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Oxidation of 2-Chlorophenol Wastewater by Hydrogen Peroxide in the Presence of Basic Oxygen Furnace Slag

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Effluent streams containing chlorinated phenols are generally present in chemical industry wastewater. Chlorinated phenols are priority pollutants and are potentially toxic to humans and aquatic life. There are stringent discharge limits for chlorinated phenols, The toxicity of chlorinated phenols decreases its biotreatability. Consequently, reducing the concentration or total mineralization of chlorinated phenol is a necessary pretreatment prior to discharge to a biological waste treatment facility. Chemical oxidation method has been used to enhance the biotreatability of wastewater containing various organic chemicals that are toxic or inhibitory to common microorganisms (Tyre et al., 1991). Of the chemical oxidants, hydrogen peroxide is a powerful oxidant that has been used to degrade organic chemicals either directly or in the presence metal catalysts (Plant & Jeff, 1994). Fenton's reagent, a mixture of ferrous ions and hydrogen peroxide, is one of the most widely used and studied catalytic treatment systems (Valentine and Wang, 1998). The ferrous ion source in the Fenton's reagent can be $FeSO_4.5H_2O$, $FeCl_2$, $Fe(ClO_4)_2.6H,O$ or other water-soluble ferrous salts. Recently, researchers find that iron oxide or iron minerals also can supply ferrous ions to react with hydrogen peroxide to degrade organic chemicals (Watts et al., 1994; Valentine and Wang, 1998). These researches showed that ferrous ions could be produced from metal oxides or supported metal oxides. In this research basic oxygen furnace slag (BOF slag) is used to produce ferrous ions in an acid solution.

BOF slag is a final waste slag in the steel making process. BOF slag has different particle sizes and has small pores in the surface. The major compositions of BOF slag are CaO, SiO_2, Fe_2O_3, FeO, MgO and MnO. 12.5 Weight % of BOF slag is FeO and 4.5 weight % of BOF slag is Fe_2O_3. FeO is slightly soluble in an acid solution to produce ferrous ion. The ferrous ion produced from the dissociation of FeO reacts with hydrogen peroxide to generate hydroxyl radicals and oxidize target pollutants.

In this paper 2-chlorophenol was used to evaluate the oxidation ability of BOF slag with hydrogen peroxide. 2-chlorophenol is a biorefractory organic chemical and a suspected carcinogen. The variety of factors that effect on the degradation of 2-chlorophenol wastewater were investigated including: hydrogen peroxide concentration, BOF slag concentration, pH value of solution and initial

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concentration of 2-chlorophenol. A kinetic reaction model was proposed and studied in the degradation process. The reaction rate constants were calculated using the Rosen-Brock Optimization Algorithm with 4th order Runge-Kutta method based on the experimental data.

MATERIALS AND METHODS

2-chlorophenol(C_6H_5ClO, FW=128.56, mp. 8 °C , bp. 175 ~ 176 °C), chlorohydroquinone (CHQ), 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) were purchased from Fisher Scientific (Pittsburge PA). 35% hydrogen peroxide was purchased from Shimakyu Co. (Japan). The BOF slag was obtained from China Steel Corp., Taiwan. 2-chlorophenol concentration was determined by HPLC (Hitachi L7110 pump with L7400 UV detector) on a 15 cm × 4.6 mm ID, 5μm Supelcosil LC 8 column with UV detection at 280 nm. The mobile phase (2.0 ml/min) was in the ratio 1% acetic acid/methanol : 1% acetic acid/water = 60 : 40. Ferrous iron was quantified by spectrophotometric measurements (HACH DR-2000) of the Fe^{2+}/TPTZ complex at 510nm. Hydrogen peroxide concentration was measured by the potassium iodide method with sodium thiosulfate titration and starch as an indicator (Shaw, 1967). The chemical oxygen demand (COD) of wastewater was determined by the dichromate reflux method.

The BOF slag obtained from the China Steel Corp. was washed with distilled water to remove the adhering dust and dried at 103°C. The heated BOF slag was cooled and separated with No. 10 (opening 2mm) and No. 18 (opening 1 mm) mesh sieve to get uniform particle size. The particle sizes used in the experiments were between 1-2mm. The batch oxidation reaction was conducted in a 1L well-mixed round-bottle glass flask. Mixing was provided by a variable speed motor connected to a stainless steel shaft. A pH controller was used to control pH value of solution by adding 1M HCl or NaOH solution into the reactor. The reaction temperature was maintained at 25°C by a constant temperature water circulator. Four different concentrations of 2-chlorophenol wastewater [25, 50, 100 and 150 mg/L] with 0.352g/L hydrogen peroxide and pH value of 2.8±0.2 were tested to assess the effect of initial concentration. The effect of pH value of solution was studied at 2.8, 3.8, 4.8 and 5.8 ±0.2 with log/L BOF slag, 0.352g/L hydrogen peroxide and 100mg/L 2-chlorophenol. The influence of hydrogen peroxide was studied by dosing different hydrogen peroxide concentrations [0.008, 0.176, 0.352, 0.704, 1.056 g/L] into the reactor. The BOF slag used in the experiments was 5, 10 and 15g/L dependent on the experimental purpose.

RESULTS AND DISCUSSION

BOF slag contains 12.5 weight percentage of FeO and 4.5 weight percentage of Fe_2O_3. In an acid solution, ferrous ion and ferric ion are produced from the dissociation of FeO and Fe_2O_3. The results of the experiments conducted at pH = 2.8±0.2 in the presence of different concentrations of BOF slag [4, 8, 15 and 20 g/L] and 0.35gL hydrogen peroxide are presented in Figure 1 and Figure 2. In the figures, the Fe^{2+} and Fe^{3+} concentration are plotted as a function of reaction time. The data show that both of the Fe^{2+} and Fe^{3+} concentration are linear proportional to reaction time. Fe0 and Fe_2O_3 dissociation equations are as follows:

$$FeO + 2H^+ \rightarrow Fe^{2+} + H_2O \qquad (1)$$

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \qquad (2)$$

In the presence of hydrogen peroxide, ferrous ion reacts with hydrogen peroxide to form "Fenton's reagents" and ferric ion reacts with hydrogen peroxide to form "Fenton's like reagents" that shown in equation 3 and equation 4. As hydroxyl radicals are produced from the reaction of ferrous ion with hydrogen peroxide, a chain reaction occurs between hydroxyl radical hydroperoxide radical ($HO_2\cdot$), hydrogen peroxide, ferric ion and ferrous ion (Watts et. al, 1994) :

$$Fe^{2+} + H_2O_2 \text{ ® } Fe^{3+} + OH\cdot + OH^- \qquad (3)$$

$$Fe^{3+} + H_2O_2 \text{ ® } Fe^{2+} + HO_2\cdot + H^+ \qquad (4)$$

$$Fe^{2+} + OH. \text{ ® } Fe^{3+} + OH^- \qquad (5)$$

$$HO_2\cdot + Fe^{3+} \text{ ® } O^2 + Fe^{2+} + H^+ \qquad (6)$$

$$H_2O_2 + OH\cdot \text{ ® } H_2O + HO_2. \qquad (7)$$

From the above reaction mechanisms we can conclude that in the absence of organic chemicals, hydroxyl radicals are further consumed by ferrous ion, hydrogen peroxide, ferric ion or other intermediates to form a final, stable, oxidized product. The following reaction illustrates the reaction:

$$OH\cdot + \xrightarrow{Fe^{2+}, H_2O_2, HO_2\cdot} Terminate \qquad (8)$$

The degradation of 2-chlorophenol wastewater was conducted in a batch reactor with the operation conditions: log/L BOF slag, 0.352g/L hydrogen peroxide, 100mg/L 2-chlorophenol and pH = 2.8±0.2. As discussed in the previous section, ferrous ion generated from the dissociation of Fe0 or other chain reactions reacts with hydrogen peroxide to form hydroxyl radicals. Hydroxyl radicals react with 2-chlorophenol and oxidize it. A reaction intermediate, chlorohydroquinone (CHQ) with distinguished concentration was detected during the process. Figure 3 shows the degradation rate of 2-chlorophenol, concentration changes of CHQ and changes of solution COD value. As depicted in Figure 3, 2-chlorophenol was totally decomposed after 30 minutes reaction time. The reactions of 2-chlorophenol and CHQ with hydroxyl radicals can be written down as follows:

$$2-CP \xrightarrow{OH\cdot} CHQ \xrightarrow{OH\cdot} Final\ products$$

The reaction intermediate, CHQ, has the highest concentration 38.3 mg/L at 25 minutes reaction time and is reduced to 2.7 mg/L at the end of reaction time, 70 minutes. The COD value of the solution changes from 254 mg/L to 76 mg/L with 70 % COD removal efficiency after 70-minute reaction time. The high COD

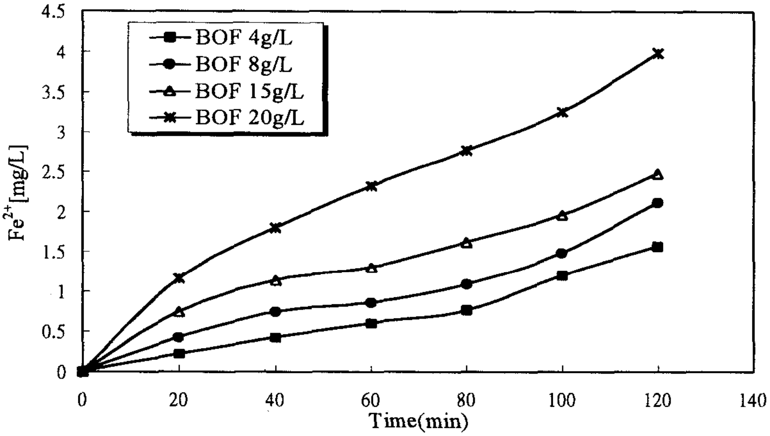

Figure 1. Ferrous ion production rate by different BOF slag concentration with 0.352g/L H_2O_2 and pH=2.8

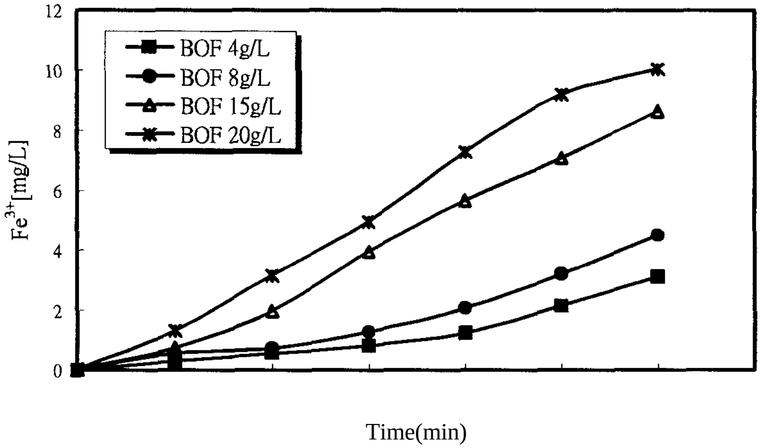

Figure 2. Ferric ion production rate by different BOF slag with 0.352g/L H_2O_2 and pH=2.8

removal efficiency proves that BOF slag with hydrogen peroxide can be used in the 2-chlorophenol wastewater treatment effectively.

Equation 1 shows that the stoichiometric molar ratio between depletion of ferrous ion and hydrogen peroxide is 1. Thus a higher dosage of hydrogen peroxide will not affect the production rate of hydroxyl radical. However, ferric ion that is produced by the reaction of ferrous with hydrogen peroxide or the dissociation of Fe_2O_3 from BOF slag will also react with hydrogen peroxide to produce ferrous ion. Thus a higher dosage of hydrogen peroxide can produce a higher concentration of hydroxyl radicals. The effect of hydrogen peroxide dosage on the

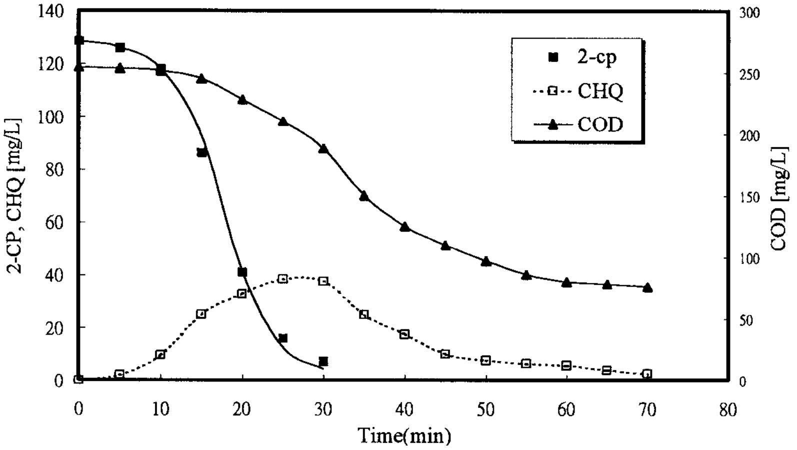

Figure 3. The degradation of 2-chlorophenol, CHQ and the changes of COD value of solution during the oxidation process by log/L BOF slag, 0.352g/L H_2O_2 and pH=2.8

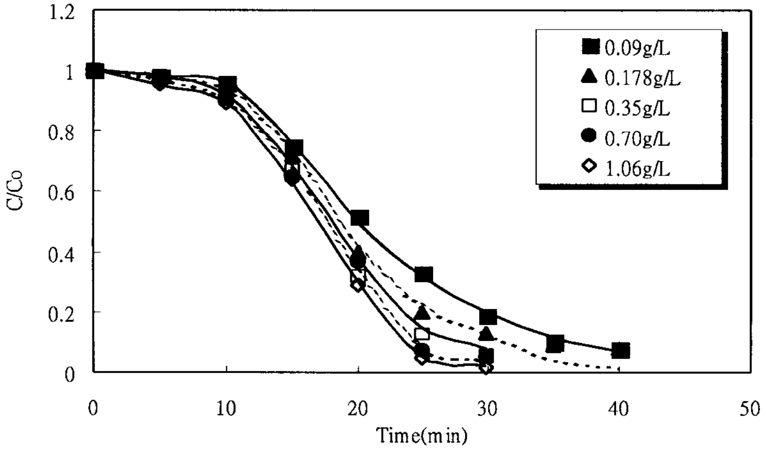

Figure 4. The degradation of 2-chlorophenol by different H_2O_2 concentration with log/L BOF slag, 100mg/L 2-cp and pH=2.8

degradation of 2-chlorophenol is shown in Figure 4. In the experiment, different concentrations of hydrogen peroxide [0.09, 0.18, 0.35, 0.70 and 1.06 g/L] were studied. The results indicate that a higher hydrogen peroxide concentration has a higher 2-chlorophenol degradation efficiency. However, the relationship is not linear. As hydrogen peroxide dosage higher than 0.352g/L, the difference of degradation efficiency of 2-chlorophenol is not apparent.

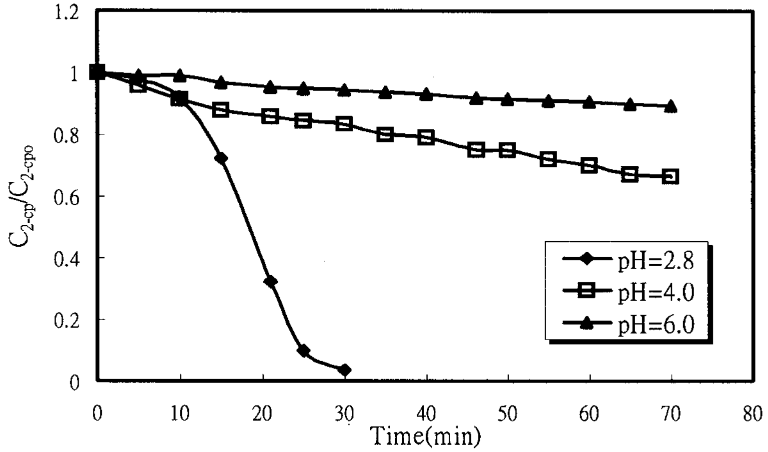

Figure 5. The pH value of solution effects on the degradation of 2-chlorophenol by log/L BOF slag, 100mg/L 2-cp and 0.352g/L H_2O_2

The dissolution of BOF slag to produce ferrous ion or ferric ion occurs only in an acid solution. Only in an acid condition, ferrous ion will react with hydrogen peroxide to produce hydroxyl radicals. Thus, the degradation process should be down under acid conditions. As shown in Figure 5, the degradation rate increases with acidity. The degradation efficiency is dramatically reduced to 34% at a pH value of 4 and is only 10% at a pH value of 6 after 70-minute reaction time. Thus, of the pH values tested the recommended pH value is 2~3.

The relationship between degradation of 2-chlorophenol and BOF slag concentration was studied at BOF slag concentrations of 5, 10 and 15g/L with 0.352g/L hydrogen peroxide dosage, 100mg/L 2,4-dichlorophenol and pH=2.8±0.2. As shown in Figure 4, 0.352g/L hydrogen peroxide is at a sufficient high concentration to react with ferrous ions to produce hydroxyl radicals. The degradation rate-limiting factor becomes ferrous ion concentration. At a higher concentration of ferrous ion presence in the solution, the degradation efficiency can be promoted. Thus, the degradation rate of 2-chlorophenol is proportional to the concentration of BOF slag concentration. The effect of BOF slag concentration on the degradation is shown in Figure 6. As depicted in Figure 6, the reaction time needed to totally degrade 2-chlorophenol is 15 minutes for 15g/L BOF slag, 35 minutes for 10g/L BOF slag and 60 minutes for 5g/L of BOF slag. There is an apparent improvement in the degradation as BOF slag concentration increases to 15g/L Since BOF slag is a waste material, it is recommended to use high concentration of BOF slag to accelerate the degradation of 2-chlorophenol wastewater.

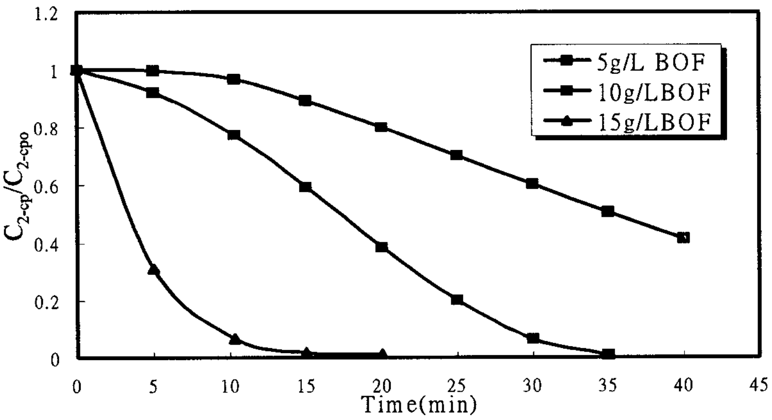

Figure 6. Degradation of 2-chlorophenol by different concentration of BOF slag with 0.352g/L H_2O_2, 100mg/L 2-cp and pH=2.8

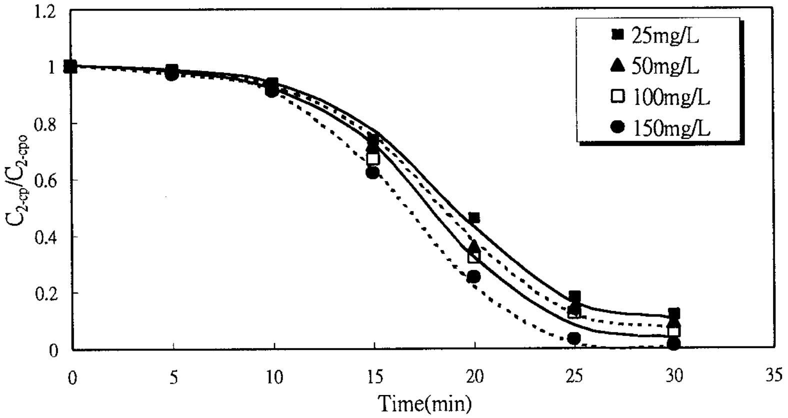

Figure 7. Degradation of 2-chlorophenol with different initial concentration of 2-chlorophenol with log/L, BOF slag, 0.352g/L H_2O_2 and pH=2.8

Figure 7 shows the degradation rate of 2-chlorophenol with different initial concentrations of 2-chlorophenol: 25, 50, 100 and 150 mg/L by 10g/L BOF slag, 0.352g/L hydrogen peroxide and pH=2.8±0.2. The experimental data show that a higher initial concentration of 2-chlorophenol has a higher degradation rate. However, the difference is not significant. The degradation effkiency is 90% for the initial concentration of 2-chlorophenol 25mg/L and is 99% for 150mg/L The results indicate that degradation rate can be promoted by the presence of high concentration of 2-chlorophennol.

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