

## Oxidation of Phenolic Wastewater by Fenton's Reagent

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### Abstract

Phenol oxidation by Fenton's reagent ( $H_2O_2 + Fe^{+2}$ ) in aqueous solution has been studied for the purpose of learning more about the reactions involved and the extent of the oxidation process, under various operating conditions. An initial phenol concentration of 100 mg/L was used as representative of a phenolic industrial wastewater. Working temperature of 25 °C was tested, and initial pH was set at 5.6. The  $H_2O_2$  and the  $Fe^{+2}$  doses were varied in the range of ( $H_2O_2/Fe^{+2}/phenol = 3/0.25/1$  to  $5/0.5/1$ ). Keeping the stirring speed of 200 rpm. The results exhibit that the highest phenol conversion (100%) was obtained under ( $H_2O_2/Fe^{+2}/phenol$  ratio of  $5/0.5/1$ ) at about 180 min. The study has indicated that Fenton's oxidation is first order with respect to the phenol concentration and the rate constant  $K$ , was found to be  $0.0325s^{-1}$ .

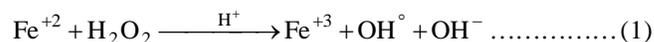
### Introduction

Increasing concern about environmental and health risks demand a more rigorous control of industrial wastewater, promoting the development and implementation of new treatment technologies capable to deal with toxic pollutants resistant to the widely established conventional methods. Among this type of pollutants, phenol and phenolic compounds have attracted much attention in the last two decades. This interest arises from their relative frequency in the aqueous effluent of the chemical industry. Moreover, phenol is considered to be an intermediate in the oxidation pathway of high molecular weight aromatic hydrocarbons, and thus it is frequently used as a model compound for advanced wastewater studies(1).

Advanced oxidation processes (AOPs) are an interesting treatment option for this type of wastewaters, because of their great potential to oxidize, partially or totally, numerous organic compounds(2-4). These processes are based on the generation of hydroxyl radicals ( $OH^\bullet$ ). This

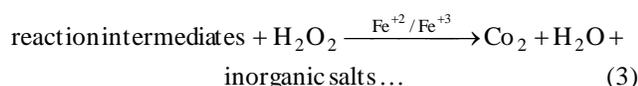
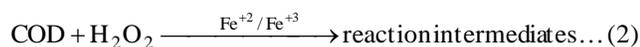
species is a more powerful oxidant ( $E^\circ 2.8V$ ) than the chemical reagents commonly used for this purpose, such as ozone ( $E^\circ 2.0V$ ) or  $H_2O_2$  ( $E^\circ 1.8V$ ). Rate constants in AOPs for organic compounds are several orders of magnitude higher than those reported for others processes such as ozonation(5). Due to its high reactivity, the hydroxyl radical is very unstable and must be continuously produced in situ by means of chemical or photochemical reactions(3). The main methods to generate this radical consist of the use of  $O_3$  at elevated pH ( $> 8.5$ ),  $O_3/H_2O$ ,  $O_3/catalyst$ , Fenton's Reagent ( $Fe^{+2}/H_2O_2$ ),  $O_3/UV$ ,  $H_2O_2/UV$ ,  $O_3/H_2O_3/UV$ , photo-Fenton/Fenton-like systems, and photocatalytic oxidation ( $UV/TiO_2$ )(6).

One of the most effective AOPs consist of the use of Fenton's reagent, a combination of  $H_2O_2$  and  $Fe^{+2}$ . In this process,  $H_2O_2$  decomposes catalytically by means of  $Fe^{+2}$  at acid pH, giving rise to hydroxyl radicals.



The application of Fenton's reagent as an oxidant for wastewater treatment is attractive, in principle, due to the fact that Fe is a widely available and nontoxic element, and hydrogen peroxide is easy to handle and the excess decomposes to environmentally safe products(7). Among the advantages of Fenton's process relative to other oxidation techniques are the simplicity of equipment and the mild operation conditions (atmospheric pressure and room temperature); mainly for these reasons Fenton's process has been regarded as the most economical alternative(8).

Numerous authors have studied the mechanism of oxidation of organic compounds by Fenton's reagent. The number of reactions is high, and the schemes of reaction are generally complex. In an overall view, the process can be represented by the following reactions(9) :



The oxidation of the substrate completely to Co<sub>2</sub> becomes, in general, uneconomical due to high H<sub>2</sub>O<sub>2</sub> consumption. Thus, this process has been mostly proposed as a pretreatment to reduce the effluent toxicity to safe levels for further biological treatment(10). For this reason, it is necessary to study the reaction pathway in depth, as the toxicity of some intermediate can be higher than that of the initial compound. This is the case in the oxidation of phenol, where hydroquinone and p-benzoquinone are formed, the toxicities of which are several orders of magnitude higher than that of phenol itself(11).

Due to the complexity of the whole process, the various reaction schemes found in the literature refer to partial studies, with specific objectives. For some of them, the aim was to detect the reaction intermediates, whereas others studied the influence of these products in the evolution of the process.

The aim of the present work is to study the oxidation of phenol with Fenton's reagent. First, the intermediates from phenol oxidation were identified, using different concentration of catalyst (Fe<sup>+2</sup>) and oxidant (H<sub>2</sub>O<sub>2</sub>). Finally a kinetic study was carried out, to obtain the kinetic rate constant for the oxidation of phenol.

## Experimental Work

Experiments were carried out in 100 ml glass batch reactor shaken in a constant temperature bath (25°C) at an equivalent stirring velocity around 200 rpm for 4 hour. The reaction volume was 50 ml, and the reactants were added simultaneously at the beginning of each run. The starting phenol concentration was 100 mg/L and 300 to 500 mg/L of H<sub>2</sub>O<sub>2</sub> (which corresponds to the stoichiometric amount of H<sub>2</sub>O<sub>2</sub> necessary to oxidize phenol to Co<sub>2</sub> and H<sub>2</sub>O. The Fe<sup>+2</sup> dose was varied between 25 and 50 mg/L.

The sample was analyzed after the reaction. Phenol and aromatic intermediates identified and quantified by means of UV-spectrophotometer and high-performance liquid chromatography.

## Results and Discussion

Evolution of phenol oxidation: It is obvious that the effect of H<sub>2</sub>O<sub>2</sub>/Fe<sup>+2</sup>/phenol ratio is the predominate factor in oxidation of phenol. Keeping other factors constant (pH=5.6, temperature = 25°C, and stirring speed = 200 rpm).

Fig. 1 shows the conversion of phenol versus time for different ratios of H<sub>2</sub>O<sub>2</sub>/Fe<sup>+2</sup>/phenol. The total phenol oxidation was obtained with 5/0.5/1 ratio at about 180 min.

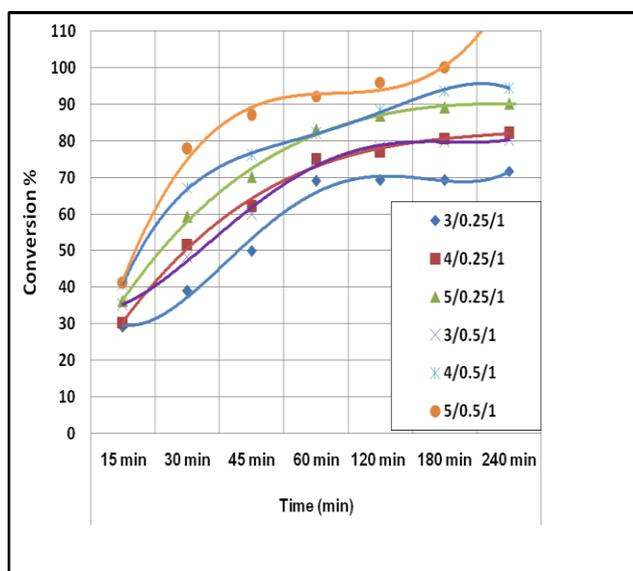
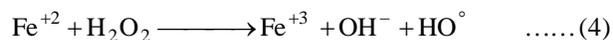


Fig. 1 Effect of H<sub>2</sub>O<sub>2</sub>/Fe<sup>+2</sup>/phenol ratio on the phenol oxidation.

Fenton's reagent of hydrogen peroxide and an iron catalyst which will rapidly oxidize phenol over wide range of concentration and temperatures. Iron is one of the most common metals that have special oxygen transfer properties which improve the utility of hydrogen peroxide. This iron-catalyzed hydrogen peroxide is (Fe+2), hydroperoxyl radicals (HO°), and/or superoxide radicals ( $O_2^-$ ) according to the following reaction:



Super oxide radicals are dominating at neutral pH and hydrogen peroxide also may contribute to hydroxyl radical formation by the following overall equation:



Evolution of intermediate compounds: Figures (2) and (3) summarize the evolution of the oxidation reaction of phenol with Fenton's reagent under the experimental conditions (H<sub>2</sub>O<sub>2</sub>/Fe+2/phenol of 5/0.5/1, pH = 5.6, Temperature = 25°C, and stirring speed = 200 rpm).

As can be seen, under these experimental conditions close to 80% of phenol is converted in about 30 min, giving rise to dihydroxybenzenes upon hydroxylation of the aromatic ring. Catechol is main primary oxidation product, indicating that hydroxylation takes place predominantly in the ortho position. The peak concentration of hydroquinone was about one-tenth that of catechol.

Ring-Opening of the aromatic intermediates leads to the formation of organic acids. As a result, a pH decrease takes place, although it remained always within the optimum range, above 2. These compounds are intermediates and/or final oxidation products. Maleic, acetic, and formic acids were the earlier and more abundant products of the acid formation stage. Oxalic acid was appearing at a lower rate, although it reached a high relative concentration as the oxidation reaction proceeded.

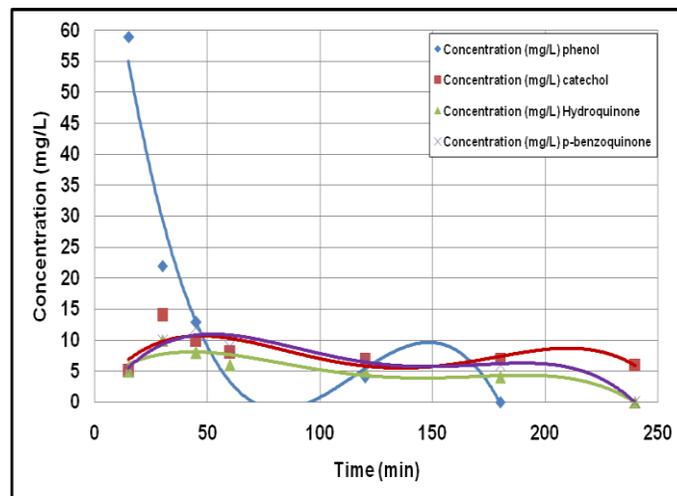


Fig. 2 Evolution of aromatic compounds identified in phenol oxidation with Fenton's reagent.

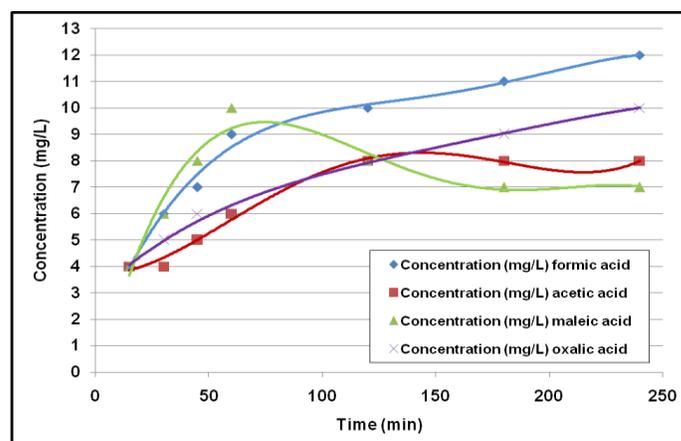


Fig. 3 Evolution of organic acids identified in phenol oxidation with Fenton's reagent.

Figure (4) summarizes the scheme of reaction proposed for phenol oxidation with Fenton's reagent, according to our results.



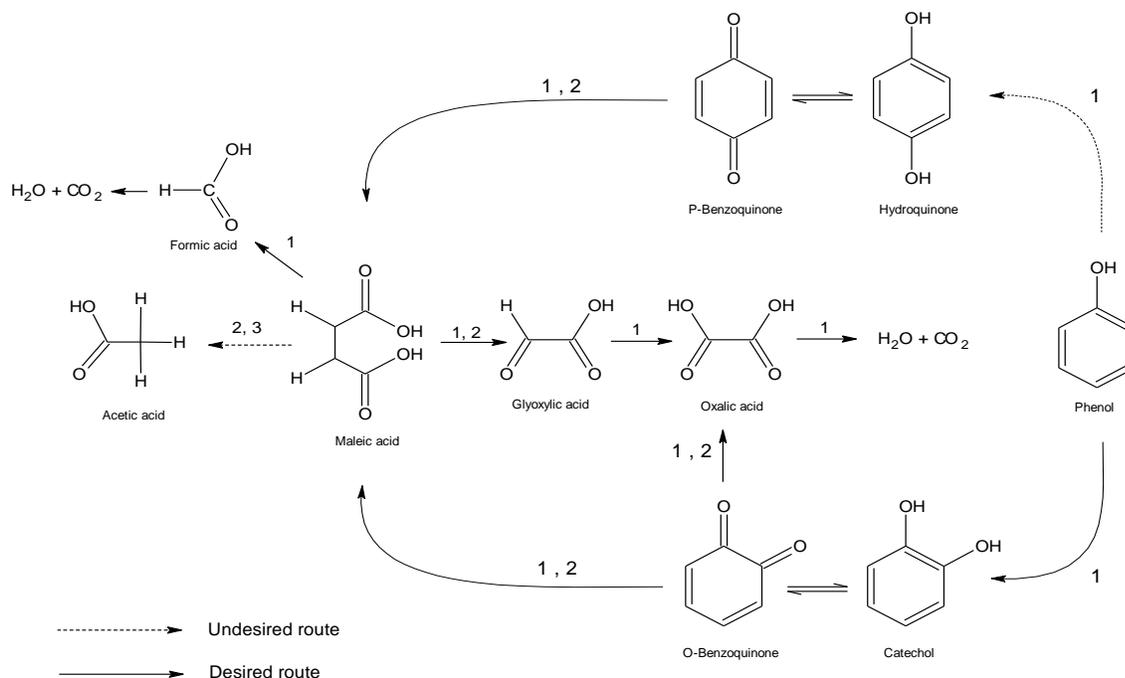


Fig. (4) : proposed reaction scheme in this work.

Reaction steps include: 1- oxidation 2- c-c bond cleavage. 3- transfer hydrogenation.

## Conclusions

This study indicated that the phenol in aqueous solutions can be oxidized by Fenton's reagent. The results showed that the degree of phenol oxidation depends to large extent on  $H_2O_2/Fe^{+2}/phenol$  ratio.

During destruction by  $H_2O_2$  in Fenton's reagent system, phenol undergoes a transformation through a variety of chemical intermediates, leading in the production of  $CO_2$  and  $H_2O$  which is relatively harmless by product.

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