.*, 1995; Benitez *et al.*, 2001). It implies that all reactions probably occur following the same mechanism, i.e. electrophilic attack of hydroxyl radical on the phenol or its oxidation product.

CONCLUSION

Degradation of phenol using anolyte produced by electrochemical process was found possible under an optimized condition. The 20% anolyte was found to be the optimal concentration giving 98% destruction of phenol after 60 minutes reaction time.

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