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A Comparative Study on Phenolic Wastewater Treatment by Advanced Electrochemical Oxidation Processes

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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 a 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 β-PbO_2 anode and stainless steel cathode. Along with the specific application of indirect electro-oxidation (electro-Fenton process) using sacrificed Fe anode and O_2 diffusion carbon felt cathode performs *in situ* electrogeneration of hydroxyl radical $OH^{\bullet}$. In all extensive experiments, sodium sulfate was used as a supportive electrolyte to sufficient increase conductivity. Considering each process, the kinetic and therefore the reaction rate constant was 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) $mAcm^{-2}$, and electrolyte circulation (6, 9, 12) L/hr. It was estimated that, for 180 min oxidation time, 70 $mAcm^{-2}$ current density, 12 L/hr flowrate, and 100 mg/L initial phenol concentration, the direct anodic oxidation achieved phenol degradation efficiency of 74.4% with graphite and 83.7% with β-PbO_2 anodes. Otherwise, the indirect oxidation at the same condition achieved phenol degradation efficiency of 88.9% with Fe anode and carbon felt cathode.

Keywords: AEOP, Anodic Oxidation (AO), Electro-Fenton (EF), Phenol, Radical ($OH^{\bullet}$)

1 Introduction

Human industrial activities have affected the surface and the groundwaters' 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 to minimize their organic and frequently quite toxic content. There are many recovery/reuse methods in water and wastewater treatment including incineration, adsorption, biological treatment, and chemical or electrochemical oxidation. The choice of the treatment depends on the economics, as well as the reliability and the treatment efficiency [1].

One of the toxic organic pollutants is phenol (C_6H_5OH) and its derivatives. Phenols are probably the most extensively 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 [2]. It was found that phenol could be almost completely converted to organic aromatic products (hydroquinone, benzoquinone, and catechol). Therefore, the removal of phenol and its derivatives is significant in environmental protection [3]. The interest in developing new and more efficient methods for the destruction of hazardous waste such as phenol and the conversion of mixed waste to low-level toxicity waste has significantly increased [4]. However, electrochemical oxidation methods could be used for aqueous wastes containing non-biodegradable organics such as phenol [5]. Advanced electrochemical oxidation processes (AEOP's) are the well-known electrochemical producer of hydroxyl radical $OH^{\bullet}$ oxidants. Hydroxyl radicals are highly oxidative agents, E°=2.80 V for mineralizing organic compounds [6]. Moreover, hydroxyl radicals $OH^{\bullet}$ are reactive electrophiles (electron preferring) that react rapidly and non-selectively with nearly all electron-rich organic compounds [7]. Electro-oxidation of pollutants can occur directly at the anode. In anodic oxidation (AO), heterogeneous hydroxyl radicals $M(OH^{\bullet})$ are generated by the electrochemical discharge of water Eq. (1) or OH^- Eq. (2) on a high O_2 evolution overvoltage anode (M) [8].

$$M + H_2O \rightarrow M(OH^{\bullet})_{ads} + H^+ + e^- \quad (1)$$

$$M + OH^- \rightarrow M(OH^{\bullet})_{ads} + e^- \quad (2)$$

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The availability and efficiency of these radicals depend on anode material [9]. Indirect oxidation of pollutants can perform in different ways. One of the powerful and environmentally friendly emerging technologies for remediation of wastewater is electro-Fenton, especially hazardous organic pollutants [10]. On contrary, homogeneous hydroxyl radicals ($OH^{\bullet}$) are generating by electro-Fenton (EF) based on the *in situ* and continuous electrogeneration of H_2O_2 from a two-electron reduction of O_2. The peroxide reacts with the electrogenerated ferrous iron catalyst (Eq. 4) to form $OH^{\bullet}$ [11]:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (3)$$

$$Fe^{2+} + H_2O_2 + H^{+} \rightarrow Fe^{3+} + OH^{\bullet} + H_2O \quad (4)$$

The $OH^{\bullet}$ thus formed will react with organic pollutants present in the medium until their mineralization, i.e., transformation to CO_2, H_2O, and inorganic ions [7]. One of the main advantages of this process is the electrocatalytic and continuous regeneration of ferrous iron from Fe^{3+} produced by Fenton's reaction [12] according to Eq. (5):

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (5)$$

This study aims to compare phenol degradation efficiencies in synthetic wastewater using direct anodic oxidation (AO-graphite and AO- β-PbO_2) and indirect oxidation by electro-Fenton (EF process). Batch experiments were executed to investigate the effect of the most significant parameters on the degradation efficiency of phenol, such as electrode type, current density, electrolyte circulation flowrate, and initial phenol concentration. The batch parallel plate electrochemical reactor with internal circulation is used in both the AO and EF processes.

2 Materials and methods

2.1. Chemicals

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 a 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 $C_{11}H_{13}N_3O$ min. assay 99%, potassium ferricyanide III $K_3Fe(CN)_6$ min. assay 99%, ammonium chloride NH_4Cl purity >99%, sodium sulfate salt purity >99%, sulfuric acid H_2SO_4 min. assay 98%, ammonia solution NH_4OH 28-30%. Finally, some drops of concentrated analytical grade H_2SO_4 or NH_4OH could be used to control pH.

2.2. Electrodes

Some materials were purchased from local markets with the following specifications: Iron plate C 2.1%, Stainless steel ANSI (304), Graphite sheet. Carbon felt has been supplied from (Shanghai Qijle Carbon Material Co. Ltd). The β-PbO_2 electrode was prepared from a thick lead plate of purity 99.5%. Lead plate (after wash) was anodized under 40 mA cm^{-2} current density in 0.1 M H_2SO_4 solution for 2 h and finally washed with distilled water. The β-PbO_2 material was tested by X-ray diffraction (XRD) analysis.

2.3. Equipment and procedure

Oxidation experiments have a variety of conditions using an undivided parallel plate batch electrochemical reactor made of Teflon with dimensions (60×34×20) mm with hold-up of 40.8 cm^3. The anode and the cathode were positioned vertically and parallel to each other with an inner interelectrode gap of 1 cm (Fig.1). The charge would be supplied by galvanostatic transient technique in which the anode has been connected directly to a rheostat (Cambridge 0.8Ω-30kΩ) and then to a 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).

The electrolyte is frequently pumped from the agitated reservoir to the feed tank using a solenoid dosing pump (Microdos ME1-CA, Italy), then enters the reactor and back into a closed loop. The recycled electrolyte in the reservoir can even be agitated with a 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.

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_2 and flowmeter were properly positioned. However, in the presence of $K_3Fe(CN)_6$ at pH 10, phenolic materials react with 4-aminoantipyrine to form a stable reddish-brown colored antipyrine dye. The phenolic concentration was estimated according to the standard methods for the examination of water and wastewater method 5530 D [13]. The absorbance measurement would be determined using a double-beam UV-6800 model spectrophotometer (Jenway, Staffordshire, UK).

3. Results and discussion

3.1. Effect of electrode type on oxidative degradation of phenol

For the AO process, the behavior of electrode pair graphite/graphite and β-PbO_2/St-St has been tested. The performance of the anodes would be analyzed and compared under the same conditions. 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 ($OH^{\bullet}$)/M($OH^{\bullet}$) generated by the AO process was estimated at current densities 30, 50, and 70 $mAcm^{-2}$ with 0.050 M of Na_2SO_4 supportive electrolyte.

Fig. 2 shows the efficiency of the oxidative degradation of phenol by AO process using graphite and β-PbO_2 anodes and EF process with Fe anode and carbon felt cathode. In these two cases, the best degradation of phenol at i =70 $mAcm^{-2}$ was attained after 180 min with β-PbO_2 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 ($OH^{\bullet}$) generated by the EF process. The required oxidation time for most phenol degradation was getting shorter when the applied current density was higher. However, this time is comparatively similar for both anodes in the AO process under the same operating conditions. These results could be clarified by increasing the rate of electrochemical reactions (1) and (2) and supporting the creation of excessive amount of ($OH^{\bullet}$)/M($OH^{\bullet}$) or ($OH^{\bullet}$) and prompting the quick oxidation of phenol.

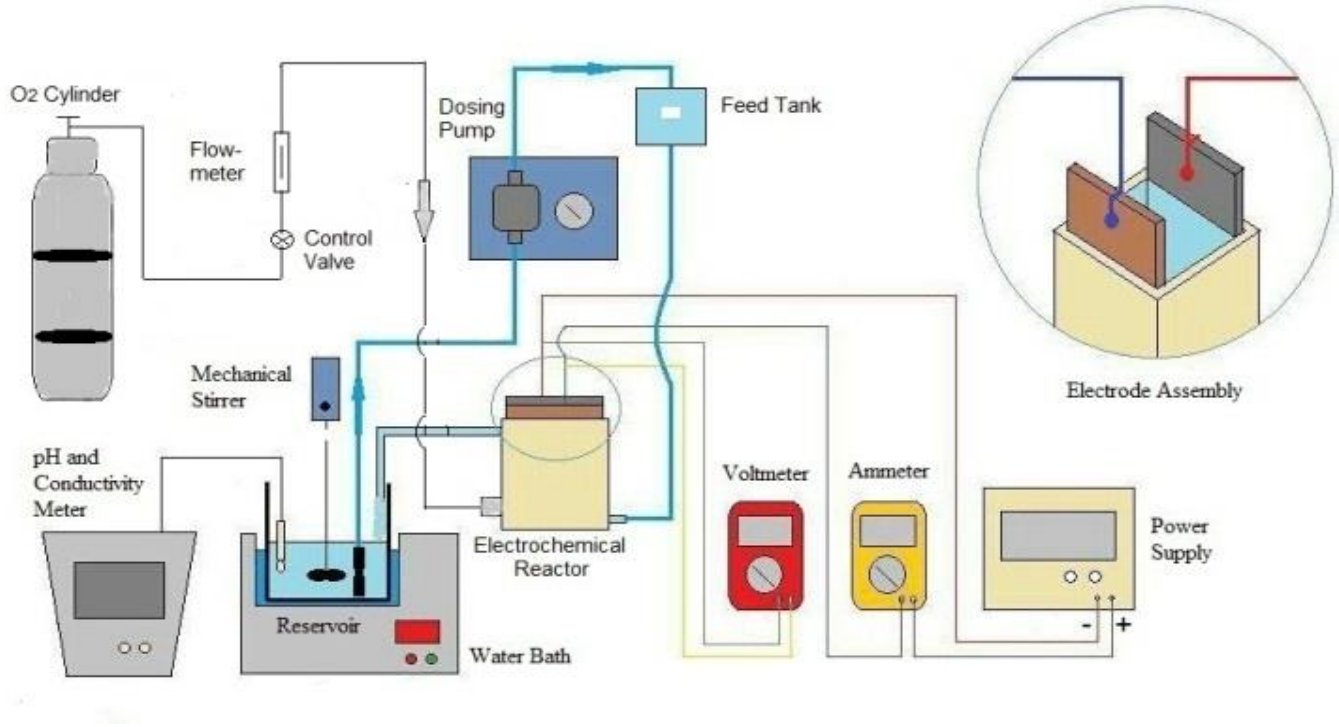

Figure 1: Schematic of the experimental set-up

On the other hand, the observed valuable effect of current ascent progress toward becoming non-noteworthy for current densities over 70 mA cm^{-2}. This phenomenon could be interpreted by the gradual enhancement of the rate of side reactions such as the OH^- oxidation or the evolution of O_2 and H_2 gases at the anode and the cathode, respectively.

In the EF process (Fig. 2) the use of the peroxi-coagulation method is based on utilizes of sacrificial Fe anode. This anode is electrodissolved, supplying stoichiometric amounts of Fe^{2+} ions to the bulk, and has a higher degradation power, allowing more pollutants to be removed [14]. Fe^{2+} ions merely react with the *in situ* electrogenerated H_2O_2 produced by O_2 diffusion cathode (carbon felt) and the excess of Fe^{3+} formed precipitates as $Fe(OH)_3$. Phenol and its derivative are then expected to be degraded by the unified action of their homogeneous oxidation with $OH^•$ generated by reaction (4) and their coagulation with the $Fe(OH)_3$ 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 the reaction rate. Different current densities have been studied to investigate their effect on the direct and indirect oxidation of phenol. To clarify the effect of current density on phenol degradation efficiency, many experiments got to be completely realized using AO-graphite, AO-βPbO_2, and EF processes for the applied current densities of 30, 50, and 70 mAcm-2 as shown in Fig. 3. As a result of the AO process, the phenol degradation efficiency increased with a marked increase in current density due to the release of heterogeneous graphite ($OH^•$) or β-PbO_2($OH^•$) at the anode surface. The highest phenol degradation efficiency of 74.4% for graphite and 83.7% for β-PbO_2 obtained at 70 mA cm^{-2} current density, 100 mg/L initial phenol concentration, and 12 L/hr flow rate. The enhancement of the parasitic reaction Eq. (6) could explain the relatively lower degradation kinetics of the AO-graphite process.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (6)$$

In this case, the observed increase in applied current density reduces H_2O_2 generation in the reactor. On contrary, the possible creation of more β-PbO_2($OH^•$) radical at high current density, as in the AO-βPbO_2 process, recovers the loss of efficiency in the bulk of the solution. The obtained phenol degradation efficiency by indirect oxidation increased with increasing current density, but in this case, due to the release of homogeneous $OH^•$ with higher quantities to the bulk of solution according to Eq. (1). At 70 $mAcm^{-2}$ current density, 100 mg/L initial phenol concentration, and flow rate of 12 L/hr, indirect oxidation provided the best phenol degradation efficiency of 88.9% for Fe anode versus carbon felt cathode. Moreover, the indirect oxidation by EF at high current density promoted H_2O_2 generation with Eq. (7):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (7)$$

It is noteworthy to remark, that the formed H_2O_2 from Eq. (7) with ferrous Fe^{2+} generated from Eq. (3), leads to the formation of more $OH^•$ according to Eq. (4). However, the $OH^•$ formation reaction enhances the higher degradation efficiency in an acidic medium with pH 3. The excess of Fe^{2+} ions precipitates as hydrated Fe(III) oxide ($Fe(OH)_3$). The oxidation products could then be expelled by mineralization or coagulation by the formed

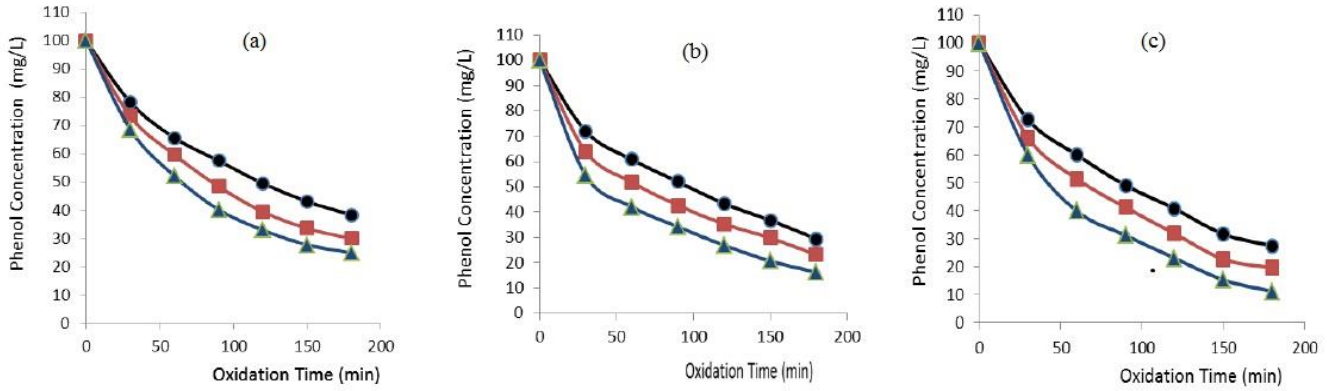

Figure 2: Effect of applied current density on phenol degradation with different processes. Conditions: current density ●30 mAcm^{-2}, ■ 50 mAcm^{-2}, ▲70 mAcm^{-2}; $[Ph]_o$ = 100 (mg/L); Na_2SO_4 0.05 M; pH 7; temp. 25°C; flow rate 12 L/hr: (a) AO-graphite process (b) AO-βPbO_2 (c) EF process

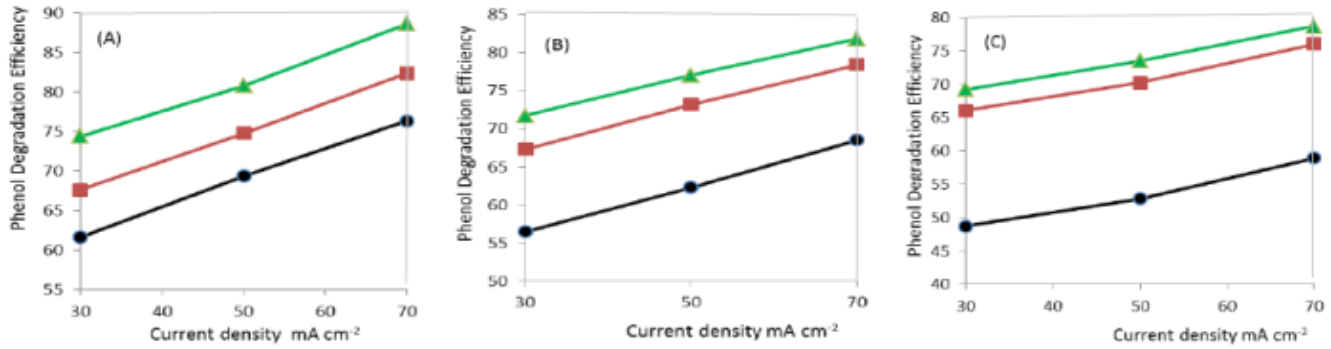

Figure 3: Effect of applied current density on phenol degradation efficiency. Conditions: (A) $[Ph]_o$= 100 mg/L; (B) $[Ph]_o$ = 250 mg/L; (C) $[Ph]_o$= 500 mg/L; ● AO-graphite, ■ AO- βPbO_2, ▲EF process; Na_2SO_4 0.05 M; pH 7; temp. 25°C; flow rate 12 L/hr

Fe(OH)$_3$ precipitate. In contrast to AO, degradation kinetics of phenol in the EF process were significantly higher, with the applied range of current density. However, when the oxidation time is compared at 70 mA cm^{-2}, OH$^{\bullet}$ radicals in the EF process are predominantly formed at the bulk of the electrolyte rather than at the anode surface. Hence, the oxidation power of the tried AEOPs extends in the sequence EF > AO-βPbO_2 > AO-graphite. These states of oxidation occur at a high applied current density of more than the limiting one, and this case is said to be diffusion transfer behavior. However, the current efficiency permanently decreased during oxidation time being less than 100% for AO-graphite, AO-βPbO_2, and EF processes confirmed that the phenol degradation work under mass transfer control.

3.3. Kinetic study of phenol degradation

With all tested processes, the phenol concentration decay would be comfortably fitted to pseudo-first-order reaction kinetics, as confirmed by Polcaro and Palmas, 1997 [15]. Principally, the apparent rate constant K_{app} of the oxidation reaction of phenol is determined with Eq. (8):

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

The K_{app} values were calculated by plotting $\ln(C_{pho}/C_{pht})$ versus time. As shown in Fig. 4, the correlation coefficients (R^2) for straight lines are greater than 98.8%. This reaction order could be justified by the fact that the lifetime of OH$^{\bullet}$ radical is dependent on the activity of the anode type. However, for non-active electrodes, it has been proposed that OH$^{\bullet}$ cannot combine with the anode surface and then become available to oxidize organics in a very short time [16]. This explains the phenomena of radical oxidant formation and the change of efficiency with anode type. The results presented in Table 1 (obtained from Fig. 2) at the same current density confirm that the oxidation ability follows the order EF > AO-βPbO_2 > AO-graphite, indicating that peroxi-coagulation electrodes and the β-PbO_2 anode have the larger oxidizing power than graphite anode.

When comparing K_{app} values 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 β-PbO_2 anodes provided almost similar oxidation efficiencies in the AO process, while the scarify Fe anode supplies a better oxidation rate in the EF process.

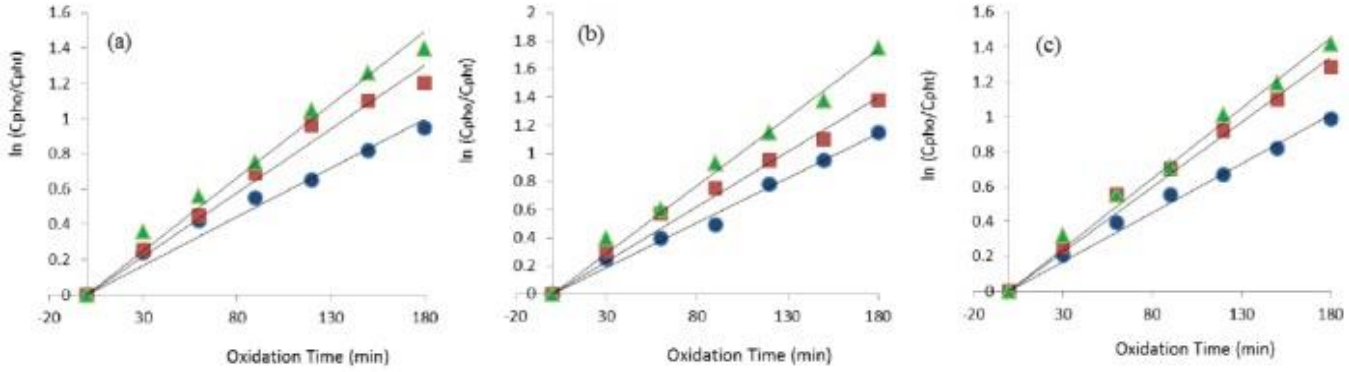

Figure 4: Linearized concentration profiles of phenol as a function of oxidation time with different processes. Condition; applied current density ● 30 mAcm^{-2}, ■ 50 mAcm^{-2}, ▲70 mAcm^{-2}; $[Ph]_o$ =100 mg/L; electrolyte 0.05 M Na_2SO_4; pH=7; temp. 25°C; flow rate 12 L/hr: (a) AO-graphite process (b) AO-βPbO_2 (c) EF process

The K_{app} values are relatively limited in the case of the AO process when using Na_2SO_4 as a supporting electrolyte. This behavior can be explained by the oxidation of SO_4^{2-} ion to $(SO_4^{-})^{\bullet}$ radical and then to $(SO_4^{-})^{\bullet}$ radical as in Eq. 9, [17]:

$$SO_4^{2-} \rightarrow (SO_4^{-})^{\bullet} + e^{-} \quad (9)$$

These radicals could be combined, according to reaction (Eq. 10), which explains occurring of stable oxidants in the reaction media, including peroxosulfate [18]:

$$(SO_4^{-})^{\bullet} + (SO_4^{-})^{\bullet} \rightarrow S_2O_8^{2-} \quad (10)$$

Table 1: Apparent rate constant of phenol degradation by different current densities (100 mg/L initial phenol concentration, flow rate12 L/h)

Current density (mA cm^{-2})	EF K_{app} (min^{-1})	AO-βPbO_2 K_{app} (min^{-1})	AO-graphite K_{app} (min^{-1})
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^{2+} Catalyst on Phenol Degradation

Catalyst concentration (i.e., Fe^{2+} ions) is an important parameter influencing EF process efficiency, particularly in the case of peroxi-coagulation. Fig. 5 shows the degradation of 100 mg/L initial phenol aqueous solution of pH 3, as a function of Fe^{2+} catalyst in EF experiments. This Fig. explains the behavior of the peroxi-coagulation method with iron Fe/carbon felt electrodes at current densities 30, 50, and 70 mAcm^{-2}. The Fe^{2+} 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), the Fenton process takes place according to Eq. (4) to generate $OH^{\bullet}$ reacting with phenol [2, 12]. Therefore, the rate of $OH^{\bullet}$ generation is entirely controlled by the rate of electrochemical generation of Fe^{2+} from Eq. (4).

Fig. 5 shows that the concentration of phenol decayed in a steep descent using a current density of 70 mA cm^{-2}, with the concentration of Fe^{2+} catalyst increasing as the current increased. As a result, the phenol degradation efficiency increased predominately with increasing of Fe^{2+} concentration. The degradation was significantly fasted down with 20 mM Fe^{2+}; 60 min were required for most oxidation of phenol, while 180 min produced enough excess with a 55.9 mM Fe^{2+}catalyst.

In general, the efficiency of the EF process increases with increasing Fe^{2+} catalyst concentration because the [$OH^{\bullet}$] radicals increase with increasing Fe^{2+} concentration. These results agreed to a large extent with Nidheesh and Gandhimathi, 2012 [10]. On the other hand, some researchers stated that excess ferrous ions in the electrolyte solution could consume the $OH^{\bullet}$ radicals and influence the extent of degradation [12].

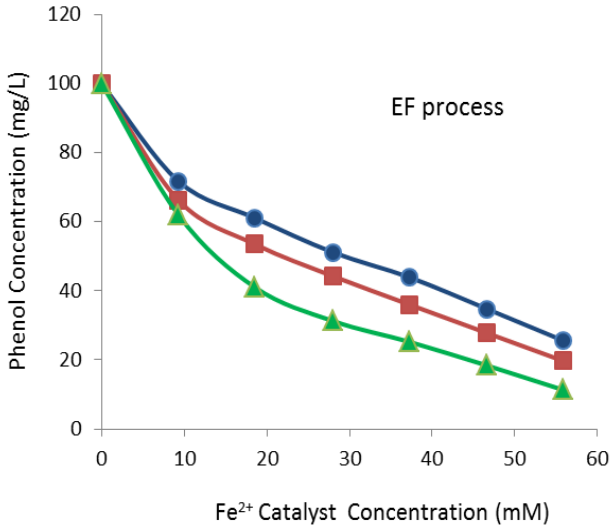

Figure 5: Effect of Fe^{2+} catalyst concentration generated during EF process for phenol degradation. Condition; current density ● 30 mAcm^{-2}, ■ 50 mAcm^{-2}, ▲70 mAcm^{-2}; $[Ph]_o$ =100 mg/L; oxidation time 180 min; electrolyte 0.05 M Na_2SO_4; pH=7; temp. 25°C; flow rate 12 L/hr

3.5. Effect of Initial Phenol Concentration

Phenol solutions of different initial concentrations of 100, 250, and 500 mg/L were used to investigate their effect on degradation efficiency. For comparison purposes, the degradation of phenol via AO-graphite, AO-βPbO_2, and EF processes was investigated. As a result, the phenol degradation efficiency for direct and thus indirect oxidation will increase as the initial phenol concentration decreases, as shown in Fig 6 (a).

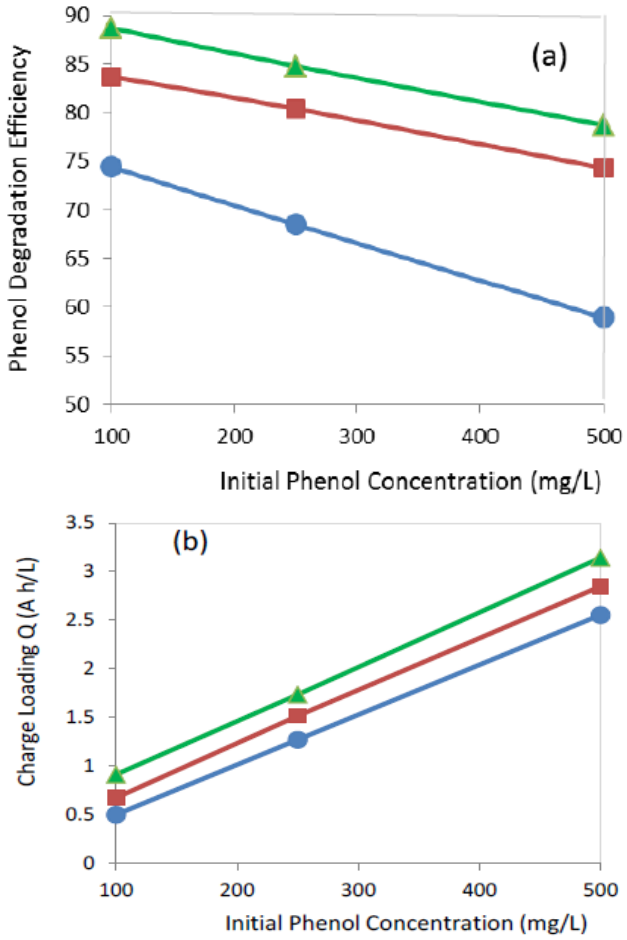

Figure 6 (a): Effect of initial phenol concentration on degradation efficiency. Conditions: ● AO-graphite, ■ AO- βPbO_2; ▲ EF process; current density 70 $mAcm^{-2}$; Na_2SO_4 0.05 M; pH 7; temp. 25°C; flow rate 12 L/hr; (b): Effect of initial phenol concentration on charge loading. Conditions: ● AO-graphite, ■ AO- βPbO_2; ▲ EF process; current density 70 $mAcm^{-2}$; Na_2SO_4 0.05 M; pH 7; temp. 25°C; flow rate 12 L/hr

In contrast, as the initial phenol concentration decreases, so does the reaction time for complete conversion. At 100 mg/L initial phenol concentration, 12 L/hr flow rate, and 70 $mAcm^{-2}$ current density, degradation efficiencies of 74.4% and 83.7% for AO-graphite and AO-PbO_2, respectively, were obtained. While at the same condition, a degradation efficiency of 88.9 was recorded for the EF process. With an initial phenol concentration of up to 500 (mg/L), the degradation efficiency decreases, with reported values of 58.9 %, 74.3 %, and 78.7 % for the AO-graphite, O-PbO2, and EF processes, respectively. However, as the initial phenol concentration increases, more intermediate products may form. The majority of the literature stated that the removal of intermediate products would be much more difficult and slower oxidized at higher initial phenol concentrations [2, 7, 19]. Fig 6 (b) shows the experimental results of charge loading (Q) variation at different initial phenol concentrations under the same operating conditions. 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-βPbO_2, and FE processes, respectively. As seen from Fig, 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 of 2.551, 2.845, and 3.141 A h/L for AO-graphite, AO-βPbO_2, and EF process, respectively. Figs. 6 (a) and (b) confirm the above-mentioned trends. The phenol degradation efficiency was, as expected, inversely proportional to the initial phenol concentration. This could be due to the availability of a constant amount of $OH^{\bullet}$ 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 [2].

3.6. Effect of Circulation Rate on kinetic of Phenol Degradation

The hydraulic residence time of wastewater in the oxidation system is expressed by the volumetric flow rate of the continuous system. However, in a batch system with internal circulation, the hydraulic residence time is the time required to keep the wastewater in the 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.

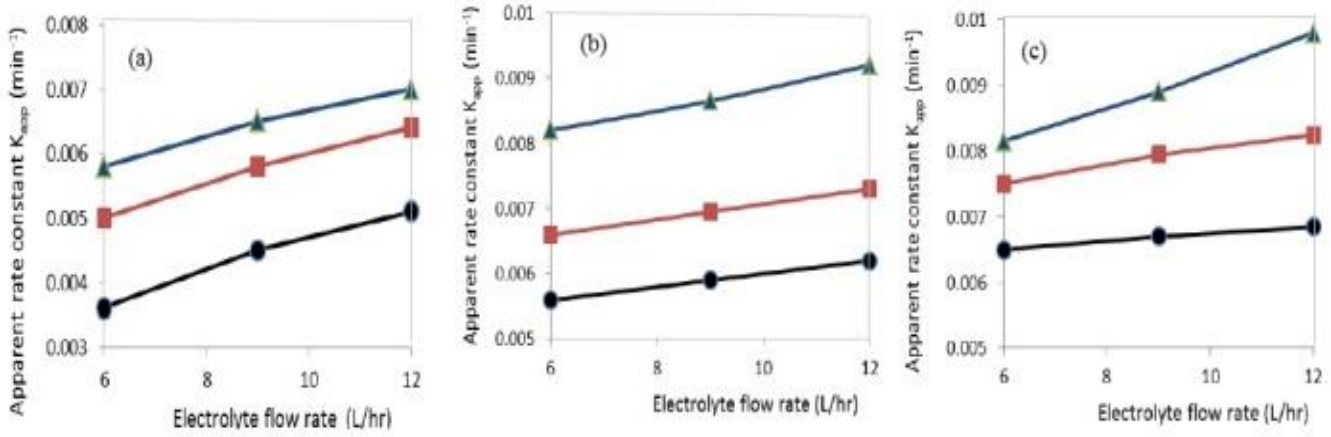

Fig. 7. Effect of circulation flow rate on apparent rate constant of phenol degradation by different processes. Conditions: current density ●30 $mAcm^{-2}$, ■ 50 $mAcm^{-2}$, ▲70 $mAcm^{-2}$; $[Ph]_o$ = 100 mg/L; Na_2SO_4 0.05 M; pH 7; temp. 25°C: (a) AO-graphite process (b) AO-βPbO_2 process (c) EF process

Fig. 7 shows the apparent rate constant K_{app} of phenol degradation versus electrolyte flow rate for AO-graphite, AO-βPbO_2, and EF processes with an initial phenol concentration of 100 mg/L. The present study found that as the electrolyte internal circulation increased, so did the phenol degradation efficiency. According to Fig. 7, increasing the electrolyte circulation flow rate from 6 to 12 L/hr can increase the apparent rate constant by 10-20% depending on the type of process. Thus, for the examined parameters, flow velocity may have a significant impact on the reaction kinetics; in fact, in the examined range of velocities, where the reaction is under mass transfer control. It should also be noted that the increase in the apparent rate constant is highly influenced by the type of oxidation process and the type of anode. Principally, increasing the electrolyte circulation flow rate could improve solution homogeneity and phenol diffusivity at the anode's surface, thereby increasing the oxidation reaction. The EF process was the most positively influenced by increasing the electrolyte circulation flow rate. Finally, at the highest current density, K_{app} of the AO-graphite and AO-βPbO_2 processes increased by 10 % when the circulation flow rate was increased from 6 to 12 L/hr under the same condition. While the K_{app} of the EF process increased by 17% when the flow rate was increased from 6 to 12 L/hr under the same operating condition.

4 Conclusions

Advanced electrochemical oxidation processes (AEOP's) were approved as effective techniques to treat synthetic phenolic wastewater of concentrations 100, 250, and 500 mg/L. Phenol degradation efficiency was investigated using the direct anodic oxidation process and indirect oxidation of the electro-Fenton process. For comparison purposes, processes of AO-graphite, AO- βPbO_2, and peroxi-coagulation were studied about several experimental parameters such as initial phenol concentration, current density, oxidation time, and electrolyte circulation flow rate. The results show that a reasonable degradation of phenolic material can be achieved using AO- βPbO_2 process and EF process (peroxi-coagulation method). The phenol degradation efficiency of 83.7% and 88.9% were predicted for βPbO_2 and EF processes, respectively, at 100 mg/L initial phenol concentration, electrolyte circulation flow rate 12 L/hr, and current density 70 $mAcm^{-2}$. In addition, the results explained the impact of Fe^{2+} catalyst concentration on phenol degradation as an important parameter influencing the EF process. Furthermore, the results show that as current density and electrolyte circulation flow rate increase, so does the efficiency of phenol degradation. In contrast, as the initial phenol concentration increases, the efficiency of phenol degradation decreases. The kinetic study revealed that the phenol degradation reaction follows pseudo-first-order reaction kinetic with AO-graphite, AO- βPbO_2, and EF processes, but with conflicting values of apparent rate constant values. In addition, confirmatory experiments showed that the phenol degradation efficiency results in an excessive apparent rate constant K_{app} that increases proportionally with a significant increase in current density. The effect of initial phenol concentration on charge loading to the reactor was also investigated, and it was shown that increasing the initial phenol concentration allowed for more charge to be required.

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Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically concerning authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution to data collection, data analyses, and manuscript writing.

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