



# Application of Advanced Electrochemical Oxidation Processes for the Treatment of Phenolic Wastewater

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## Abstract

This paper investigates the impact of using advanced electrochemical oxidation processes (AEOP's) to degrade phenol in wastewater. For comparison purposes, the direct and the indirect oxidation processes were tested to treat synthetic phenolic solution in batch parallel plate electrochemical reactor with internal circulation. Successful application of the direct anodic oxidation experiments typically achieved once with graphite electrodes and then with  $\beta$ -PbO<sub>2</sub> anode and stainless steel cathode. Along with specific application of indirect electro-oxidation (electro-Fenton process) using sacrificed Fe anode and O<sub>2</sub> diffusion carbon felt cathode performs *in situ* electrogeneration of hydroxyl radical OH<sup>•</sup>. In all extensive experiments, sodium sulfate was used as supportive electrolyte to sufficient increase of conductivity. Considering each processes, the kinetic and therefore the reaction rate constant were significantly analyzed throughout the oxidation time. The phenol degradation efficiency has been investigated during the oxidation time with varied independent parameters like initial phenol concentration (100, 250,500) mg/L, applied current density (30, 50, 70) mAcm<sup>-2</sup> and electrolyte circulation (6, 9, 12) L/hr. It was estimated that, for 180 min oxidation time, 70 mAcm<sup>-2</sup> current density, 12 L/hr flowrate, and 100 mg/L initial phenol concentration, the direct anodic oxidation achieved phenol degradation efficiency of 74.4% and 83.7% with each graphite and  $\beta$ -PbO<sub>2</sub> anode, respectively. Otherwise, the indirect oxidation at the same condition achieved phenol degradation efficiency of 88.9% with Fe anode and carbon felt cathode.

## 1. Introduction

The human industrial activities have affected the surface and the ground waters quality day by day. Several industries such as textile, refineries, chemical, plastic and food-processing plants produce phenolic wastewaters. Such wastewaters usually have to be treated in order to minimize their organic and frequently quite toxic content. There are many recovery/reuse methods in water and wastewater treatment including incineration, adsorption, osmosis inverse, filtration, catalytic degradation, microbiological and chemical or electrochemical oxidation. The choice of the treatment depends on the economics, as well as the reliability and the treatment efficiency [1, 2].

One of the toxic organic pollutants is phenol (C<sub>6</sub>H<sub>5</sub>OH) and its derivatives. Phenols are probably the most extensive studied compounds with high toxicity that release in wastewaters. The presence of phenol in drinking water and irrigation water represents a serious health hazard to humans, animals, plants and microorganisms. Phenol is a potential carcinogen of a human, which raises considerable health concerns, even at low concentrations [3]. Therefore, the removal of phenol and its derivatives is significant in the environmental protection [4].

The interest in developing new and more efficient methods for destruction of hazardous waste such as phenol and the conversion of mixed waste to low level toxicity waste has significantly increased [5]. However, electrochemical oxidation methods could be used for aqueous wastes containing non-biodegradable organics such as phenol [6].

AEOP's typically provide the promising approaches for possible prevention of pollution problems. Advanced electrochemical oxidation processes (AEOP's) are well-known electrochemical producer of hydroxyl radical OH<sup>•</sup> oxidant. Hydroxyl radicals are highly oxidative agents, E<sup>o</sup>=2.80 V for mineralizing organic compounds [7]. Moreover, hydroxyl radicals OH<sup>•</sup> are reactive electrophiles (electron preferring) that react rapidly and non-selectively with nearly all electron-rich organic compounds [8].

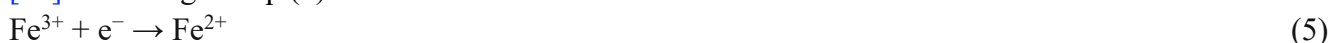
Electro-oxidation of pollutants can occur directly at anode. In anodic oxidation (AO), heterogeneous hydroxyl radicals M(OH<sup>•</sup>) are generated by electrochemical discharge of water Eq. (1) or OH<sup>-</sup> Eq. (2) on a high O<sub>2</sub> evolution overvoltage anode (M) [9].



The availability and efficiency of these radicals depend on anode material [10]. Indirect oxidation of pollutant can perform through different ways. One of the powerful and environmentally friendly emerging technologies for remediation of wastewater is electro-Fenton, especially hazardous organic pollutants [11]. In contrary, homogeneous hydroxyl radicals (OH<sup>•</sup>) are generating by electro-Fenton (EF) that based on the *in situ* and continuous electrogeneration of H<sub>2</sub>O<sub>2</sub> from two-electron reduction of O<sub>2</sub>. Peroxide reacts with the electrogenerated ferrous iron catalyst (Eq. 4) to form OH<sup>•</sup> [12].



The OH<sup>•</sup> thus formed will react with organic pollutants present in medium until their mineralization, i.e., transformation to CO<sub>2</sub>, H<sub>2</sub>O and inorganic ions [8]. One of the main advantages of this process is the electrocatalytic and continuous regeneration of ferrous iron from Fe<sup>3+</sup> produced by Fenton's reaction [13] according to Eq. (5):



The aim of this work is to comparatively assess phenol degradation in synthetic wastewater using the direct anodic oxidation (AO-graphite and AO- β-PbO<sub>2</sub>) and the indirect oxidation by electro-Fenton (EF process). Batch experiments were executed to investigate the effect of most significant parameters such as electrode type, current density, electrolyte circulation flowrate and initial phenol concentration on the degradation efficiency of phenol. Each of AO and EF processes employs batch parallel plate electrochemical reactor with internal circulation.

## 2. Material and Methods

### 2.1. Chemical

Wastewater samples containing 100, 250, and 500 mg/l of phenol have prepared by dissolving 50, 125, and 250 mg of laboratory grade phenol in 500 ml double distilled water. Sodium sulfate was added to wastewater forming 0.05 M supportive electrolyte of 2500 μs/cm electrical conductivity. However, all the used chemicals reagent grade were purchased from Merck, Germany, (phenol min. assay 98%, 4-aminoantipyrine C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O min. assay 99%, potassium ferricyanide III K<sub>3</sub>Fe(CN)<sub>6</sub> min. assay 99%, ammonium chloride NH<sub>4</sub>Cl purity >99%, sodium sulfate salt purity >99%, sulfuric acid H<sub>2</sub>SO<sub>4</sub> min. assay 98%, ammonia solution NH<sub>4</sub>OH 28-30%. Finally, some drops of concentrated analytical grade H<sub>2</sub>SO<sub>4</sub> or NH<sub>4</sub>OH could be used to control pH.

## 2.2. Electrodes

Some materials have purchased from local markets with specification: Iron plate C 2.1%, Stainless steel ANSI (304), Graphite sheet. Carbon felt has been supplied from (Shanghai Qijle Carbon Material Co. Ltd). The  $\beta$ -PbO<sub>2</sub> electrode was prepared from thick lead plate of purity 99.5%. Lead plate (after wash) was anodized under 40 mA cm<sup>-2</sup> current density in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution for 2 h and finally washed with distilled water. The  $\beta$ -PbO<sub>2</sub> material was tested by X-ray diffraction (XRD) analysis.

## 2.3. Equipment and procedure

Oxidation experiments have a variety of conditions using undivided parallel plate batch electrochemical reactor made of Teflon with dimensions (60×34×20) mm with hold-up of 40.8 cm<sup>3</sup>. The anode and the cathode were positioned vertically and parallel to each other with an inner interelectrode gap of 1 cm (Figure 1). The charge would be supplied by galvanostatic transient technique, where the anode has been connected directly to a rheostat (Cambridge 0.8Ω-30kΩ) and then to multi-range ammeter (DT830-D Hewlett-Packard) to limit and measure the applied anodic current. Conversely, the cathode was connected directly to a DC power supply (MCH-305DII, 30V, 5A, China).

Starting from the agitated reservoir, the electrolyte was often pumped to the feed tank, using solenoid dosing pump (Microdos ME1-CA, Italy), then enter the reactor and return back into a closed loop. The recycled electrolyte in the reservoir can even be agitated with mechanical stirrer (RW 16 basic-UK). A digital thermometer (VWR type) and pH meter (Model 3540 Jenway-UK) were appropriately introduced into the reservoir to precisely measure the temperature and pH.

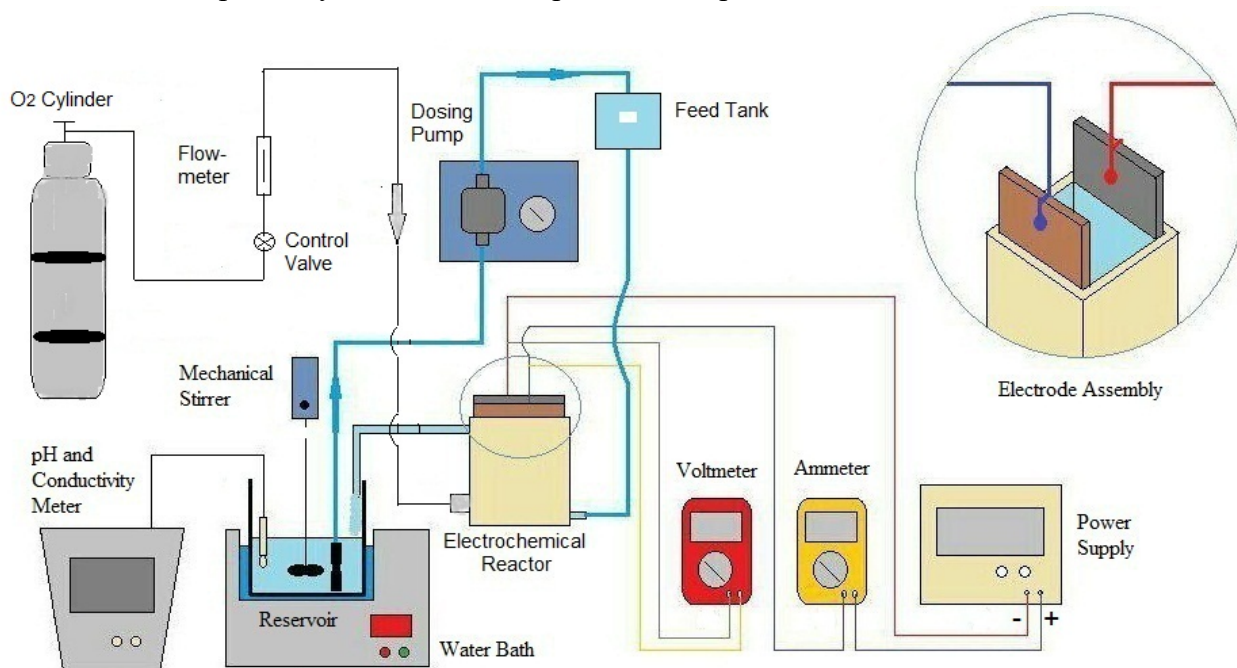


Figure 1: Schematic of experimental set up

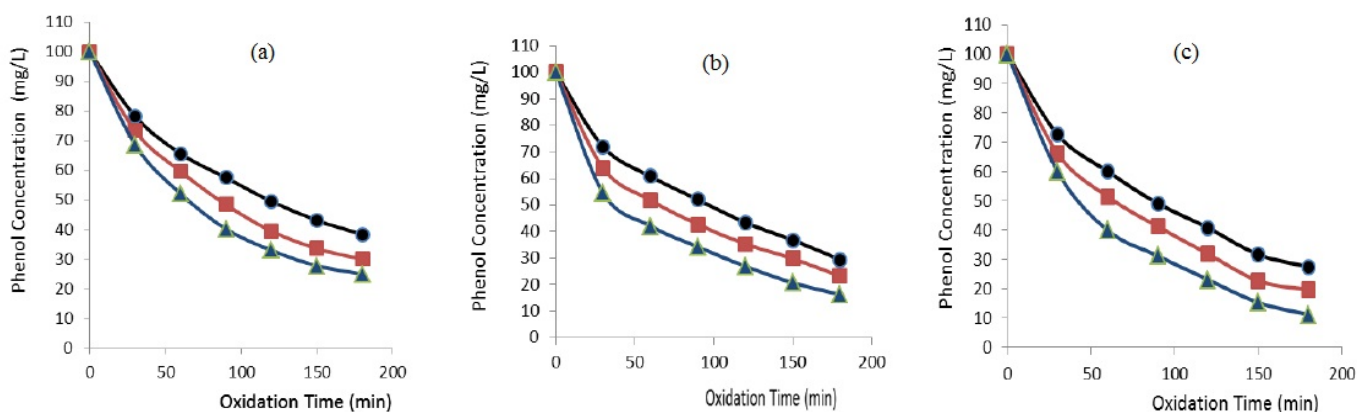
A sample of 5 ml withdraws by standard pipette from the reservoir at every 30 min along the oxidation time. Further, in electro-Fenton experiments a source of pure O<sub>2</sub> and flowmeter were properly positioned. However, phenolic materials react with 4-aminoantipyrine on presence of K<sub>3</sub>Fe(CN)<sub>6</sub> at pH 10 to form a stable reddish-brown colored antipyrine dye. The phenolic concentration was estimated according to the standard methods for examination of water and wastewater (1999) Method 5530 D [14]. The absorbance measurement would be determined by double-beam UV-6800 model spectrophotometer (Jenway, Staffordshire, UK).

### 3. Results and discussion

#### 3.1. Effect of electrode type on oxidative degradation of phenol

The behavior of electrode pair graphite/graphite and  $\beta$ -PbO<sub>2</sub>/St-St has been tested for AO process. The achievement of the anodes would be analyzed and then compared at the same condition in order to optimize the degradation of phenol in solution. All experiments have carried out with 500 mL of 100, 250, 500 mg/L phenol concentration at pH 7.0. The decay kinetics of phenol concentration with the heterogeneous oxidant (OH<sup>•</sup>)/M(OH<sup>•</sup>) generated by AO process was estimated at current densities 30, 50 and 70 mAcm<sup>-2</sup> with 0.050 M of Na<sub>2</sub>SO<sub>4</sub> supportive electrolyte.

Figure 2 shows the efficiency of the oxidative degradation of phenol by AO process using graphite and  $\beta$ -PbO<sub>2</sub> anodes and EF process with Fe anode and carbon felt cathode. In these two cases, the best degradation of phenol at  $i = 70$  mAcm<sup>-2</sup> was attained after 180 min with  $\beta$ -PbO<sub>2</sub> and Fe anode. Furthermore, Fig. 2 also shows the effect of the applied current on the behavior of degradation curves of phenol oxidation by the homogeneous (OH<sup>•</sup>) generated by EF process. The required oxidation time for most phenol degradation was getting shorter when the applied current density was higher.



**Figure 2:** Effect of applied current density on phenol degradation with different processes. Conditions: current density ● 30 mAcm<sup>-2</sup>, ■ 50 mAcm<sup>-2</sup>, ▲ 70 mAcm<sup>-2</sup>; [Ph]<sub>0</sub> = 100 (mg/L); Na<sub>2</sub>SO<sub>4</sub> 0.05 M; pH 7; temp. 25°C; flow rate 12 L/hr: (a) represent AO-graphite process (b) represent AO- $\beta$ PbO<sub>2</sub> (c) represent EF process.

However, this time is comparatively similar for both anodes in AO under the same operating conditions. These results could be clarified by increasing the rate of electrochemical reactions (1) and (2) and supporting the create of excessive amount of (OH<sup>•</sup>)/M(OH<sup>•</sup>) or (OH<sup>•</sup>) and prompting to the quick oxidation of phenol.

On the other hand, the observed valuable effect of current ascent progress toward becoming non-noteworthy for current densities over 70 mAcm<sup>-2</sup>. This phenomenon could be interpreted by the gradual enhancement of the rate of side reactions such as the OH<sup>-</sup> oxidation or the evolution of O<sub>2</sub> and H<sub>2</sub> gases at the anode and the cathode, respectively.

In EF process (Fig. 2) the use of peroxi-coagulation method is based on utilizes of sacrificial Fe anode. This anode is electrodisolved supplying stoichiometric amounts of Fe<sup>2+</sup> ions to the bulk and has a higher degradation power allowing remove more of pollutant [15].

Fe<sup>2+</sup> ions merely reacts with the *in situ* electrogenerated H<sub>2</sub>O<sub>2</sub> produced by O<sub>2</sub> diffusion cathode (carbon felt) and the excess of Fe<sup>3+</sup> formed precipitates as Fe(OH)<sub>3</sub>. Phenol and its derivative are then expected to be degraded by the unified action of their homogeneous oxidation with OH<sup>•</sup> generated by reaction (4) and their coagulation with the Fe(OH)<sub>3</sub> precipitate.

### 3.2. Effect of applied current density on phenol degradation efficiency

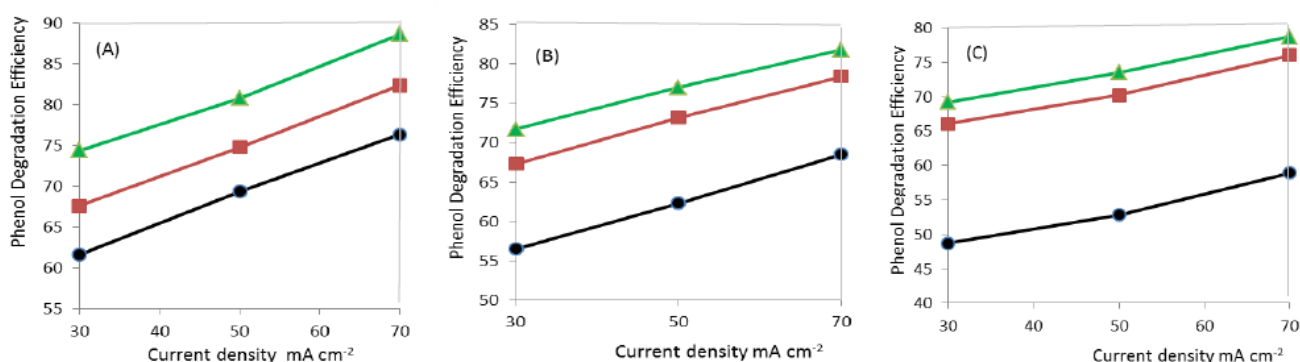
Among various operation parameters that affected the efficiency of phenol oxidation, current density seems to be the most key factor to control reaction rate. Different current densities have been studied to investigate its effect on the direct and the indirect oxidation of phenol. To clarify the effect of current density on phenol degradation efficiency, many experiments got to be complete realized using AO-graphite, AO- $\beta$ PbO<sub>2</sub> and EF processes for the applied current densities of 30, 50 and 70 mAcm<sup>-2</sup> as shown in Figure 3.

AO resulted that, the phenol degradation efficiency increased with marked increase in current density due to release of heterogeneous graphite(OH<sup>•</sup>) or  $\beta$ -PbO<sub>2</sub>(OH<sup>•</sup>) at the anode surface. The highest phenol degradation efficiency of 74.4% for graphite and 83.7% for  $\beta$ -PbO<sub>2</sub> obtained at 70 mAcm<sup>-2</sup> current density, 100 mg/L initial phenol concentration and 12 L/hr flow rate.

The relatively lower degradation kinetics of AO-graphite process could explain by the enhancement of the parasitic reaction Eq. (6):



Where, the observed increase of applied current density reduces the H<sub>2</sub>O<sub>2</sub> generation in the reactor. In contrary, possible creation of more  $\beta$ -PbO<sub>2</sub>(OH<sup>•</sup>) radical at high current density, as in AO- $\beta$ PbO<sub>2</sub> process, recovers the loss of efficiency in the bulk of solution.



**Figure 3:** Effect of applied current density on phenol degradation efficiency. Conditions: (A) [Ph]<sub>0</sub> = 100 mg/L; (B) [Ph]<sub>0</sub> = 250 mg/L; (C) [Ph]<sub>0</sub> = 500 mg/L; ● AO-graphite, ■ AO-  $\beta$ PbO<sub>2</sub>, ▲ EF process; Na<sub>2</sub>SO<sub>4</sub> 0.05 M; pH 7; temp. 25°C; flow rate 12 L/hr.

The obtained phenol degradation efficiency through indirect oxidation increased with the increasing of current density, however for this case, due to release of homogeneous OH<sup>•</sup> with more significant quantity to the bulk of solution according to Eq. (1). The indirect oxidation gave the best phenol degradation efficiency of 88.9% with Fe anode versus carbon felt cathode at 70 mAcm<sup>-2</sup> current density, 100 mg/L initial phenol concentration and 12 L/hr flow rate. Moreover, the indirect oxidation by EF at high current density promoted H<sub>2</sub>O<sub>2</sub> generation with Eq. (7):



It is noteworthy to remark, that the formed H<sub>2</sub>O<sub>2</sub> from Eq. (7) with ferrous Fe<sup>2+</sup> generated from Eq. (3), lead to the formation of more OH<sup>•</sup> according to Eq. (4). However, OH<sup>•</sup> formation reaction enhances the higher degradation efficiency in acidic medium with pH 3. The excess of Fe<sup>2+</sup> ions precipitates as hydrated Fe(III) oxide (Fe(OH)<sub>3</sub>). The oxidation products could then be expelled by mineralization or coagulation by the formed Fe(OH)<sub>3</sub> precipitate. In contrast to AO, degradation kinetics of phenol in EF process was significantly higher, with the applied range of current density.

However, by the compare of oxidation time at  $70 \text{ mA cm}^{-2}$ ,  $\text{OH}^\bullet$  radicals in EF process are predominantly formed at the bulk of the electrolyte rather at anode surface. Hence, the oxidation power of the tried AEOPs extends in the sequence  $\text{EF} > \text{AO-}\beta\text{PbO}_2 > \text{AO-graphite}$ .

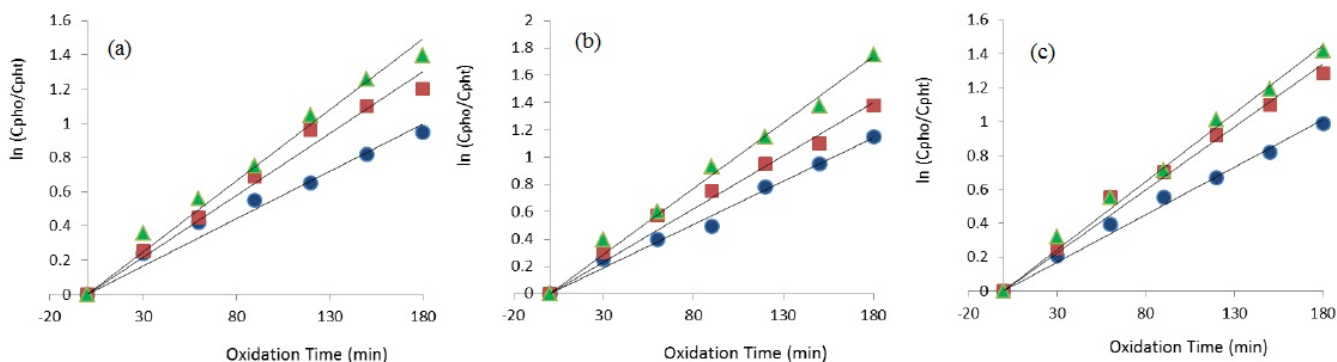
Obviously, these states of oxidation occur at high applied current density of more than the limiting one and this case said to be diffusion transfer behavior. However, the current efficiency permanently decreased during oxidation time being less than 100% for AO-graphite, AO- $\beta\text{PbO}_2$  and EF processes, confirmed that the phenol degradation work under mass transfer control [16].

### 3.3. Kinetic study of phenol degradation

The phenol concentration decay would be comfortably fitted to pseudo-first-order reaction kinetics, as well confirmed by Polcaro and Palmas, 1997 [17]) with the all tested processes. Principally, the apparent rate constant  $K_{app}$  of the oxidation reaction of phenol was determined with Eq. (8):

$$\ln \frac{C_{pho}}{C_{pht}} = K_{app} t \quad (8)$$

The  $K_{app}$  values have been estimated by plotting  $\ln(C_{pho}/C_{pht})$  versus time. As shown in Figure 4, the correlation coefficients ( $R^2$ ) for the straight lines of more than 98.8%. This reaction order could be justified by the life time of  $\text{OH}^\bullet$  radical depends on the activity of anode type. However, for non- active electrode, it has been proposed that  $\text{OH}^\bullet$  cannot combine with the anode surface and then, during a very short time, they are available to oxidize organics [18]. This explains the formation of radical oxidant and the efficiency change depends on anode type.



**Figure 4:** Linearized concentration profiles of phenol as a function of oxidation time with different processes. Condition; applied current density  $\bullet$   $30 \text{ mAcm}^{-2}$ ,  $\blacksquare$   $50 \text{ mAcm}^{-2}$ ,  $\blacktriangle$   $70 \text{ mAcm}^{-2}$ ;  $[\text{Ph}]_0 = 100 \text{ mg/L}$ ; electrolyte  $0.05 \text{ M Na}_2\text{SO}_4$ ;  $\text{pH}=7$ ; temp.  $25^\circ\text{C}$ ; flow rate  $12 \text{ L/hr}$ : (a) represent AO-graphite process (b) represent AO- $\beta\text{PbO}_2$  (c) represent EF process.

The results presented in Table 1 (obtained from Fig. 2) at the same current density confirm that the oxidation ability follows the order  $\text{EF} > \text{AO-}\beta\text{PbO}_2 > \text{AO-graphite}$ , indicating that peroxi-coagulation electrodes and the  $\beta\text{-PbO}_2$  anode have the larger oxidizing power than graphite anode.

From the comparative values of  $K_{app}$  for phenol oxidation by each OA and EF processes, one can remark that, the  $K_{app}$  increased at higher current density and lower phenol content. Furthermore, the oxidation efficiency is mainly affected by the current density and the type of the anode. Graphite and  $\beta\text{-PbO}_2$  anodes provided almost similar oxidation efficiencies in AO process, while the scarified Fe anode supplies better oxidation rate in EF process.

The  $K_{app}$  values are relatively limited in the case of AO when using  $\text{Na}_2\text{SO}_4$  as supporting electrolyte. This behavior could be explained by the oxidation of  $\text{SO}_4^{2-}$  ion to  $(\text{SO}_4^-)^\bullet$  radical as in Eq. 9, [19]:



These radicals could be combined, according to reaction (Eq. 10), which explains occurring of stable oxidants in the reaction media, including peroxosulfate [20]:



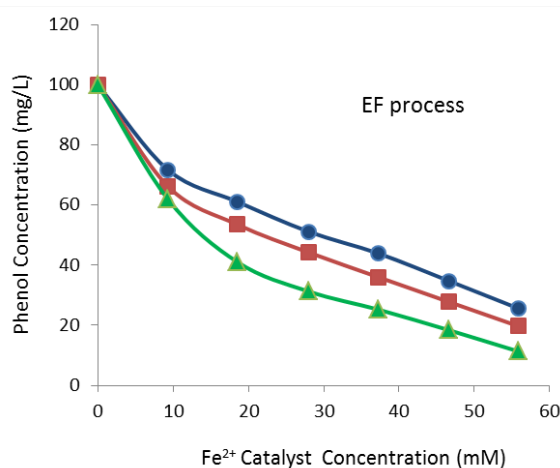
**Table 1:** Apparent rate constant of phenol degradation by different current densities (100 mg/L initial phenol concentration, flow rate 12 L/h)

Current density (mAcm <sup>-2</sup> )	$K_{app}$ (min <sup>-1</sup> ) EF	$K_{app}$ (min <sup>-1</sup> ) AO-βPbO <sub>2</sub>	$K_{app}$ (min <sup>-1</sup> ) AO-graphite
30	0.0068	0.0062	0.0051
50	0.0083	0.0074	0.0067
70	0.0150	0.0094	0.0072

### 3.4. Effect of Fe<sup>2+</sup> Catalyst on Phenol Degradation

Catalyst concentration (i.e., Fe<sup>2+</sup> ions) is an important parameter influencing EF process efficiency, particularly in the case of peroxi-coagulation. Figure 5 shows the degradation of 100 mg/L initial phenol aqueous solution of pH 3, as function of Fe<sup>2+</sup> catalyst in EF experiments. This Figure explains the behavior of peroxi-coagulation method with iron Fe/carbon felt electrodes at current densities 30, 50, and 70 mAcm<sup>-2</sup>. The Fe<sup>2+</sup> catalyst concentrations ranging from 9.3 mM generated at the first 30 min to 55.9 mM through the entire time of oxidation (180 min).

At optimum pH condition (pH=3.0), Fenton process takes place according to Eq. (4) [13, 3] to generate OH<sup>•</sup> reacting with phenol. Therefore, the rate of OH<sup>•</sup> generation is entirely controlled by the rate of electrochemical generation of Fe<sup>2+</sup> from Eq. (4) [16].



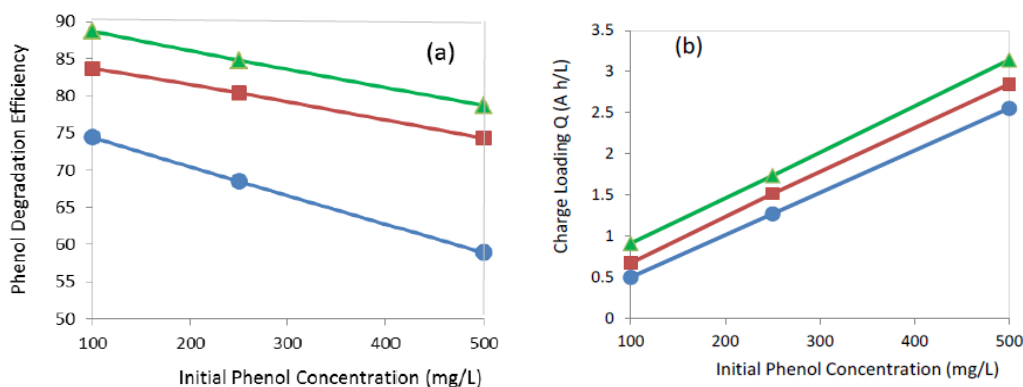
**Figure 5:** Effect of Fe<sup>2+</sup> catalyst concentration generated during EF process for phenol degradation. Condition; current density ● 30 mAcm<sup>-2</sup>, ■ 50 mAcm<sup>-2</sup>, ▲ 70 mAcm<sup>-2</sup>; [Ph]<sub>0</sub> =100 mg/L; oxidation time 180 min; electrolyte 0.05 M Na<sub>2</sub>SO<sub>4</sub>; pH=7; temp. 25°C; flow rate 12 L/hr.

Figure 5 shows that the concentration of phenol decayed in steep descent using current density 70 mA cm<sup>-1</sup>, where Fe<sup>2+</sup> catalyst concentration increased with the increasing of current. Hence, the phenol degradation efficiency increased predominately with the increasing of Fe<sup>2+</sup> concentration. The degradation was significantly fasted down with 20 mM Fe<sup>2+</sup>; 60 min required for most oxidation of phenol, while 180 min produces enough excess with 55.9 mM Fe<sup>2+</sup> catalyst.

Generally, the efficiency of EF increases with  $\text{Fe}^{2+}$  catalyst increase, because the  $[\text{OH}^{\bullet}]$  radicals increase with the increasing in  $\text{Fe}^{2+}$  concentration. These results agreed to large extent with Nidheesh and Gandhimathi, 2012 [11]. On the other hand, some researchers stated that excess ferrous ions in the electrolyte solution could consume the  $\text{OH}^{\bullet}$  radicals and influence the extent of degradation [13].

### 3.5. Effect of Initial Phenol Concentration

Phenol solutions of different initial concentrations of 100, 250 and 500 mg/L used to investigate their effect on degradation efficiency. For comparison purposes the degradation of phenol via AO-graphite, AO- $\beta\text{PbO}_2$  and EF processes have been studied. As a result, the phenol degradation efficiency for the direct and therefore the indirect oxidation will increase in step with the decrease of initial phenol concentration, as shown in Figure 6 (a). Conversely, the reaction time for complete conversion decreases with the decrease of initial phenol concentration.



**Fig. 6.** (a) Effect of initial phenol concentration on degradation efficiency. (b) Effect of initial phenol concentration on charge loading. Conditions: ● AO-graphite, ■ AO- $\beta\text{PbO}_2$ ; ▲ EF process; current density  $70 \text{ mAcm}^{-2}$ ;  $\text{Na}_2\text{SO}_4$  0.05 M; pH 7; temp.  $25^\circ\text{C}$ ; flow rate 12 L/hr.

Results appeared that, the degradation efficiencies of 74.4% and 83.7% for AO-graphite and AO- $\beta\text{PbO}_2$ , respectively, could be obtained at 100 mg/L initial phenol concentration, 12 L/hr flow rate and  $70 \text{ mAcm}^{-2}$  current density. While at the same condition, a degradation efficiency of 88.9 was recorded for EF process. The decrease on degradation efficiency with an initial phenol concentration up to 500 (mg/L), reported values of 58.9%, 74.3% and 78.7% for AO-graphite, O- $\beta\text{PbO}_2$ , and EF processes, respectively. However, with an increase of initial phenol concentration, more intermediate products could be formed. Most literature stated that at the higher initial phenol concentration, the removal of intermediate products would be much more difficult and slower oxidized [3, 8, and 21].

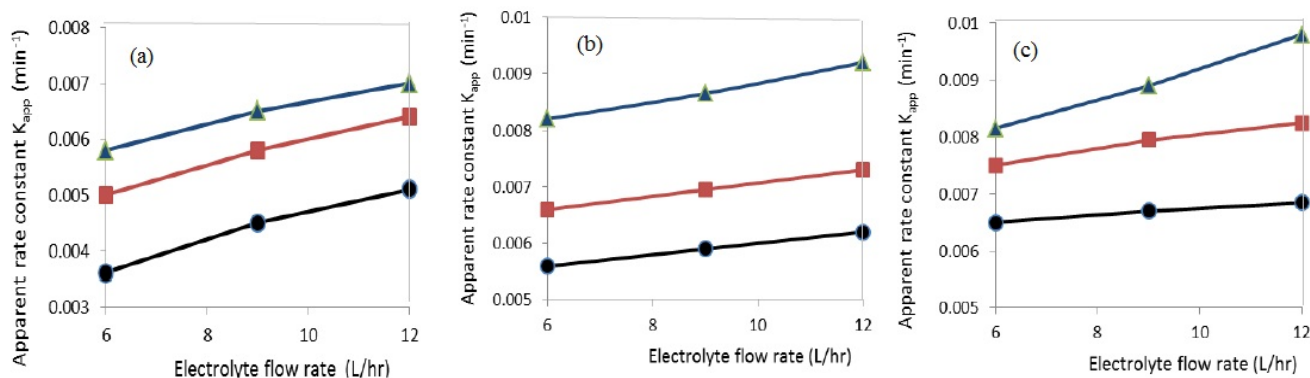
The experimental results of charge loading ( $Q$ ) variation at different initial phenol concentration with the same operating condition are showing in Figure 6 (b). The result shows that the charge loading has low starting values 0.494, 0.668, and 0.908 A h/L for AO-graphite, AO- $\beta\text{PbO}_2$  and FE process, respectively. As seen from Figure, when the initial phenol concentration increased to 500 mg/L, the same increment of ( $Q$ ) could be obtained for each tested process giving high final charge loading values 2.551, 2.845 and 3.141 A h/L for AO-graphite, AO- $\beta\text{PbO}_2$  and EF process, respectively. Figure 6 (a) and Figure 6 (b) confirm the above-mentioned trends.

As expected, the phenol degradation efficiency was inversely proportional to the initial phenol concentration. This might be proper to the available of constant amount of  $\text{OH}^{\bullet}$  radicals irrespective of the phenol concentration and hence, the degradation rate was decreased. However, these results are in good agreement with Gümüs and Akbal, 2016 [3].



### 3.6. Effect of Circulation Rate on kinetic of Phenol Degradation

The volumetric flowrate of continuous system expresses the hydraulic residence time of wastewater in the oxidation system. But, in batch system with internal circulation, the hydraulic residence time, in this case, is the time to keep the wastewater in a system. The effect of electrolyte internal circulation on phenol degradation has been studied with flowrates 6, 9, and 12 L/hr for total (oxidation/residence) time 180 min. Figure 7 shows the apparent rate constant  $K_{app}$  of phenol degradation versus electrolyte flow rate for AO-graphite, AO- $\beta$ PbO<sub>2</sub> and EF processes with an initial phenol concentration 100 mg/L.



**Figure 7:** Effect of circulation flow rate on apparent rate constant of phenol degradation by different processes. Conditions: current density ●30 mAcm<sup>-2</sup>, ■ 50 mAcm<sup>-2</sup>, ▲ 70 mAcm<sup>-2</sup>; [Ph]<sub>0</sub> = 100 mg/L; Na<sub>2</sub>SO<sub>4</sub> 0.05 M; pH 7; temp. 25°C: (a) represent AO-graphite process (b) represent AO- $\beta$ PbO<sub>2</sub> process (c) represent EF process.

In the present work it was found that, the phenol degradation efficiency increased with the increasing of electrolyte internal circulation. It can be seen from Figure 7 that the increase of electrolyte circulation flow rate from 6 to 12 L/hr could increase the apparent rate constant of 10-20% depending on the type of process. Thus, for the examined parameters, the flow velocity may appreciably affect the reaction kinetics; in fact, in the examined range of velocities, where the reaction is under mass transfer control. It must also be mentioned that the increasing of apparent rate constant depends largely on the type of oxidation process and the type of anode [9, 10, and 12].

Principally, the increasing of electrolyte circulation flow rate could increase the homogeneity of solution and the diffusivity of phenol at the surface of the anode, so increasing the oxidation reaction. EF process was positively the most process influenced by increasing the circulation flow rate of the electrolyte. At largest current density, it was found that  $K_{app}$  of AO-graphite and AO- $\beta$ PbO<sub>2</sub> processes increased by 10 % with increasing circulation flow rate from 6 to 12 L/hr at the same condition. In contrast, the  $K_{app}$  of EF process increased by  $\geq 17\%$  with increasing flow rate from 6 to 12 L/hr also at the same operating condition.

## Conclusions

Phenol degradation was investigated using direct anodic oxidation process and indirect oxidation of electro-Fenton process. For comparison purposes, processes of AO-graphite, AO-  $\beta$ PbO<sub>2</sub> and peroxi-coagulation were studied in accordance to several experimental parameters like initial phenol concentration, current density, oxidation time, and electrolyte circulation flow rate. The investigation of the mentioned processes for phenol degradation leads to the following conclusions:

The examination of the behavior of both chlorophenols leads to some final considerations:

1. Advanced electrochemical oxidation processes (AEOP's) were proved as effective techniques to treat synthetic phenolic wastewater of concentration 100, 250 and 500 mg/L.

2. A reasonable degradation of phenolic material could be achieved using AO-  $\beta\text{PbO}_2$  process and EF process (peroxi-coagulation method). Phenol degradation efficiency of 83.7% and 88.9% was predicated for  $\beta\text{PbO}_2$  and EF processes, respectively, at 100 mg/L initial phenol concentration, electrolyte circulation flow rate 12 L/hr and current density 70  $\text{mAcm}^{-2}$ . In addition, the results explained that the impact of  $\text{Fe}^{2+}$  catalyst concentration on phenol degradation as an important parameter influencing EF process.
3. The phenol degradation efficiency increases with increasing of current density and electrolyte circulation flow rate. Conversely, the phenol degradation efficiency decreases with the increasing of initial phenol concentration.
4. The phenol degradation reaction could follow a pseudo first-order reaction kinetic with AO-graphite, AO-  $\beta\text{PbO}_2$  and EF processes, but of conflicting values of apparent rate constant. In addition, confirmatory experiments showed that the phenol degradation efficiency cause excessive apparent rate constant  $K_{app}$  that increase proportionally with the marked increase of current density.
5. The effect of initial phenol concentration on charge load to the reactor was also investigated and resulted in such a way that the increasing of initial phenol concentration would allow to more charge required.

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