



Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 11(3), 2015 [083-088]

Investigation the performance of advanced oxidation processes for degradation of phenol from water

Ahmad Reza Yazdanbakhsh¹, Hasti Daraei^{1*}, Masomeh Davoodabadi²

¹Department of Environmental Health Engineering, Shahid Beheshti University of Medical Sciences, Tehran, (IRAN)

²Department of Environmental Health Engineering, Alborz University of Medical Sciences, Karaj, (IRAN)
E-mail: Ha.daraei@sbm.ac.ir

ABSTRACT

Background and Objective: Phenol is one of the serious pollutants from the chemical and petrochemical industries. This pollutant due to its convoluted structure is resistant to biodegradation. One of the methods that is useful to removal this pollutant is advanced oxidation (AOP).

Materials and Methods: A laboratory scale study was done on a synthetic wastewater containing phenol. All experiments was done in batch conditions and effect of variables pH, amount of hydrogen peroxide, iron dosage, contact time and initial concentration on the phenol removal were tested. The remaining phenol concentration was measured using the DR-5000 device.

Results and Discussion: In order to effect of these parameters, the experiment was performance at pH 2 to 6, 5 to 45 ml of peroxide, time of 5 to 60 minutes with 2 to 15 g iron powder. The optimum pH, ratio of hydrogen, hydrogen, iron powder and time were 3, 15 mg/l, 8g and 5 minutes respectively. In order of COD test was done to confirm the complete mineralization and result shown that mineralization of phenol was not complete.

Conclusion: According to the results of this study and high preference, Fenton-like process can be used for conversion organic resistant compounds to other compounds with lower toxicity.

© 2015 Trade Science Inc. - INDIA

KEYWORDS

Fenton-like;
Advance oxidation;
Phenol;
Pollutant.

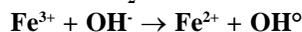
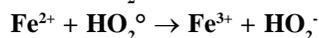
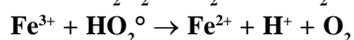
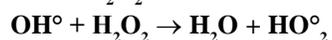
INTRODUCTION

Phenol and its derivatives are aromatic and toxic compounds to the environment, aquatic organisms and human life. This organic substance is a priority pollutant in EPA list and its concentration in drinking water should not surpass the order of $\mu\text{g/L}$ ^[1].

Phenolic combinations are generated in the oil refineries, pulp and paper, pharmaceutical, pesticide industries and by several other chemical plants^[2]. Widely Technologies used for the removal of phenol such as biological methods^[3], the manufacture of dyes and plastic^[4], adsorption^[5] and wet oxidation^[6]. Also, advanced oxidation processes (AOPs)

Current Research Paper

such as Fenton and Fenton-like^[7] is successfully used for the removal of this compound. Fenton or Fenton-like are solutions of hydrogen peroxide and Fe^{2+} ^[8]. The Fenton process is a catalytic procedure for the generation of hydroxyl radicals. Fenton and Fenton-like processes are based on electron transmission between hydrogen peroxide (H_2O_2) and a metallic ion (Fe^{2+})^[9]. These ions are very stable in an acid environment. Because of the oxidation reactions with H_2O_2 are not possible for high concentration of pollutants due to its low reaction rate at passable H_2O_2 concentration. Hence, transition metal salts such as ferrous ions are imperative to activate breakup of H_2O_2 to produce reactive radicals responsible for compound demolition^[10]. Usually, when these compounds are added to aqueous solution a redox reaction will occur^[11]. Hydroxyl radical can attack and demolish the antibiotic. A complex redox reaction will occur as in:



The Fenton processes have several significant advantages such as the generation of hydrogen radical (which is strong oxidant), short reaction time, iron and H_2O_2 are inexpensive, and also the reaction is easily to operate^[11].

MATERIALS AND METHODS

Chemicals

Phenol (with purity 99%) dissolved in distilled water and stored in dinky bottle. hydrogen peroxide (30%, w/v), ferrous sulfate heptahydrate and other reagents were obtained from Merck Germany. All the experiments were carried out at room temperature. Determination of the optimal pH for this reaction was experimented with pH values ranging from 1 to 6 by adding 0.1 M NaOH or 0.1 M HNO_3 . After we determined the optimal pH, we only used one pH value in all subsequent experiments. Also, for other variable (H_2O_2 concentration, iron powder, contact time) used this way.

Fenton's reactions

Fenton's reagent is a composite of Hydrogen peroxide (HP) and ferrous ion. Because HP is a weak acid can be oxidized organic compounds. Nonetheless, this oxidant has a low reaction rate at conscionable HP concentration. Thus, transmittal metal ions are needful to activate severance of HP to generate reactive radicals.

Fenton process was carried out at room temperature ($32 \pm 2^\circ\text{C}$) using various Fe powder and Hydrogen peroxide (35%, w/w) dosages at various pH values in order to assess optimum values to yield better results in COD and phenol removal. During the determination of optimum pH value, Fe powder dosages and H_2O_2 concentrations were fixed at constant value.

RESULTS AND DISCUSSION

Effect of pH

The pH is an important variable that controlled

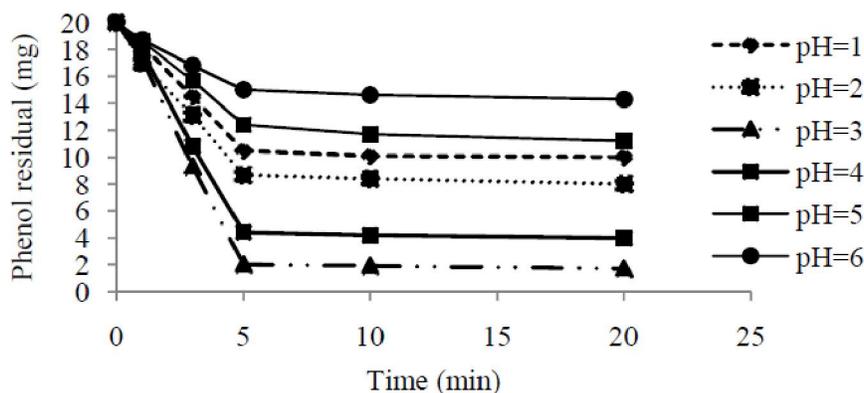


Figure 1 : Effect of initial pH on the phenol removal efficiency (Initial phenol=20 mg/L, t=5-20 min)

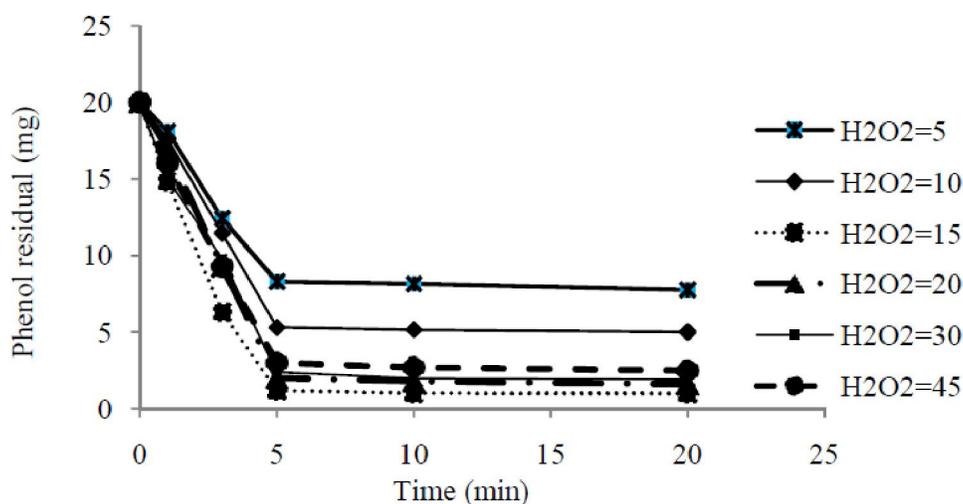


Figure 2 : Effect of H_2O_2 on the phenol removal efficiency (Initial phenol=20 mg/L, t=5-20 min)

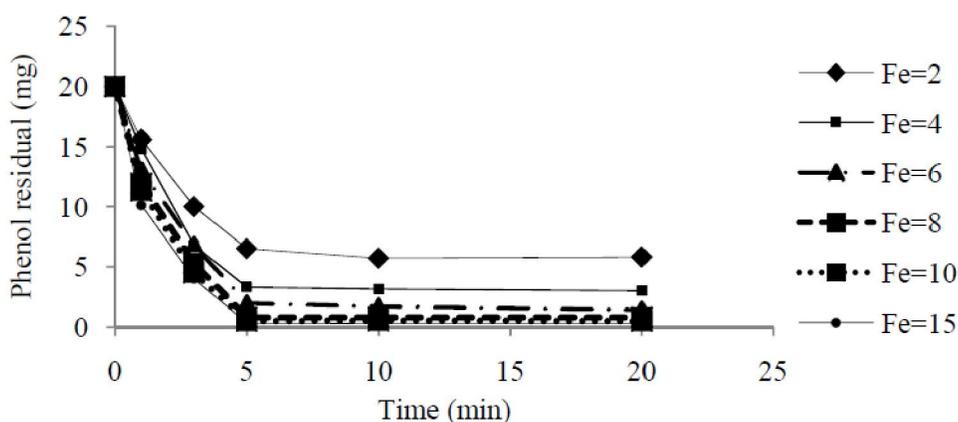


Figure 3 : Effect of Fe powder on the phenol removal efficiency (Initial phenol=20 mg/L, t=5-20 min)

the redox reaction. The solution pH directly and indirectly affects to production of hydroxyl radicals and organic oxidation. This parameter is an agent for the activity of Hydrogen and hydroxyl ions present in the aqueous solution. According to the results, the maximum efficiency for phenol removal was achieved in $pH = 3$. Fenton's reaction will be impeded at upper pH values (e.g., $pH > 4$) due to the creation of Fe^{2+} complexes, sedimentation of iron oxyhydroxides, and decreased oxidation potential of OH^\bullet . In other words, presence of this HO^\bullet is able to exchange phenol into hydroquinone and catechol. Therefore, at high pH values, Fe ions settled at the beginning of the reaction. Thus, the system requires suitable treatment for stable production of OH radicals^[12, 13]. In other hand, the low efficiency at $pH < 2$ could be ascribed to the permanency of H_2O_2 via the creation of oxonium ion $H_3O_2^+$, reducing its reactivity with ferrous ion^[14]. Also, in these pH values

the snatching effect of H^+ towards OH^\bullet becomes more visible.

Effect of H_2O_2

Experiments were done at a pH of 3.0 using the batch dosing mode. It is found from Figure 2. that the concentrations of phenol decrease with an increase of H_2O_2 concentration to 15cc. This increase in efficiency is due to the availability of sufficiency HO^\bullet radical required for the degradation. The maximum phenol degradation of 95% was observed for Fenton process with 15 mg/L of H_2O_2 . The maximum phenol degradation is due to the addition of hydroxyl radicals. During this process by increase of H_2O_2 concentration, highest amount of Fe^{2+} ions will react with H_2O_2 to generate further amount of hydroxyl radicals. However scavenging effect of H_2O_2 towards HO^\bullet occurs at higher concentrations, but when hydrogen peroxide concentration exceeded

Current Research Paper

the optimum amount, the phenol concentration increase^[15]. This reduction in efficiency observed can be due to the reaction of hydroxyl radicals and hydrogen peroxide and mixture hydroxyl radicals to compose H_2O_2 ^[16]. Also in this reaction, HOO° radicals will be generated that are substantially lesser reactive than HO° radicals, thus reduces the reaction rate. Therefore, 15 mg/L of hydrogen peroxide concentration was determined as the optimum value for phenol degradation.

Effect of Fe dosage

Aqueous solution having initial concentration of phenol 20 mg/L done by Fenton-like process with Fe dosage ranging from 2 to 15 g, the H_2O_2 concentration 15 mg/L at pH 3. Figure 3 shows that the phenol degradation increased with the increasing dosage of iron ion β , and further increasing Fe dosage β could not noticeable raise the removal of phenol. This was due to the presence of higher amounts of ferrous ions and reactions between iron and intermediates of degradation in the Fenton reaction^[17].

Effect of contact time

The amount of the phenol degradation at definite intervals of time was monitored. Figures indicate that, with the increase in time, degradation rate of the phenol increases. It can be seen that the degradation rate initially increased rapidly, and the equilibrium value was obtained in 5 min. This is due to resulted from saturation of Fe powder surfaces with phenolic ion followed by sorption and desorption processes that arise after saturation.

Also, after 5 minutes, HO° values drastically reduced and more iron ions and HP are consumed. Thus, there isn't a significant change in removal efficiency^[17].

Effect of phenol initial concentration

Figure 5 shows the effect of the initial concentration of phenol in efficiency, it is intelligible that increases of initial concentration don't have eidetic effect in removal efficiency. At low initial concentration, the degradation efficiency is a slightly most than the higher concentration. It can be derived that removal is partly favored at lower phenol concentration^[7].

COD

Figure 5 exhibits changes in COD during Fenton process for phenol degradation. COD parameter was measured with COD syringes with colorimetric method. The samples were heated for two hours with $K_2Cr_2O_7$ in the presence of silver sulfate and mercury sulfate. The absorbance was measured at 620 nm on a spectrophotometer DR2500. Finally, according to the figure, with the high phenol removal, the removal rate of COD was about 70 %, this indicates incomplete mineralization of organic compounds. Therefore, advanced oxidation processes will be completely converted organic compounds into mineral compound (CO_2 and H_2O) or convert organic compounds into simpler compounds that are biodegradable. Therefore, this process has not been able to complete mineralization of phenol, thus this process can be used as a pre-treatment process for the removal of phenol.

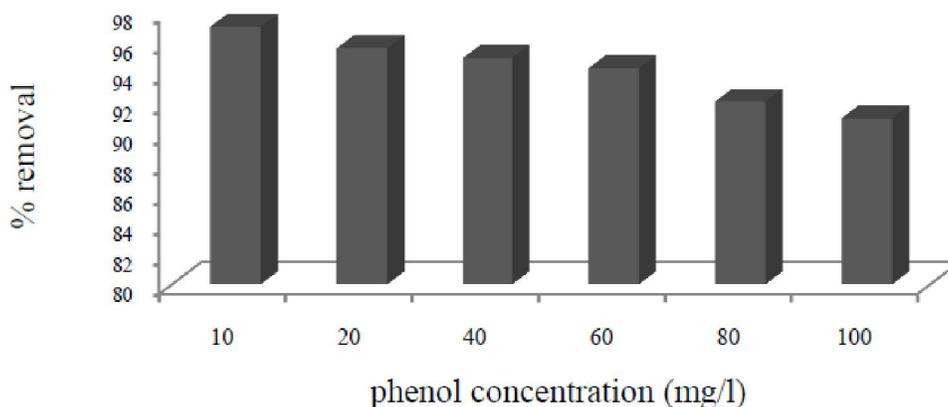


Figure 4 : Effect of phenol concentration on the removal efficiency (HP value=15 cc, t=5 min)

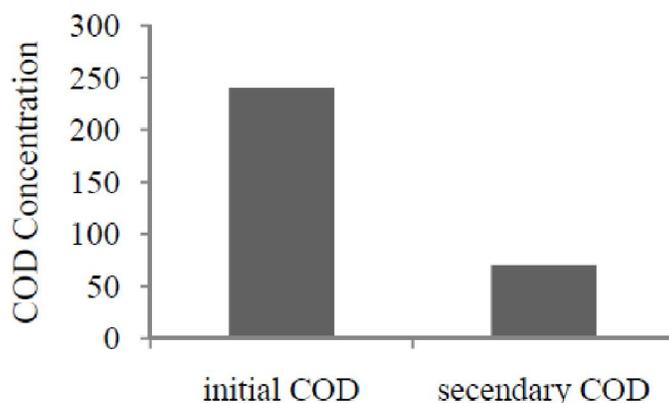


Figure 5 : COD removal rate in optimal conditions for phenol

CONCLUSION

The results presented above clearly indicate that the AOP acts as an effective process for the removal of phenol from water. The degradation is dependent upon pH, amount of iron powder, and H_2O_2 concentration. Fenton's oxidation also presented good phenol removal results. This work shows that the organic compound load can be significantly reduced by Fenton oxidation.

REFERENCES

- [1] M.Manshour, H.Daraei, A.R. Yazdanbakhsh; A feasible study on the application of raw ostrich feather, Feather treated with H_2O_2 and feather ash for removal of phenol from aqueous solution, *Desalination and Water Treatment*, **41(1-3)**, 179-185 (2012).
- [2] H.Daraei, A.Mittal, M.Noorisepehr, F.Daraei; Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste, *Environmental Science and Pollution Research*, **20(7)**, 4603-4611 (2013).
- [3] H.P.Fang, D.W.Liang, T.Zhang; Anaerobic treatment of phenol in wastewater under thermophilic condition, *Water Res.*, **40**, 427-434 (2006).
- [4] W.Kujawski, A.Warszawski, W.Ratajczak; Removal of phenol from waste water by different separation techniques, *Desalination*, **163**, 287-296 (2004).
- [5] H.Daraei, M.Manshour, A.R. Yazdanbakhsh; Removal of phenol from aqueous solution using ostrich feathers ash, *Mazand.Univ.Med.Sci.*, **20(79)**, 81-7 (2010).
- [6] A.Santos, P.Yustos, S.Gomis; Reaction network and kinetic modeling of wet oxidation of phenol catalyzed by activated carbon, *Chem.Eng.Sci.*, **61**, 2457-2467 (2006).
- [7] A.Babuponnusami, K.Muthukumar; Advanced oxidation of phenol: A comparison between Fenton, Electro-Fenton, Sono-electro-Fenton and photo-electro-Fenton processes, *Chemical Engineering Journal*, **183**, 1-9 (2012).
- [8] Venny, S.Gan, H.K.Ng; Current status and prospects of Fenton oxidation for the decontamination of persistent organic pollutants (POPs) in soils, *Chemical Engineering Journal*, **213**, 295-317 (2012).
- [9] Safarzadeh A.Amiri, J.R.Bolten, S.R.Cater; The use of iron in advanced oxidation processes, *J.Adv.Oxid.Technol.*, **1**, 18-26 (1996).
- [10] M.E.Argun, S.D.M.Karatas, M.Guru; Activation of pine cone using Fenton oxidation for Cd(II) and Pb(II) removal, *Bioresource Technology*, **99**, 8691-8698 (2008).
- [11] San N.Sebastian, J.F.Fernandez, X.F.Segura, A.S.Ferrer; Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent, *J.Hazard.Mater.*, **101**, 315-322 (2003).
- [12] W.Ben, Z.Qiang, X.Pan, M.Chen; Removal of veterinary antibiotics from sequencing batch reactor (SBR) pretreated swine wastewater by Fenton's reagent, *Water research*, **43**, 4392-4402 (2009).
- [13] A.J.Luna, O.Chiovone-Filho, A.Machulek, De E.Moraes, S.A.O.Nascimento; Photo-Fenton oxidation of phenol and organochlorides (2,4-DCP and 2,4-D) in aqueous alkaline medium with high chloride concentration, *Journal of Environmental Management*, **111**, 10-17 (2012).
- [14] M.Aleksic, H.Kusic, N.Koprivanac, D.Leszczynska, Loncaric A.Bozic; Heterogeneous Fenton type processes for the degradation of organic dye pollutant in water — The application of zeolite assisted AOPs, *Desalination*, **257**, 22-29 (2010).

Current Research Paper

- [15] A.Babuponnusami, K.Muthukumar; Advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes, *Chemical Engineering Journal*, **183**, 1–9 (2012).
- [16] X.R.Xu, X.Y.Li, X.Z.Li, H.B.Li; Degradation of melatonin by UV, UV/H₂O₂, Fe²⁺/H₂O₂ and UV/Fe²⁺/H₂O₂ processes, *Sep.Purif.Technol.*, **68**, 261–266 (2009).
- [17] H.Daraei, H.Kamali; Experimental design and response surface modeling for optimization of 2-chlorophenol removal from water by nanoscale iron and Fe Powder, *J.Environ.Anal.Toxicol.*, **4(228)**, 2161-0525 (2014).