



EXPERIMENTAL STUDY FOR OXIDATION OF PHENOL BY FENTONS REAGENT

Sama Mohammed Abdullah

Chemical Engineering Department-College of Engineering-University of Baghdad

ABSTRACT

The oxidation of phenol in aqueous solution was studied at atmospheric pressure in a batch reactor. Fenton reaction was used to degrade this component. Phenol (50 - 100 ppm) oxidation was carried out in the acidic medium range of (pH=2.7 - 5.8) under mild conditions of temperature (28 - 48°C), stoichiometric excess percentage of H₂O₂ (S.E_{H₂O₂}%) of (0 - 100%), and Fe(II) to phenol concentrations ratio of (0 - 0.63). The results indicate that the oxidation by Fenton reaction was an efficient method to eliminate phenol, also the amount of catalyst and temperature had the large effect on the phenol degradation. Finally the simple kinetic model for the reaction was established.

الخلاصة

أكسدة الفينول في الوسط المائي تمت دراستها تحت الضغط الجوي في مفاعل دفعي. تفاعلات فنتون استخدمت لمعاملة هذا المركب. الفينول (50-100 جزء بالمليون) تمت أكسدته في وسط حامضي بين (2.7-5.8) تحت ظروف معتدلة من درجات حرارة (28-48 م°) والنسبة المئوية لكمية بيروكسيد الهيدروجين الفائضة عن التفاعل (0-100%) ونسبة أيون الحديد الثنائي الى الفينول (0-0.63). بينت النتائج ان أكسدة الفينول باستخدام تفاعلات فنتون هي عملية كفوة للتخلص من الفينول، كما بينت ان كمية العامل المساعد ودرجة الحرارة لهما تأثير كبير على عملية ازالة الفينول. أخيرا تم وضع موديل مبسط لدراسة حركية التفاعل.

INTRODUCTION

In situ chemical oxidation is an evolving technology that involves the introduction of chemical oxidants into subsurface soil and groundwater to destroy organic contaminants. This technology has promise when the contamination is amenable to mineralization to carbon dioxide and water or oxidation to a relatively less harmful form that may then be suitable for subsequent treatment. Selection of oxidation as an appropriate technology and the oxidant is dependent on the nature and type of contaminant, the level of remediation required, viability of oxidant delivery, soil conditions and hydrogeology of the site (Kluck and Achari 2003).

The development of novel treatment methods encompasses investigations of advanced oxidation processes (AOPs), which are characterized by production of the hydroxyl radical (OH[•]) as a primary oxidant (Barbusiński 2005). Hydroxyl radicals are highly reactive and nonselective oxidations being able to decompose many organic compounds (Hu et al. 2002). This ability is enhanced by the presence of compounds able to activate the radical decomposition mechanisms (Chedeville et al. 2005). Fenton reaction hypothesis postulated that hydroxyl radical was the effective oxidation reagent in this reaction (Ricciardi 2006). Fenton reagent is a mixture of H₂O₂ and ferrous iron, which generates hydroxyl radical according to the reaction below:



The ferrous iron initiates and catalyzes the decomposition of H_2O_2 , resulting in the generation of hydroxyl radical. The generation of hydroxyl radical involves a completely reaction sequence in an aqueous solution (Farrokhi et al. 2003).

The use of $Fe(II)/H_2O_2$ as an oxidant for waste water treatment is attractive due to the facts that: (1) iron is a highly abundant and non-toxic element, and (2) hydrogen peroxide is easy to handle and environmentally benign (Munter 2001). Factors that influence Fenton processes are pH, contaminant character and concentration, $Fe(II)$ concentration, hydrogen peroxide quantity required for complete oxidation and temperature (Paradowska 2004).

The optimum pH of Fenton oxidations is usually reported in the acidic range between 2 and 4. Groundwater and soil may possess a high buffer capacity. Therefore, the necessity to acidify the reaction medium limits the applicability of the Fenton process in environmental technology. The main reason for the low reactivity at circumneutral pH is the precipitation of $Fe(III)$ as hydrous oxyhydroxides $Fe_2O_3 \cdot nH_2O$ which inhibits the recycling process of $Fe(III)/Fe(II)$ (Georgi et al. 2006).

The stoichiometric amount of H_2O_2 required for the total oxidation of phenol was calculated by using eq. (2) (Feng, and Le-cheng 2004).



In the kinetic study the results were obtained at different temperatures, $S.E_{H_2O_2}\%$ and $[Fe^{2+}]_0/[Ph]_0$ were used. If Fenton's reaction as mentioned by former researchers (Feng, and Le-cheng 2004, Parjan Singh 2006, Kwan 2003, and Alegría et al. 2003) was pseudo-first order, then the mention integral rate equation can be described by the eq. (3):

$$\ln \frac{[Ph]_0}{[Ph]} = K_{obs} t \quad (3)$$

At these different conditions the pseudo-first order rate constants (K_{obs}) were obtained from plotting $\ln [Ph]_0/[Ph]$ vs. t as shown in Fig. 7.

In this study, the expression of K_{obs} can incorporate the effect of H_2O_2 and $Fe(II)$ in addition to temperature effect and as follows:

$$K_{obs} = k_0 [H_2O_2]_0^\alpha [Fe^{2+}]_0^\beta \exp\left[\frac{-E_a}{RT}\right] \quad (4)$$

To calculate the values of K_{obs} , α , β , and E_a eq. (4) must be linearized in the following way:

$$\ln K_{obs} = \ln k_0 + \alpha \ln [H_2O_2]_0 + \beta \ln [Fe^{2+}]_0 - \frac{E_a}{RT} \quad (5)$$

This work deals with phenol oxidation in aqueous phase using Fenton reaction and aims to quantify the influence of feed solution acidity (pH), hydrogen peroxide stoichiometric excess percent ($S.E_{H_2O_2}\%$), iron to phenol concentration ratio, initial phenol concentration, and temperature. The reaction kinetic was also studied.



EXPERIMENTAL

Materials

Phenol with 99.5% purity was chosen as wastewater model compound and was purchased from Griffin. Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) with 99% purity was used as catalyst was purchased from BDH chemical LTD. Hydrogen peroxide with 99.5% purity was used as oxidizing agent was purchased from Keny chemicals-company. Sulfuric acid 95.97% purity was purchased from Fluka was used to adjust solutions acidity. All chemical work was carried out using distilled water.

Experimental Set-up And Procedure

All oxidation runs were conducted using three-neck Pyrex round-bottle flask (500 ml). One neck was used for introducing the reactants solutions and the catalyst as well as taking out the samples by Syringe. Through the second and third necks quick fit thermometer and reflux condenser were fixed. The flask was heated with a hot plate stirred magnetically (T.Jlassco (India), magnetic stirrer with hot plate), as illustrated in Fig. 1.

A volume of 500 ml of phenol solution were filled into the reaction vessel. By adding 1M H_2SO_4 the solutions were adjusted to pH 2.7, 3.7 and 4.7 to keep the medium in the acidic range. Afterwards the appropriate amount of Fe(II) was added. The hydrogen peroxide was introduced in appropriate amount to start the reaction at the suitable temperature. The liquid samples were taken periodically and immediately filtrated and analyzed.

Samples Analysis

Phenol concentration in the outlet samples was analyzed using Shimadzu model UV-160A ultraviolet/visible spectrophotometer. Prior to each oxidation experiment the phenol calibration curve of UV spectrophotometer was checked to correct deviation in the peak height, which may be occurred.

Phenol calibration curve was made by taking samples of phenol solutions in the concentration range of 0.5 to 50 ppm and measured the absorbency against each concentration, and then plotting concentrations values against them absorbency in the UV spectrophotometer device. When the sample of unknown phenol concentration input to this device, it would immediately gave that concentration.

RESULTS AND DISCUSSION

Effect Of pH Solution

The degradation of phenol at three different feed solution pH of 5.8, 4.7, 3.7 and 2.7 was studied at constant other variables: $\text{S.E.}_{\text{H}_2\text{O}_2}\%$ of 0%, $[\text{Fe}^{2+}]_0/[\text{Ph}]_0$ of 0.42, temperature of 28°C , and initial phenol concentration of 50 ppm, as illustrated in Fig. 2.

The study was indicated that phenol degradation was improved at the most acidic medium (pH=2.7). Thus, at pH=2.7 the remaining phenol concentration was 4.4 ppm, while equal to 9.3, 10.1, and 10.4 ppm at for the pH 3.7, 4.7, and 5.9 respectively. Also, in the solutions with pH 5.8, 4.7 and 3.7 a precipitation of Fe(III) presumably as hydrous oxyhydroxide $\text{FeSO}_3 \cdot n\text{H}_2\text{O}$ was observed. In contrast, no precipitation occurred in the reaction solutions with pH 2.7. These results can be attributed due to low solubility of Fe^{3+} for pH higher than 3, which causes formation of Fe complexes and precipitate as hydrous oxyhydroxides $\text{FeSO}_3 \cdot n\text{H}_2\text{O}$ which inhibits the recycling process of Fe(III)/Fe(II) that can decrease the efficiency of the catalyst as represented in the reaction:

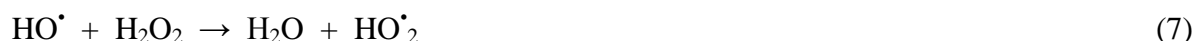


Also the acidic pH favors the formation of a stable and electrophilic structure via a solvation of a proton by an H_2O_2 molecule. These results were in agreement with Feng and Le-cheng 2004, and Kwan 2003.

Effect Of Hydrogen Peroxide Stoichiometric Excess Percent (S.E._{H₂O₂}%)

The degradation of phenol at four different S.E._{H₂O₂}% of 0%, 50% and 100% was studied at constant other variables: pH of 2.7, $[\text{Fe}^{2+}]_0/[\text{Ph}]_0$ of 0.42, temperature of 28°C, and initial phenol concentration of 50 ppm, as illustrated in Fig. 3. It can be seen that the remaining phenol concentrations of 4.4, 3.7, and 3.6 ppm were achieved when S.E._{H₂O₂}% equal to 0%, 50%, and 100% respectively.

A significant enhancement of phenol degradation was observed when S.E._{H₂O₂}% was increased from 0% to 100%. It's significant to know that the oxidant H_2O_2 should be added in an optimal dosage for the reaction due to H_2O_2 itself act as a scavenger of HO^\bullet radical at high oxidant concentration, as represented by the reaction:



Through parallel undesired reaction, the extra H_2O_2 moles will compete with phenol for the HO^\bullet . The radicals (HO_2^\bullet) are the result of this competitive reaction which are less reactive than HO^\bullet radicals and their reaction with organic dissolved carbon is negligible. . These results were in agreement with Chedeville et al. 2005, Feng and Le-cheng 2004, and Paradowska 2004.

Effect Of Fe^{2+} To Phenol Concentration Ratio $[\text{Fe}^{2+}]_0/[\text{Ph}]_0$

The degradation of phenol at three different values of $[\text{Fe}^{2+}]_0/[\text{Ph}]_0$ 0.21, 0.42 and 0.63 was studied at constant other variables: pH of 2.7, S.E._{H₂O₂}% of 50%, temperature of 28°C, and initial phenol concentration of 50 ppm, as illustrated in Fig. 4, in addition, the run without Fe^{2+} at the same above variables was carried out to demonstrated the importance of present Fe^{2+} ions when using H_2O_2 as oxidant. As clear in the Fig. 4 phenol concentration reaches to 3 ppm when $[\text{Fe}^{2+}]_0/[\text{Ph}]_0$ was 0.63, but at $[\text{Fe}^{2+}]_0/[\text{Ph}]_0$ equal to 0, 0.21, and 0.42 phenol concentrations were 47.2, 22.2, and 3.7 ppm respectively.

That considerable influence of Fe^{2+} concentration on the phenol elimination, because more radicals are produced, thus leading to a faster degradation. . These results were in agreement with Chedeville et al. 2005, and Feng and Le-cheng 2004.

Effect Of Temperature

The degradation of phenol at three different temperatures of 28, 38, and 48°C was studied at constant other variables: pH of 2.7, S.E._{H₂O₂}% of 50%, $[\text{Fe}^{2+}]_0/[\text{Ph}]_0$ of 0.63, and initial phenol concentration of 50 ppm, as illustrated in Fig. 5. This figure shows that at 48°C, phenol concentration was 0.2 ppm, while at 38, and 28°C phenol concentrations were 1.09, and 3 ppm.

The temperature showed a strong effect on the phenol elimination. This kind of effect was expected because it's known that kinetic constant (either for phenol decomposition, radicals formation or iron regeneration) have exponential dependency with reaction temperature (Arrhenius law) and this has also been reported by other authors (Chedeville et al. 2005, and Paradowska 2004).

Effect Of Initial Phenol Concentration

The degradation of phenol at three different initial phenol concentrations of 50, 75, and 100 ppm was studied at constant other variables: pH of 2.7, S.E._{H₂O₂}% of 50% , [Fe²⁺]₀/[Ph]₀ of 0.63, and temperature of 28°C. It can be seen from Fig. 6 that the remaining phenol concentrations were 6.8 and 10.6 ppm when initial phenol concentrations were 75, and 100 ppm, while its 3 ppm when initial phenol concentration was 50 ppm. This study showed nonlinear dependence on phenol initial concentration and is somewhat decreased when its concentration is increased. When phenol concentration increased, the intermediate components result throughout reaction pathway increased too, and competed with phenol for the HO[•] at this conditions which were considered the best for 50 ppm phenol concentration. These results were in agreement with Chedeville et al. 2005, and Feng and Le-cheng 2004.

Kinetic Model

The analysis curves indicate the pseudo-first order with respect to phenol concentration and 0.01 and 0.25 orders with respect to H₂O₂ and Fe(II) concentrations respectively. The orders of H₂O₂ and Fe(II) demonstrated the null and considerable effects of them respectively. While the activation energy was been 8 × 10³ J/mol. And frequency factor was 2 × 10¹⁷. This result was agreed with findings of other studies were conducted (Parjan Singh 2006, and Alegría et al. 2003).

$$-r_A = 2 \times 10^{17} \text{EXP} \left[\frac{-8 \times 10^3}{RT} \right] [H_2O_2]_0^{0.01} [Fe^{2+}]_0^{0.25} [Ph] \quad (8)$$

CONCLUSIONS

The results obtained in the chosen field of study confirm that the oxidation by Fenton's reaction in an efficient method for phenol degradation in the acidic medium, so where the lowest remaining phenol concentration (0.2 ppm) was achieved under the conditions of [pH of 2.7, S.E._{H₂O₂}% of 50%, [Fe²⁺]₀/[Ph]₀ of 0.63, temperature of 48°C, and initial phenol concentration of 50 ppm,. These results suggested that catalyst amount and reaction temperature were the predominant factors on the process, while the S.E._{H₂O₂}% and phenol initial concentration effects were relatively null.

Kinetic study showed that the reaction was 1, 0.25, and 0.01 orders with respect to phenol, Fe(II), and H₂O₂ concentrations respectively, with 8 × 10³ J/mol. activation energy and 2 × 10¹⁷ frequency factor.

REFERENCES

- Alegría Y., Liendo F., and Núñez O., "On the Fenton degradation mechanism. The role of oxalic acid", ARKIVOC x,538-549 (2003).
- Barbusiński, K., "The modified Fenton process for decolorization of dye wastewater", Polish Journal of Environmental Studies, 14 (3), 281-285, (2005).
- Chedeville, O., Tosun-Bayraktar, A., and Porte, C., "Modeling of Fenton reaction for the oxidation of phenol in water", Journal of Automated Methods and Management in Chemistry, 2, 32-36 (2005).
- Farrokhi, M., Mesdaghinia, AR., Naseri, S., and Yazdanbakhsh, AR., "Oxidation of pentachlorophenol by Fenton's reagent", Iranian J Publ Health, 32 (1), 6-10 (2003).

- Feng, H., and Le-cheng, L., "Degradation kinetics and mechanisms of phenol in photo-Fenton process", Journal of Zhejiang University SCIENCE, 5(2), 198-205 (2004).
- Georgi, A., Schierz, A., and Kopinke, F. D., "Activation of hydrogen peroxide by complexes of iron(II) with humic acid for chemical degradation of organic compounds in water", Extended abstract for a scheduled presentation at the EAAOP conference (Environmental applications of Advanced Oxidation Processes), Greece (2006).
- Hu, X., Lam, F. L. Y., Cheung, L. M., Chan, K. F., Zhao, X. S., and Lu, G. Q., "Copper/MCM-41 as catalyst for photochemically enhanced oxidation of phenol by hydrogen peroxide", Catalysis Today, 68, 129-133 (2002).
- Kluck, C., and Achari, G., "Chemical oxidation techniques for in situ remediation of hydrocarbon impacted soils", (2003).
- Kwan, W. P., "Decomposition of hydrogen peroxide and organic compounds in the presence of iron and iron oxides", Ph. D. thesis, Massachusetts Institute of technology, (2003).
- Munter, R., "Advanced oxidation processes-current status and prospects", Proc. Estonian Acad. Sci. Chem., 50, 59-80 (2001).
- Paradowska, M. A., "Tailored chemical oxidation techniques for the abatement of bio-toxic organic wastewater pollutions: An experimental study", Ph. D. thesis, Rovira i Virgili University, (2004).
- Parjan Singh D. K. A/P., "Removal of organic using solar-Fenton technology", Bachelor Thesis, University Teknologi Malaysia, (2006).
- Ricciardi, M., "Wastewater treatment by high efficiency heterogeneous photo-Fenton process", Ph. D. thesis, Degli University, (2006).

NOMENCLATURE

$[\text{Fe}^{2+}]_0$	Fe(II) initial concentration (mol./l).
$[\text{H}_2\text{O}_2]_0$	H_2O_2 initial concentration (mol./l).
$[\text{Ph}]_0$	The initial phenol concentration (mol./l).
$[\text{Ph}]$	The phenol concentration after a time interval t, (mol./l).
E_a	The activation energy (J/mol.).
k_0	The frequency factor (case dependent units).
K_{obs}	The pseudo-first order rate constant.
R	The universal gas constant, 8.314 (J/mol.K).
S.E. _{H₂O₂} %	Stoichiometric Excess Percent.
T	Temperature (K).
T	Time (min.).
α	H_2O_2 order.
β	Fe(II) order.

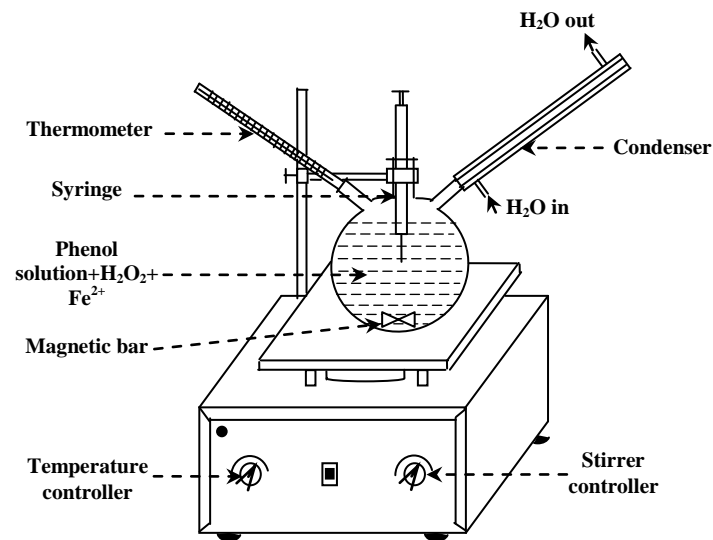


Fig. (1), Experimental set up of study

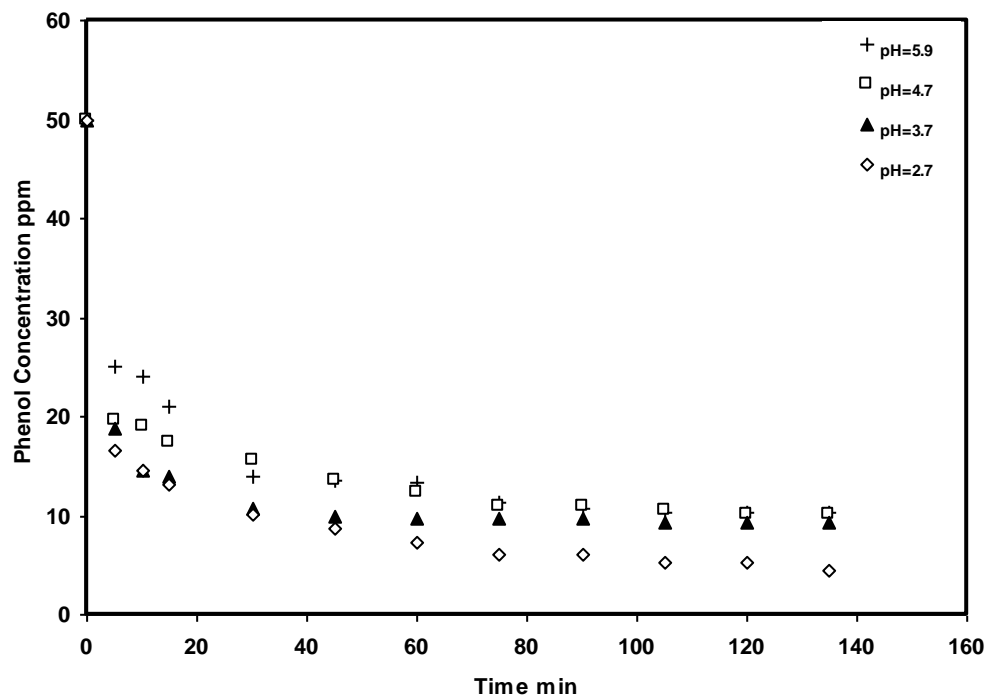


Fig. 2, Effect of feed solution pH.

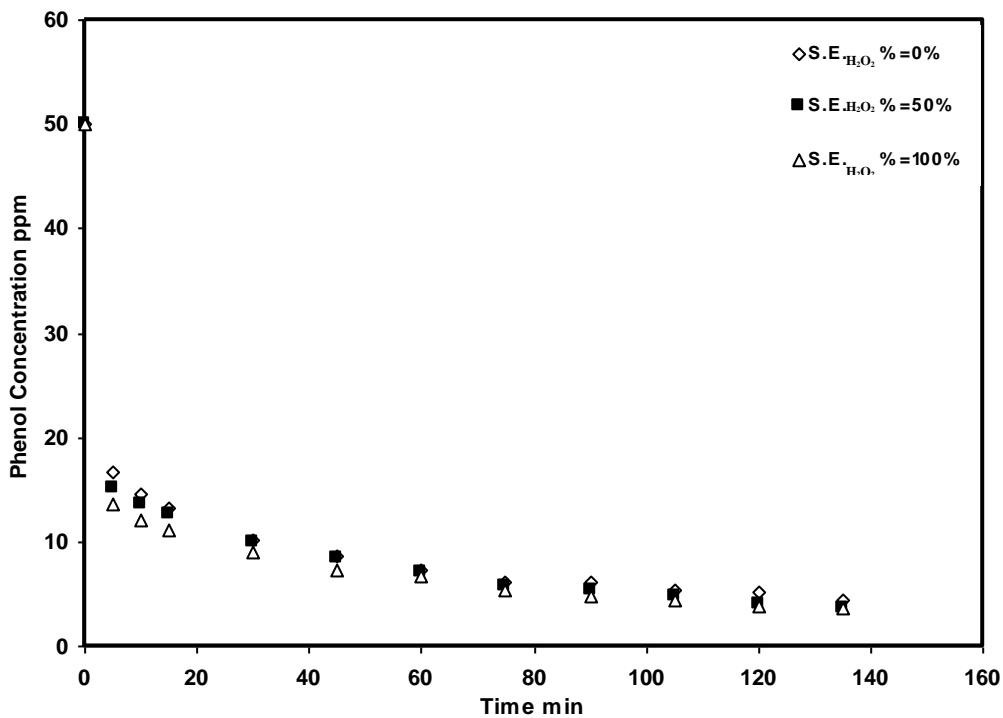


Fig. 3, Effect of hydrogen peroxide stoichiometric excess

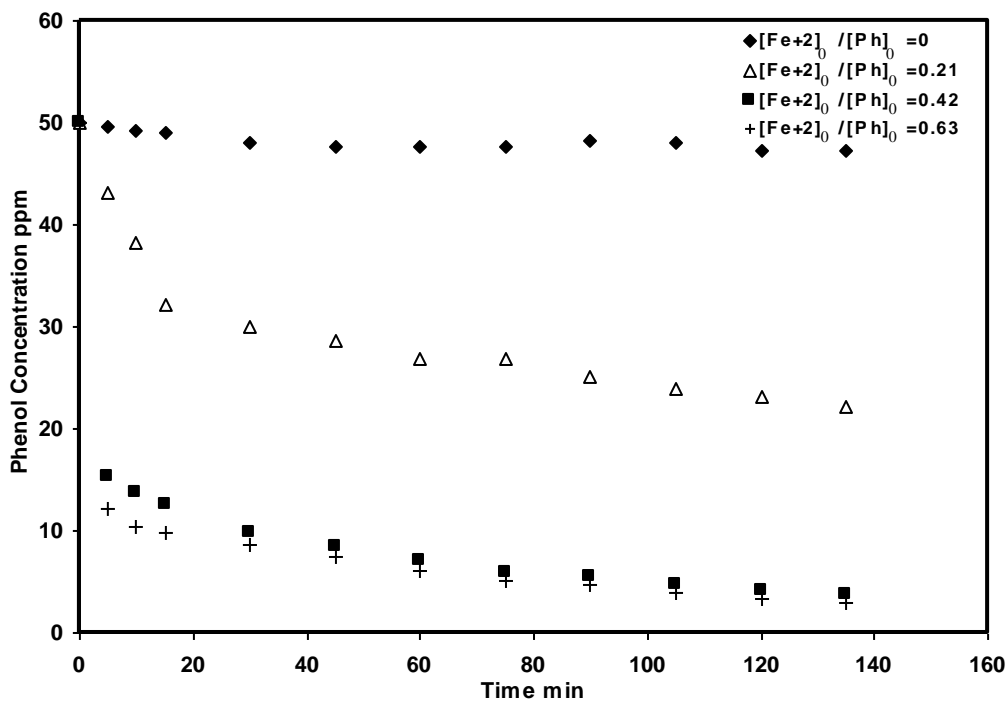


Fig. 4, Effect of Fe²⁺ to phenol concentration ratio.

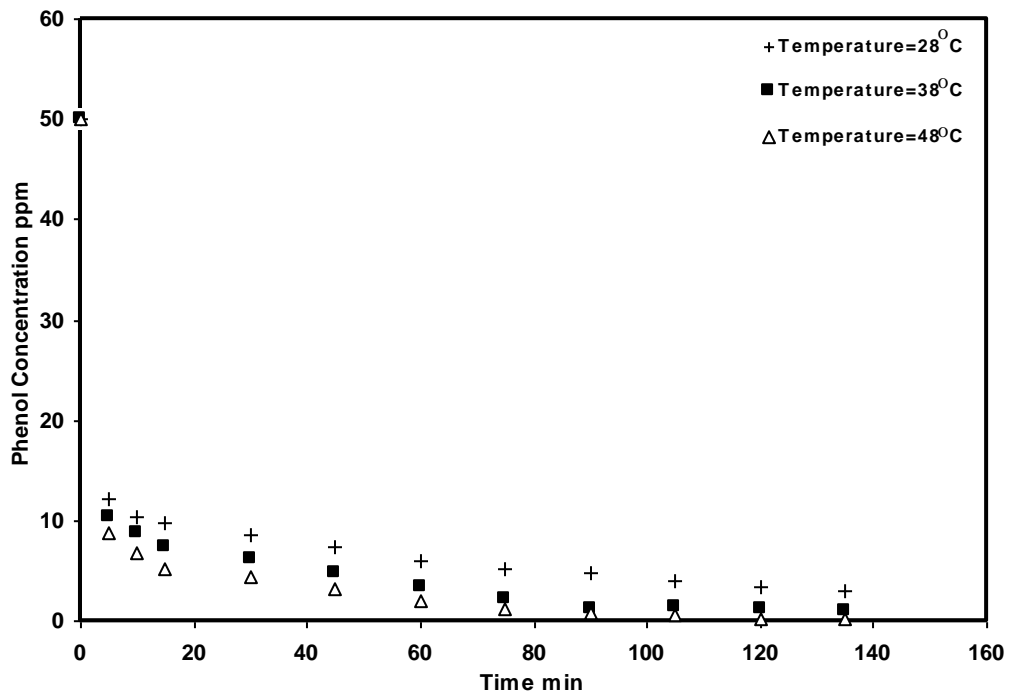


Fig. 5, Effect of temperature.

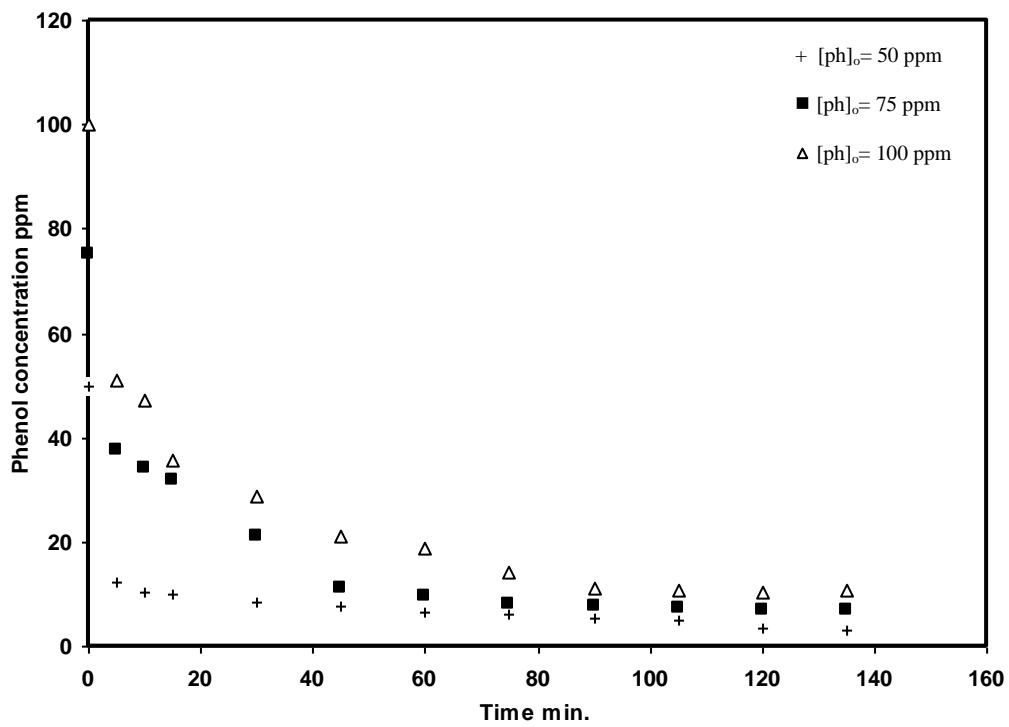


Fig. 6, Effect of initial phenol concentration.

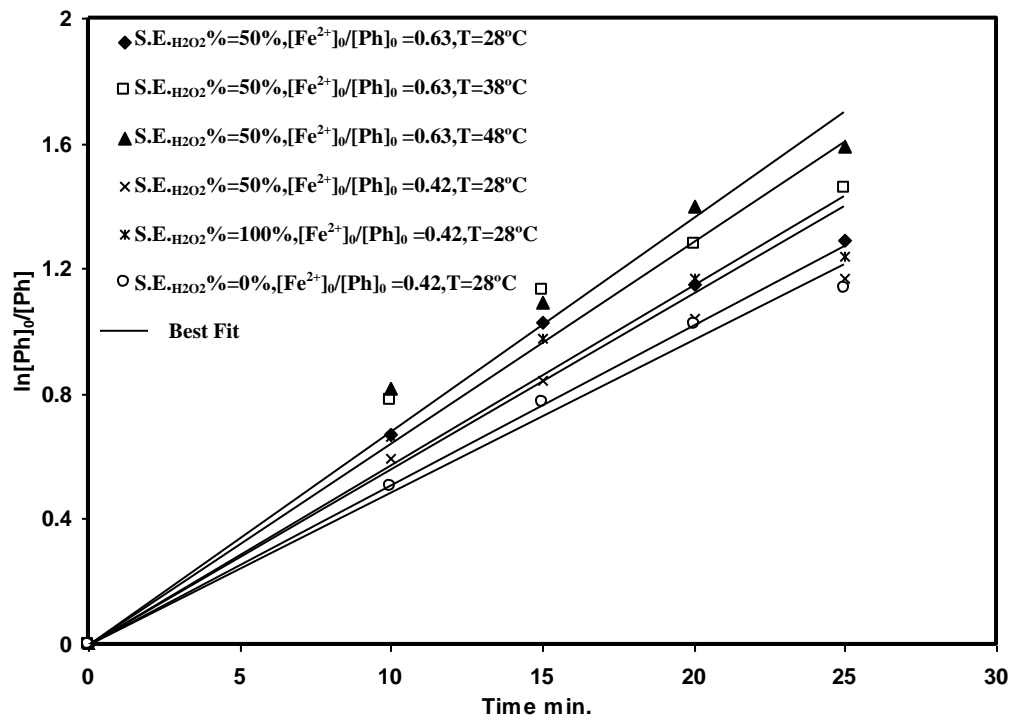


Fig. 7, $\ln[\text{Ph}]_0/[\text{Ph}]$ versus time at various conditions.