Enhanced electro-catalytic degradation and kinetics of phenol in wastewater by high-gravity field with Ti/RuO$_2$-IrO$_2$-SnO$_2$ anodes

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Received 19 December 2018; 3 June 2019

ABSTRACT

To improve electro-catalytic degradation of phenol in wastewater and enhance the mass transfer, self-made high-gravity electro-catalytic reactor with Ti/RuO$_2$-IrO$_2$-SnO$_2$ anodes was developed for the degradation of phenol in the high-gravity field. Under the optimal operating conditions, the phenol removal efficiency reached 100% after 100 min electro-catalytic degradation, and reached 96.32% in the high-gravity field which increased by 10.93% compared with that in the normal gravity field after 60 min electro-catalytic degradation. For about the same phenol removal efficiency, the electro-catalytic time was 33.33% shorter in the high-gravity field than that in the normal gravity field. Results showed that the reason for increasing phenol removal efficiency and reducing electro-catalytic time is the fast generation rate of hydroxyl radicals, and the enhanced electro-catalytic degradation and kinetics of phenol by the high-gravity field. The study provides an efficient and environment friendly way for elimination of phenol from wastewater.

Keywords: High-gravity; Phenol wastewater; Electro-catalytic oxidation; Degradation pathway; Ti/RuO$_2$-IrO$_2$-SnO$_2$ anode; Kinetics study

1. Introduction

Because phenol is a highly toxic substance, the discharges of phenolic wastewaters can lead to detrimental environmental consequences and are harmful to ocean life. Many methods, such as adsorption [1], biological treatment [2], wet oxidation [3], photo-catalytic oxidation [4] and electro-catalytic oxidation [5] have been proposed for phenolic wastewater treatment. Electro-catalytic oxidation is mediated by electron exchange with the electrode surface and hydroxyl radicals are produced on the anode to degrade pollutants, dismissing the need for the addition of chemical agents. Electro-catalytic oxidation for phenolic wastewater degradation has some advantages, such as environmental compatibility, safety, clean and amenability to automation [6], and has received increasing attention in recent years. However, low mass transfer efficiency can result in concentration polarization and low electro-catalytic efficiency [7]. Therefore, the methods which have high mass transfer efficiency should be applied to electro-catalytic oxidation of wastewater.

There are lots of studies interested in preparation of active metal oxide electrodes to improve electro-catalytic efficiency. Among the studies, Ti/RuO$_2$-IrO$_2$-SnO$_2$ electrode had good electro-catalytic properties [8], and cyclic voltammetry measurements indicated that Ti/RuO$_2$-IrO$_2$-SnO$_2$ gave the best catalytic response on the electrochemistry of phenol [9]. But there are insufficient data about phenol removal using Ti/RuO$_2$-IrO$_2$-SnO$_2$ electrode. And the bubbles generated by oxygen evolution and the mass transfer blocked in the
system can lead to the decrease in electro-catalytic efficiency. So the phenol removal using Ti/RuO$_2$-IrO$_2$-SnO$_2$ electrode and the mass transfer enhancement for electro-catalytic oxidation is necessary for wastewater degradation [10,11].

High gravity field has the advantage of highly efficient mass transfer and has been applied in gas purification [12], dust removal [13], wastewater treatment [14–16], water electrolysis [17], chlor-alkali electrolysis [18] and material preparation [19,20]. The interphase slip rate is fast in the high-gravity field [12], while the bubbles can be easily separated from the electrode surface and electrolytes, previous research had shown it [21], and the wastewater renewal rate from electrode surface is fast and interphase contact area can be increased. In this case, concentration polarization can be reduced, and the mass transfer process can be intensified in the high gravity field [13]. This will be beneficial to the pollutants in wastewater that contact with the electrode surface, proceed the rate of electro-catalytic oxidation and reduce the reaction time. Therefore, the degradation efficiency of wastewater can be improved, the degradation time and energy consumption can be reduced in the high-gravity field.

In this work, a high-gravity electro-catalytic reactor with multi-concentric cylindrical electrodes was developed to couple high gravity technology to electro-catalytic oxidation technology and degraded wastewater in the high gravity field. Ti/RuO$_2$-IrO$_2$-SnO$_2$ was used as multi-concentric cylindrical anodes. The optimal operating conditions in electro-catalytic oxidation of phenol with Ti/RuO$_2$-IrO$_2$-SnO$_2$ anodes in the high-gravity field, and the effects of high-gravity field on the degradation process and degradation kinetics of phenol were investigated. The aim of this work is to provide an efficient and environment friendly way for elimination of phenol from wastewater.

2. Experimental

2.1. High-gravity electro-catalytic reactor and degradation of phenol

The high-gravity electro-catalytic reactor with Ti/RuO$_2$-IrO$_2$-SnO$_2$ anodes was developed to degrade phenol, as shown in Fig. 1. The concentric cylindrical cathodes connected with a cathode plate. The concentric cylindrical anodes connected with an anode plate, which were connected with the shaft and could rotate to form different high-gravity fields. They arranged alternately to form a multistage high-gravity electro-catalytic reactor. The volume of the reactor was 3 L and the circular effective volume was 5 L. The inter-electrode spacing was 1.0 cm.

The cylindrical stainless steel was used as the cathode while the cylindrical Ti/RuO$_2$-IrO$_2$-SnO$_2$ was used as the anode. The Ti/RuO$_2$-IrO$_2$-SnO$_2$ anodes were prepared by thermal decomposition. Pure titanium was used as the substrate which was etched in boiling 10% oxalic acid solution for 10 h. Then, the substrate was washed with ultra-pure water and dried in air. The RuCl$_3$, H$_2$IrCl$_6$ and SnCl$_2$ (Ru:Ir:Sn molar ratio of 17:23:60) were dissolved in isopropanol solution to prepare the coating solution. Then, the coating solution was brushed onto the titanium substrate. The solvent was evaporated at 95°C for 10 min and the residue was calcined at 450°C for 15 min in a muffle furnace. Afterwards, the coatings were cooled down to room temperature naturally. The same procedure was repeated until the oxide load of 15 g/m$^2$ was obtained.

The intensity of the high-gravity field was measured by the high-gravity factor ($\beta$), which was a ratio of the centrifugal acceleration to the gravitational acceleration ($g$). It could be expressed by Eq. (1) [12]:

$$\beta = \frac{\omega^2 r}{g}$$

where $\beta$ was the high-gravity factor, $\omega$ was the rotating speed (rev/min), $r$ was the average radius of the rotor (m).

The phenol aqueous solution used as simulated phenolic wastewater where in the wastewater storage tank entered in the high-gravity electro-catalytic reactor via the pump and the flowmeter. In the reactor, the wastewater flowed through the alternate cylindrical anodes and cathodes in the S-shape in the gravity field and was subjected to shear force strongly, the electrodes surface was washed by the wastewater, and the concentration polarization was reduced, the mass transfer was enhanced. The degraded phenolic wastewater through the wastewater outlet could be directly discharged via the valve or discharged into the wastewater storage tank for recycling. The total current in the system was supplied by the DC power supply.

2.2. Analysis methods

The phenol concentration and intermediates were detected by high performance liquid chromatography (HPLC) (UltiMate 3000, Thermo Fisher, USA) with a C18 reversed-phase column (Accucore XL C$_{18}$, 250 × 4.6 mm, 4 μm) at 25°C. The mobile phase was composed of methyl alcohol and water (60:40, v/v) with a flow rate of 1.0 mL/min. The detection wavelength was 270 nm and the injection volume was 20 μL. The phenol removal efficiency ($\eta$) was defined as Eq. (2):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

where $C_0$ and $C_t$ were the phenol concentration before and after electro-catalytic oxidation at time $t$ (mg/L), respectively.

Amounts of hydroxyl radicals generated at the anode surfaces were evaluated by an electron spin resonance (ESR) spectrometer (JESEFA200, JEOL, Japan). The hydroxyl radical spin adduct of 5-dimethyl-1-pirroline-N-oxide (DMPO) was prepared through sampling the solution with DMPO.

The analysis of intermediates were done by gas chromatography and mass spectrometry (GC-MS) on an Agilent 7890B gas chromatograph coupled to an Agilent 5977A mass detector. The sample was withdrawn with a 10 mL pipette and passed through a 0.45 μm membrane filter, then preconcentrated by liquid–liquid extraction with pentane for gas chromatography analysis. Chromatographic separations were carried out on an HP-5MS (30 m × 250 μm × 0.25 μm).
3. Results and discussion

3.1. Effect of high-gravity factor

The effect of high-gravity factor on phenol removal in the electro-catalytic oxidation is presented in Fig. 2. It can be seen that an increase in high-gravity factor results in an increase in the phenol removal efficiency when the high-gravity factor is less than and equal to 20. This is because with the increase in high-gravity factor, wastewater flowed through the alternate cylindrical anodes and cathodes and was subjected to shear force strongly, the rates of interphase slip and mass transfer were increased, the effects of bubbles and concentration polarization were reduced by the high-gravity field. Then the phenol removal efficiency decreased when a further increase in high-gravity factor because the residence time in the reactor was reduced. So the suitable high-gravity factor was 20, the phenol removal efficiency reached 96.32%, which increased by 10.93% over in the normal gravity field (85.77%) after 60 min electro-catalytic oxidation. When the phenol removal efficiency in the high-gravity field was 86.49%, which was near to that in the normal gravity field (85.77%), only 40 min was to be used, which had a 33.33% shorter electro-catalytic time. Results indicate that the phenol removal efficiency was improved, the time was reduced during the electro-catalytic oxidation in the high-gravity field.

3.2. Effect of initial phenol concentration

Fig. 3 shows the effect of initial phenol concentration on the phenol removal efficiency.

The phenol removal efficiency decreased slowly as the initial phenol concentration varies from 100 to 1,000 mg/L,
for lower initial phenol concentration, more phenol was expected to be degraded easily. Then the phenol removal efficiency decreased fast as the initial phenol concentration varied from 1,000 to 2,000 mg/L, because more intermediates would be generated at a high phenol concentration and exceeded relative to hydroxyl radicals and active chlorine species. It indicates that the phenol is degraded easily at low and medium concentration levels. Generally, the phenol concentration of wastewater which is pretreated or biochemically treated is around 500 mg/L. So initial phenol concentration of 500 mg/L was selected for the experimental research.

3.3. Effect of the current density

The effect of current density on phenol removal in the electro-catalytic oxidation in the high-gravity field is shown in Fig. 4.

The phenol removal efficiency increased when the current density increases from 150 to 350 A/m², then increased slowly. The higher current density indicates the more charges on the electrode and the more easily generated •OH and CIO⁻, and side reactions rarely occur. So the electro-catalytic oxidation of phenol and intermediate products can be promoted. But the higher current density leads to the side reactions easily occur, for example, the oxygen evolution reaction and heat loss (Eq. (3)), which can lead to the higher cell voltage and energy consumption. Considering the energy consumption and phenol removal efficiency, the appropriate current density was 350 A/m².

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- + \text{heat} \uparrow
\]  

(3)

3.4. Effect of NaCl dosage

NaCl often exists in actual phenolic wastewater and has an effect on the wastewater treatment. So the effect of NaCl dosage on the electro-catalytic oxidation of phenol was investigated (Fig. 5).

The phenol removal efficiency increased as the NaCl dosage increased because the amount of CIO⁻ increased and the more phenol could be degraded (Eqs. (6)–(8)). But when the NaCl dosage was over 8.5 g/L, the phenol removal efficiency decreased. This is because the excess NaCl dosage may lead to side reaction (Eq. (5)) and affect the phenol degradation. When the NaCl dosage was 6.5 g/L, the phenol removal efficiency was next to the value of NaCl dosage of 8.5 g/L after 120 min electro-catalytic degradation. The phenol removal efficiency was high at a shorter electro-catalytic time of 60 min when the NaCl dosage was 8.5 g/L. Therefore, 8.5 g/L was considered for the experimental research. In practical applications, the appropriate NaCl dosage should be used according to the dosage in actual phenolic wastewater.

\[
2\text{Cl}^- \rightarrow \text{Cl}_2(\text{aq}) + 2e^- 
\]  

(4)

\[
\text{Cl}_2(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) \uparrow 
\]  

(5)

\[
\text{Cl}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{Cl}^- + \text{H}^+ 
\]  

(6)

\[
\text{HOCl} \rightarrow \text{CIO}^- + \text{H}^+ 
\]  

(7)

\[
\text{R} + \text{ClO}^- \rightarrow \text{RO} + \text{Cl}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^- 
\]  

(8)

where R represents organics.

3.5. Effect of initial pH value

Fig. 6 shows the effect of initial pH value on the phenol removal in the electro-catalytic oxidation in the high-gravity field.

It shows that the acidic condition is beneficial for the phenol removal efficiency. This is because Cl⁻ can be hydrolyzed to produce HClO which is favorable to the formation in the acidic conditions (Eq. (7)), at the same time, the
oxygen evolution potential was high. Low pH can inhibit the oxygen evolution reaction and improve the phenol removal efficiency. The alkaline condition is beneficial for the generation of hydroxyl radicals, meanwhile the oxygen evolution potential was low and oxygen evolution could occur easily [22], so few phenol species were oxidized directly on the anode. As shown in Fig. 6, the phenol removal efficiency increased with the increase of initial pH value and then decreased over pH 6.5, it is the result of the mutual effects of the above influence factors. So the optimum initial pH value was 6.5.

3.6. Effect of high-gravity field on the generation rate of hydroxyl radicals

The elimination of phenol and other pollutants from wastewater mainly relies on the hydroxyl radicals produced on the anode. So, the generation rate of hydroxyl radicals in high-gravity field and normal gravity field was investigated to evaluate the effect of high-gravity field at the optimal operational conditions, as shown in Fig. 7. The spectrum was composed of quartet lines having a peak height ratio of 1:2:2:1. The amounts of DMPO-OH and hydroxyl radicals were more at the same electro-catalytic time in the high-gravity field than that in the normal gravity field (β = 1). This is because the wastewater flows through the alternate cylindrical anodes and cathodes in the S-shape and is subjected to shear force strongly in the gravity field. In this situation, mass transfer is improved and renewal rate of electrode surface is increased. So the bubbles generated by oxygen evolution on the anode and in the phenolic wastewater can be easily separated from them, the concentration polarization can be reduced. Therefore, there is less competition for the generation of hydroxyl radicals on the anode, the generation rate of hydroxyl radicals which reacted with phenol or intermediates is fast, resulting in the increase in the phenol removal efficiency, as shown in Fig. 2.

3.7. Effect of high-gravity field on the degradation process of phenol

GC-MS analysis was performed at the optimal operation conditions and degradation time of 40 min to research the effect of high-gravity field on the degradation process of phenol. The main intermediates were identified by comparing the retention time of the standard compounds. Fig. 8 gives the GC-MS chromatograms of phenol degradation in the high-gravity field and normal gravity field. It can be seen that the main intermediates were hydroquinone, catechol, resorcinol and benzoquinone, maleic acid, fumaric acid, succinic acid, malonic acid and oxalic acid which were same whether in the high-gravity field or in the normal gravity field. It means the same phenol degradation pathway which is proposed in Fig. 9. The hydroxyl radicals attack benzene rings to produce hydroquinone, catechol and resorcinol, which were easily further oxidized to benzoquinone. Then the benzoquinone was degraded to carboxylic acids such as maleic acid and fumaric acid, and further oxidized to produce succinic acid, malonic acid and oxalic acid. These carboxylic acids mineralized into CO₂ and H₂O. Although the degradation process was unchanged, the peak areas of phenol and intermediates decreased rapidly and the degradation rate of phenol and intermediates were fast in the high-gravity field.

3.8. Effect of high-gravity field on the degradation kinetics of phenol

The experimental data obtained at the optimal operation conditions were used to determine the order of the reaction and the effect of high-gravity field on the degradation kinetics of phenol. The exponential decay of phenol concentration as a function of time was observed and fitted to a pseudo-first-order kinetic model whether in the high-gravity field or in the normal gravity field (Fig. 10). The apparent rate
Fig. 8. GC/MS chromatograms of phenol degradation in the high-gravity field ($\beta = 20$) and normal gravity field ($\beta = 1$) (initial phenol concentration: 500 mg/L; current density: 350 A/m²; NaCl dosage: 8.5 g/L; initial pH value: 6.5; degradation time: 40 min).

Fig. 9. Degradation pathway of phenol.
constant (k) was calculated according to the rate equation (Eqs. (9) and (10)):

$$\frac{dC}{dt} = -kC$$

Integrating:

$$\ln\left(\frac{C}{C_0}\right) = kt$$

where $C_i$ and $C_0$ are the concentration of phenol at time $t$ and time zero, respectively, and $t$ is the reaction time. The $k$ values for the high-gravity field and normal gravity field were 0.052 min$^{-1}$ ($R^2 = 0.991$) and 0.033 min$^{-1}$ ($R^2 = 0.997$), respectively. The reaction rate constant obtained in the high-gravity field is higher than that obtained in the normal gravity field. It indicates that high-gravity field can accelerate the wastewater degradation rate. Thus, the phenol removal efficiency was improved, the time was reduced in the high-gravity field, as shown in Fig. 2.

4. Conclusions

The results of the self-made high-gravity electro-catalytic reactor with Ti/RuO$_2$-IrO$_2$-SnO$_2$ anodes demonstrated that the mass transfer was enhanced and the degradation efficiency of phenol was improved in the high-gravity field, because the generation rate of hydroxyl radicals and the degradation process of phenol was fast, the kinetic laws of phenol degradation fitted to the pseudo-first-order kinetic model and the reaction rate constant is high.

The phenol removal efficiency reached 100% after 100 min electro-catalytic degradation, and reached 96.32% in the high-gravity field ($\beta = 20$) which increased by 10.93% over in the normal gravity field after 60 min electro-catalytic degradation at an initial phenol concentration of 500 mg/L, a current density of 35 A/m$^2$, a sodium chloride concentration of 8.5 g/L, and an initial pH value of 6.5. For about the same phenol removal efficiency, the electro-catalytic time was 33.33% shorter in the high-gravity field than that in the normal gravity field.

Results showed that the high-gravity field affected electro-catalytic degradation and kinetics of phenol positively, and electro-catalytic degradation of phenol in the high-gravity field is efficient and environment friendly.

Acknowledgment

This study was supported by the National Natural Science Foundation of China (No. U1610106, No. 21703208), the Natural Science Foundation for Young Scientists of Shanxi Province, China (No. 201701D221047) and the Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (201802077).

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