Isabela B. S. Will, Joanna Yu, José E. F. de Moraes, Antonio C. S. Teixeira, Roberto Guardani

DEGRADATION OF ORGANIC COMPOUNDS IN WATER BY THE PHOTO-FENTON PROCESS

Isabela B. S. Will[*], *Joanna Yu, José E. F. de Moraes, Antonio C. S. Teixeira, Roberto Guardani*

Escola Politécnica da USP, Departamento de Engenharia Química,
Laboratório de Simulação e Controle de Processos,
Av. Prof. Luciano Gualberto, Trav. 3, n° 380, CEP 05508-900, São Paulo-SP, Brasil.
E-mail[*]: isabelawill@zipmail.com.br

ABSTRACT

Advanced Oxidation Processes for wastewater treatment have been attracting growing interest for the degradation of hazardous compounds for which biological treatment is often not efficient. Organic pollutants, generated by many industrial processes, can be oxidized in a number of reactions, which can lead to carbon dioxide and water.

In this work, the photo-Fenton oxidation of phenol, taken as model pollutant, has been investigated using combinations of Fe (II), H_2O_2 and UV-visible light. The experimental program involved photochemical experiments in a bench-scale reactor in order to obtain the rate of phenol degradation. The influence of the following parameters was examined: initial phenol concentration, H_2O_2 and Fe (II) concentrations, light wavelength range and temperature.

The results indicated that the photo-Fenton oxidation is an effective treatment for industrial wastewater containing phenol. The technology represents a feasible route to treat wastewater containing organic toxic compounds, originating from a number of industrial activities.

INTRODUCTION

In recent years, phothochemically initiated degradation processes, referred to as Advanced Oxidation Processes (AOP), have been proposed for the treatment of wastewater containing non-biodegradable organic compounds (Esplugas et al., 1994, Sýkora et al., 1997, Lei et al., 1998). According to Esplugas et al., AOPs are methods for the production of highly reactive intermediates, mainly the hydroxyl ($OH^•$) radical, which is able to oxidize the pollutants to yield CO_2, H_2O and a small amount of acids or salts.

The hydroxyl radical can be produced by homogeneous processes, such as O_3/UV, H_2O_2/UV,

$H_2O_2/Fe(II)$ (Fenton), $H_2O_2/Fe(II)/UV$ (Photo-Fenton) (Esplugas et al., 1994 and Benitez et al., 1999), and heterogeneous processes, such as TiO_2/UV (Ruppert and Bauer, 1993; Bauer and Fallmann, 1997; Martyanov, et al., 1997 and Rideh et al., 1997).

A combination of H_2O_2 and UV radiation with Fe(II), the so called photo-Fenton process, produces more hydroxyl radicals in comparison with the systems $H_2O_2/Fe(II)$ or H_2O_2/UV, thus promoting the rate of degradation of organic pollutants. Fig. 1 shows the proposed reaction pathways for the photo-Fenton process starting with the Fenton reaction (reaction 1) (Kim and Volgelpohl, 1998).

Fe (III) photolysis takes place under irradiation with light (adsorption range: 290 to 400nm), producing Fe (II). Fe (II) ions in the presence of H_2O_2 provide a continuous source of hydroxyl radicals. Hydrogen peroxide is decomposed by Fe(II) (known as Fenton reagent), producing hydroxyl radicals according to:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH^• \qquad (1)$$
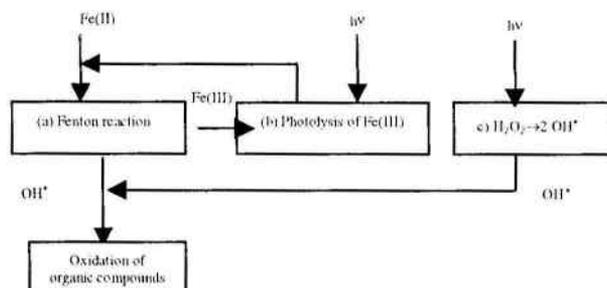
(a) Fenton Reaction

(b) Photolysis of Fe(III): $[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + OH^•$

(c) $H_2O_2 + h\nu \rightarrow 2\,OH^•$ ($\lambda < 400nm$)

(d) Oxidation

Fig.1 – Reaction pathways for the photo-Fenton process

The highly reactive hydroxyl radicals formed in the photo-Fenton process initiate the oxidative destruction of organic substances (RH) in water, which may lead to the total oxidation of organic pollutants.

$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \qquad (2)$$

The $R^{\bullet}$ radical reacts with other substances generating oxidized compounds.

In this work, the photo-Fenton oxidation of aqueous phenol solutions, with total organic carbon (TOC) between 100 and 1000 ppm (in terms of carbon), has been investigated using Fe (II), H_2O_2 and UV-visible light. Phenol, taken as a model pollutant, can be found in industrial wastewater, and poses a significant threat to the environment. Phenolic compounds are toxic to aquatic life and have the ability to impart taste and odor to drinking water, even at parts per billion levels.

The experimental program involved photochemical experiments in a bench-scale reactor in order to investigate the phenol degradation rate. The influence of the following parameters was examined: initial phenol concentration, H_2O_2 and Fe (II) concentrations, light wavelength range and temperature.

EXPERIMENTAL METHODS

Materials

Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) and hydrogen peroxide (30%) were used as a source of hydroxyl radicals. KI, Na_2SO_3 and $Na_3PO_4.12H_2O$ (or $NaH_2PO_4.H_2O$), were added to samples taken at different reaction times, in order to stop the reaction (quenching agents). All reagents, including phenol, are analytical grade.

Photochemical experiments

The laboratory unit consists of an annular photochemical reactor with a net volume of 1 L. A medium pressure mercury vapor lamp of 550W was used as light source. The light wavelength range depended on the choice of the lamp immersion well (quartz or borosilicate) which acts as a filter. The photochemical reactor is connected to a jacketed recirculation tank with a net volume of 5 L. The solution in the tank is well mixed and its temperature can be controlled by means of a thermostatic bath.

The reaction was monitored by measuring the total organic carbon (TOC) in the solution.

The experimental procedure was based on previous work of the authors (Göb et al., 1999). The initial pH of the phenol solution (total volume = 3 L) was adjusted to 3.0 by adding H_2SO_4 and the light was turned on. Ferrous sulphate heptahydrate was added at the beginning of the experiment and hydrogen peroxide

was continuously fed. Samples were taken at different times along the reaction. The sample preparation involved adding the reaction quenching agents, followed by filtration (0.22 μm Durapore membrane, Millipore) to remove precipitated iron salt, prior to feeding to the TOC analyzer (TOC-5000A, Shimadzu). In some experiments the phenol content was also analyzed by gas chromatography (3300, Varian).

The experimental program involved three factorial designs. The first one was a fractional factorial design at two levels to investigate the influence of the following parameters: initial phenol concentration ($C_{ph,0}$), H_2O_2 and Fe(II) concentrations (C_{H2O2} and C_{Fe}, respectively), light wavelength range and temperature.

The second one was a full factorial design at two levels in which the effects of initial phenol, H_2O_2 and Fe(II) concentrations were studied in detail. Preliminary experiments were carried out at central point conditions, in order to evaluate the experimental errors associated with the process, sample preparation and analysis. The average deviations are about $\pm$ 38.6 ppm, of the measured TOC values.

In the third factorial design, Fe (II) concentration was reduced and only H_2O_2 and Fe(II) concentrations were varied.

The values of the parameters in each factorial design are shown in Table 1.

Table 1 – Factorial design parameters

| Parameter	Level	1st Factorial Design	2nd Factorial Design	3rd Factorial Design
$C_{ph,0}$ (ppm)	−	500	100	
	+	1000	1000	1000 (fixed)
Total amount of H_2O_2 (mmol)	−	150	30	30
	+	450	300	300
C_{Fe} (mmol/L)	−	1,0	0.3	0.01
	+	5,0	1.0	0.1
Light wavelength range	−	visible	visible (fixed)	visible (fixed)
	+	UV+visible		
Temperature (°C)	−	30	30 (fixed)	
	+	50		30 (fixed)

RESULTS AND DISCUSSION

1st Factorial Design

In this factorial design, 16 experiments (2^{5-1}) were performed. During the experiments, a change of solution color from transparent to dark was noticed, which is probably an evidence of the formation of intermediate organic compounds, such as quinones and/or iron complexes. This behavior is also observed by GC analysis. Fig. 2 shows the TOC and the normal phenol concentration vs. reaction time for two experiments at different conditions.
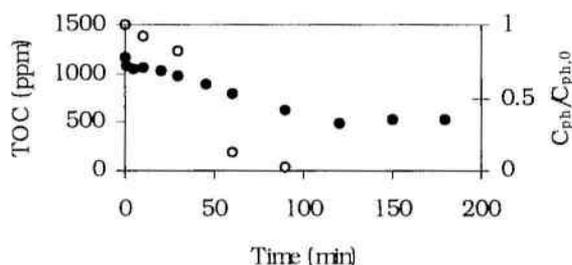
Case A: ● TOC   ○ GC - $C_{ph,0} = 1000$ ppm, Total amount of $H_2O_2 = 150$ mmol, $C_{Fe} = 5$ mM , T = 50°C, visible light, total time of reaction = 180 minutes.
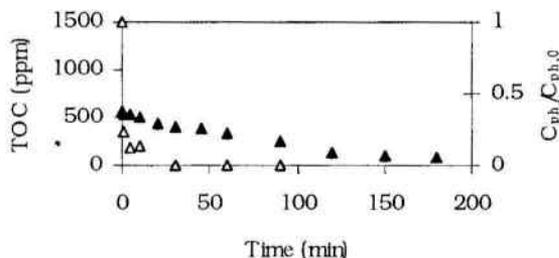
Case B: ▲ TOC   △ GC - $C_{ph,0} = 500$ ppm, Total amount of $H_2O_2 = 150$ mmol, $C_{Fe} = 1$ mM , T = 50°C, visible light, total time of reaction = 180 minutes.

Fig 2 – TOC and GC analysis results for 2 experiments of the first factorial design.

In both cases, a clear decrease in TOC and phenol concentrations is observed. TOC decreases rapidly in the first 10 minutes, followed by a less intense degradation in the last 90 minutes. Practically no significant degradation is observed during the last 30 minutes of the experiments.

In case A, 54% of TOC is degraded in 3 hours of reaction, which corresponds to an average rate of 7.23 ppm/min; in experiment B, these values are 86% and 5.36 ppm/min, respectively. Also, a total conversion of organic carbon into CO_2 is observed for the last case.

The increased degradation rate in experiment A is due to the increased phenol and iron concentrations.

As shown by chromatographic analysis (Fig. 2) phenol concentration is below the detection limit after 30 minutes (case B) and 90 minutes (case A). The plateaus observed in TOC curves are possibly related to the formation of intermediate organic compounds, which are more difficult to degrade.

The experimental results were evaluated by means of a pareto chart (Fig 3), showing the effects of single factors and two-factors combinations.
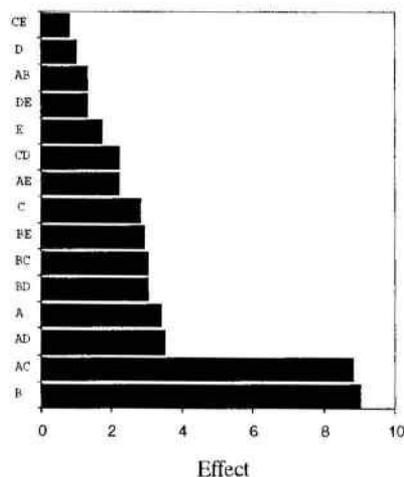
A: Phenol; B: Peroxide; C: Iron; D: Temperature; E: Light wavelenght range

Figure 3 – Pareto chart for average rate 1st Factorial Design

It can be observed that peroxide concentrations, as well as the phenol-iron interactions are the most important factors in the process. This is in agreement with the results shown in Fig. 2, in which phenol and iron concentrations are the only factors affecting the average degradation rate, which is greater when both variables are at their maximum levels (case A).

The effects of temperature and light wavelength range were not important in this experimental domain although there is evidence of interactions between them and other effects.

2nd Factorial Design

In this factorial design 8 experiments (2^3) were performed. The effects of initial phenol concentration, in a broader experimental domain; H_2O_2 and Fe(II) concentrations at lower levels, were studied. A broader phenol concentration range (from 500-1000 to 100-1000 ppm TOC) was adopted to enable a better evaluation of

this effect on the degradation process. The use of reduced amounts of Fe is also beneficial in terms of final disposal of the wastewater.

The results shown in Fig. 4 are in agreement with the ones shown in Fig 3, with H_2O_2 as the main factor affecting the process. This is expected, since H_2O_2 takes part in the reactions that generate hydroxyl radical.
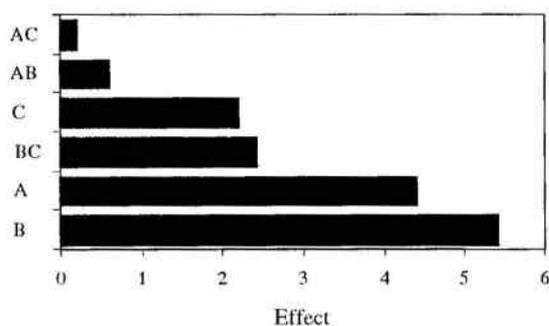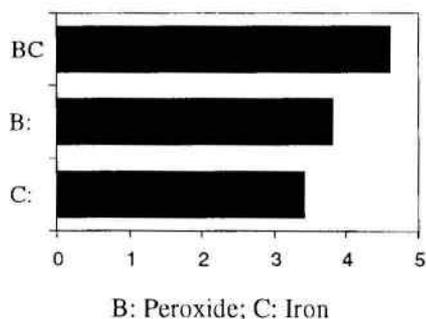

A: Phenol; B: Peroxide; C: Iron

Fig. 4 - Pareto chart for average **rate 2nd Factorial Design**

The effect of phenol concentration is more adequately estimated in this 2nd design, since its concentration range is broader.

3rd Factorial Design

The third factorial design was performed in order to evaluate peroxide and iron interactions at lower iron levels (0.1 mM – 0.01 mM). As in the previous designs, the effect of the peroxide and its interaction with iron is still more important than the effect of iron alone (Fig. 5). In this experimental domain the combined action of H_2O_2 and iron is expected since these compounds are involved in a redox cycle (reaction 1).

B: Peroxide; C: Iron

Figure 5 – Pareto chart for average rate 3rd Factorial Design

CONCLUSIONS

The results indicated that the photo-Fenton oxidation is an effective treatment for industrial wastewater containing phenol. More than 85% of the phenol could be degraded to other organic compounds in 10 minutes of experiment. Moreover, about 90% of the total organic carbon could be converted into inorganic carbon in 3 hours, at nearly ambient temperature under visible light. These conditions are favorable for the application of photo-Fenton reactions.

The results enabled the evaluation of the relative influence of some parameters on the efficiency of photo-Fenton process. It was noted that the amount of iron salt added could be minimized, which is important to minimize costs associated with separation, as well as to attain maximum discharge limits imposed by environmental regulations. Others analyses, such as biochemical oxygen demand (BOD) and toxicity, should be carried out to confirm the effectiveness of the treatment.

REFERENCES

Bauer, R and Fallmann, H., The photo-Fenton oxidation - A cheap and efficient wastewater treatment method., Res. Chem. Intermed., 23 (4), 341-354, 1997.

Benitez, F. J., Beltran-Heredia, J., Acero, J. L. and Rubio, F. J., Chemical decomposition of 2,4,6-trichlorophenol by ozone, Fenton´s reagent and UV radiation. Ind. Eng. Chem. Res., 38, 1341-1349, 1999.

Bigda, R. J., Consider Fenton´s Chemistry for wastewater treatment, Chemical Engineering Progress, december, 62-66, 1995.

Esplugas, S., Yue, P. L. and Pervez, M. I., Degradation of 4-chlorophenol by photolytic oxidation., Wat. Res., 28 (6), 1323-1328, 1994.

Göb, S., Oliveros, E., Bossmann, S. H., Braun, A. M., Guardani, R., Nascimento, C. A. O., Modeling the kinetics of a photochemical water treatment

process by means of artificial neural networks, Chem. Eng. Proc., 38, 373-382, 1999.

Kim, S. and Vogelpohl, A., Degradation of pollutants by the photo-Fenton-process, Chem. Eng. Technol, 21, 187-191, 1998.

Lei, L., Hu, X., Yue, P. L., Bossmann, S. H., Göb, S. and Braun, A. M., Oxidative degradation of polyvinyl alcohol by the photochemically enhanced Fenton reaction. J. Photochem. Photobiol. A.: Chem., 116, 159-166, 1998.

Martyanov, I. N., Savinov, E. N. and Parmon, V. N., A comparative study of efficiency of photooxidation or organic contaminants in water solutions in various photochemical and photocatalytic systems. 1. Phenol photooxidation promoted by hydrogen peroxide in a flow reactor. J. Photochem. Photobiol. A.: Chem., 107, 227-231, 1997.

Rideh, L., Wehrer, A., Ronze, D. and Zoulalian, A., Photocatalytic degradation of 2-chlorophenol in TiO2 aqueous suspension: modeling of reaction rate. Ind. Eng. Chem. Res., 36, 4712-4718, 1997.

Ruppert, G., Bauer, R. and Heisler G., The photo-Fenton reaction- na effective photochemical wastewater treatment process. J. Photochem. Photobiol. A.: Chem., 73, 75-78, 1993.

Sýkora, J., Pado, M., Tatarko, M. and Izakovic, M., Homogeneous photo-oxidation of phenols: influence of metals[1]. J. Photochem. Photobiol. A.: Chem., 110, 167-175, 1997.