Evaluation of Efficacy of Advanced Oxidation Processes Fenton, Fenton-like and Photo-Fenton for Removal of Phenol from Aqueous Solutions

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Summary: Contamination of water, soil and groundwater caused by aromatic compounds induces great concern in most world areas .Among organic pollutants, phenol is mostly considered dangerous due to its high toxicity for human and animal. Advanced oxidation processes (AOPs) is considered as a most efficient method also the best one for purifying organic compounds which are resistant to conventional physical and chemical processes. This experimental study was carried out in laboratory scale. First, a synthetic solution was made of phenol. Then, Fenton, Fenton-like and photo-Fenton processes were applied removing phenol from aquatic solution. The effects of Hydrogen Peroxide concentration, catalyst, pH and time were studied to phenol removal efficiency. Results showed that Photo-Fenton process with removal efficiency (97.5%) is more efficient than Fenton and Fenton-like processes with removal efficiency (78.7% and 82.5% respectively), in pH=3, $[H_2O_2]$= 3mM, $[Fe^{2+}]$= 0.1 mM, phenol concentration 100 mg L^{-1} and time reaction 60 min, the phenol removal was 97.5%.

Keywords: Aqueous Solution, Advanced oxidation processes, Fenton; Fenton-like, Photo-Fenton.

Introduction

Contamination of water, soil and groundwater caused by aromatic compounds induces great concern in most world areas. Among organic pollutants, phenol is mostly considered dangerous due to its high toxicity for human and animal. [1] Phenol compounds are resistant organic pollutants which include low biodegradable and serious damages to environment when are discharged to natural waters body. [2] Also, it is an aromatic hydrocarbon that with its derivations considered a common pollutant in most industrials sewages including petrochemical, oil refinery, steel, coal processes, dying, textiles, paper-mill, leather industry and polymer resins. Also, due to its anesthetic effects, it widely is used in pharmaceutical industries. [3-5] Due to their particular characteristic such as toxicity, their adverse effects on human being and other animals, phenol compounds are considered as priority pollutants according to the United States Environmental Protection Agency (EPA). [6, 7] It was considered as a irritant and eatable material in high concentration which has toxicity for human and animal mucous. [4] World Health Organization (WHO) has prescribed a concentration of 1μg as the guideline concentration for drinking water. [8].

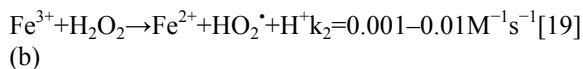There are various methods for removal of phenol in wastewaters including chlorination, ozonation, adsorption, solvent extraction, membrane filter process, coagulation, flocculation and biological treatment. [6] Since phenol compounds have low biodegradability therefore it needs an effective treatment process for their removal [9], an effective process for removing these pollutants is substituting process in Advanced Oxidation Processes (AOPs) which are the excellent choice for removal of organic compounds which are resistant to biodegradation or conventional physical and chemical processes. [10] AOPs, also, generate ·OH which accelerate oxidative degradation of numerous organic compounds soluble in wastewater. [11].

Among Advanced Oxidation Processes, Fenton is used as an effective chemical process for removing aromatic compounds existing in aquatic environment. [12] Fenton process, which is a reaction between ferrous and hydrogen peroxide for generating hydroxyl radical, under acidic condition [13, 14] is efficiently used for destroying organic and inorganic pollutant by using the capacity of oxidation of hydroxyl radicals generated from catalytically destroying H_2O_2 by iron ion. Hydroxyl radicals by having 2.8V oxidation potential are more powerful than H_2O_2. [15] The main drawback of this technique is represented by the cost of the reactants, H_2O_2 and Fe^{2+}. Therefore, various methods are presented for using Fe^{3+} which has fewer costs. [16, 17] Fe^{3+} also can be used for the destruction of hydrogen peroxide

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and hydroxyl radical production. This process is known as Fenton-like process. [18]

$$Fe^{2+}+H_2O_2\rightarrow Fe^{3+}+^{\bullet}OH+OH^- \quad k_1=51M^{-1}s^{-1}[19] \quad (a)$$

$$Fe^{3+}+H_2O_2\rightarrow Fe^{2+}+HO_2^{\bullet}+H^+ k_2=0.001-0.01M^{-1}s^{-1}[19] \quad (b)$$

Although Fenton has a high oxidation efficiency, its function is limited by the final production of ferric iron sludge. It seems that radiation UV combined with Fenton reagent could be a promising alternative since it allows the reduction of ferric to ferrous iron. [10].

$$Fe(III)OH^{2+} + uv \rightarrow Fe(II) + ^{\bullet}OH \quad (c)$$
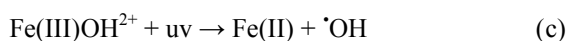
By considering the fact that phenol and its derivation are considered the major environmental pollutants and other studies suggest that treatment of Fenton, Fenton-like as well as Photo-Fenton is effective in treatment different sewages, Therefore, in this study, the performance of three advanced oxidation processes Fenton, Fenton-like and Photo-Fenton processes in removing phenol from synthetic solutions are examined and compared and the optimal conditions of removing phenol in the processes and the effectiveness of various parameters on removal efficiency are determined.

Experimental

Materials are used in the study were provided by German Factory, MERC. Hydrogen peroxide (30%) was used as an oxidizing agent and iron (II) and (III) Sulfate as iron resources. Phenol is used for examine was selected with purity of 98% and initial concentration of 100 mg L^{-1}. Acid sulfuric and sodium hydroxide 0.1 N were used for controlling pH. All experiments were carried out at (25±2℃) room temperature.

Fenton and Fenton-like experiments were performed at Jar Test equipment under agitation at 80 rpm. The reactor for Photo-Fenton experiment was made of Pyrex and consisted of two parts: The exterior including 1 liter of phenol and the inner chamber for mounted lamp UV. The exterior has been set at larger reactor (5 liter) containing water for maintaining solution at the temperature 25℃. During the experiment solution is continuously was done mixed with the help of magnet and magnetic stirrer. The used light to produce UV rays making NARVA German company with 254 nm and 125 watt power supply provided continuous UV radiation. All

solutions are prepared daily and were kept at a temperature 4℃.

All experiments were initiated by 1000 mg L^{-1} phenol solution. In each of the oxidation processes, first determine the ratio of optimized H_2O_2/Fe at pH=3 and reaction time 60 min was selected and optimizing of H_2O_2 and Fe concentration in 4 hydrogen peroxide (0.5, 1, 3 and 4 mM) as well as 4 iron concentration (0.05, 0.1, 0.2 and 0.4 mM) were conducted. After determining optimum H_2O_2/Fe ratio, as well as the best pH and reaction time, experiments were performed by considering stable determinate optimum H_2O_2/Fe at previous stages and changing of pH (2, 3, 4 and 5) and reaction time (10, 20, 30 and 60 min). sample was taken from the remained phenol determined based on photometric process on basis of 5530 D standard methods examination of water and wastewater by using 4-amino antipyrine and Potassium ferric cyanide reagents as well as Spectrophotometer model HACH(Dr/2010) in 500 nm length wave [20] pH was measured by pH instrument model pH262 made by Sanjesh Instrument Company and With buffers 4 and 7 was calibrated. Each experiment was repeated 3 times.

Result and Discussion

Effect of hydrogen peroxide concentration

In order to study the effect of H_2O_2 in phenol degradation, four different concentration of hydrogen peroxide were added to the samples. As shown in Fig. 1, with increasing of hydrogen peroxide concentration from 0.5 mM to 3 mM, phenol removal was increased in all three methods but with its increasing to 4 mM caused the removal to be decreased. production of hydroxyl radicals act a major role in degradation organic pollutants. In Photo- Fenton process, additional sources of $^{\bullet}$OH radicals should be considered: through photolysis of H_2O_2, reaction of (d), and through reduction of Fe^{3+} ions under UV light, reaction of (e). [21]

$$H_2O_2 + uv \rightarrow ^{\bullet}OH + ^{\bullet}OH \quad (d)$$

$$Fe^{3+} + H_2O + uv \rightarrow Fe^{2+} + ^{\bullet}OH + H^+ \quad (e)$$
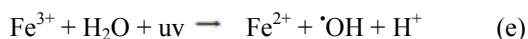
As hydrogen peroxide acts as an oxidant and a source of producing hydrogen radicals, when its concentration is increased leads to more hydroxyl radicals which result in removal increasing. But by increasing peroxide more than optimal amount, it acts as scavenger of hydroxyl radicals. [21] Hydrogen

radicals reacts with H_2O_2 and H_2O_2 itself acts as scavenger radicals, reaction of (f). Also, hydroxyl radicals can be recombined together another and hydrogen peroxide generation which has less oxidation than hydroxyl radical, reaction of (g). [22, 23] The presence of excess H_2O_2 can lead to the production of other radical (HO_2, $^{\bullet}O_2^-$) with much less activity reaction of (h). [24]
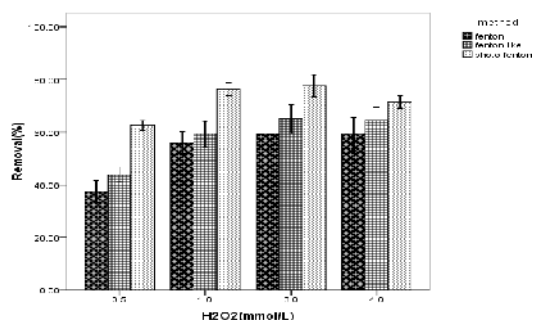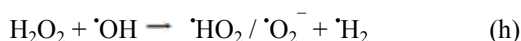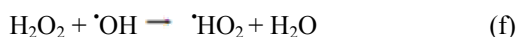
$$H_2O_2 + ^{\bullet}OH \rightarrow ^{\bullet}HO_2 + H_2O \qquad (f)$$

$$OH + ^{\bullet}OH \rightarrow H_2O_2 \qquad (g)$$

$$H_2O_2 + ^{\bullet}OH \rightarrow ^{\bullet}HO_2 / ^{\bullet}O_2^- + ^{\bullet}H_2 \qquad (h)$$

Fig. 1:   Removal percent of phenol based on H_2O_2 concentration (t= 60 min, pH= 3).

Thus, the amount of H_2O_2 should be considered not just due to optimum treatment efficiency but for its economical costs of the process. So its rate optimization for Determination optimum concentration is necessary. Regard to toxicity of phenol compounds for human and other living organisms, if the processes is done in optimal condition the residual of H_2O_2 in treated effluent is negligible and dissociate in environment spontaneously [14, 19, 22].

Effect of Temperature

Although temperature has a positive effects on reaction rate Fenton and Photo- Fenton processes but this matter is not the subject of our study, so, as mentioned in material and methods section all experiments has been done in room temperature. In addition, full scale wastewater treatment is totally operated in ambient air temperature since artificially increases of wastewater temperature is not economically feasible [8, 11, 19, 23].

Effect of Iron Concentration

Since the amount of hydrogen peroxide degradation by catalyst is a very most important factor, to examine the effect of iron dosage on the

processes, iron is also added at four various concentrations to the samples. As shown in Fig. 2, iron also acts like hydrogen peroxide *i.e.* by increasing its concentration, the removal percentage also increases but when its concentration is more than optimum leads to decreased removal of the process. Since iron play a catalyst role in the processes, therefore increased iron ions concentration to optimum level causes the hydrogen peroxide degradation to increase which leads to increased efficiency removal, but the very highest concentration of iron can also as scavenger hydroxyl radicals and causes an efficiency loss of the Fenton process which is due to compete between iron ions and organic materials in the case of an insufficient quantity of H_2O_2 added to the reactor. [25] In other words, the low efficiency due to limited catalytic action of iron ions in the presence of high concentrations, because the presence of excess ions cause their combine with $^{\bullet}OH$ radicals and them out makes from the operate act. According to the following equation [23]:
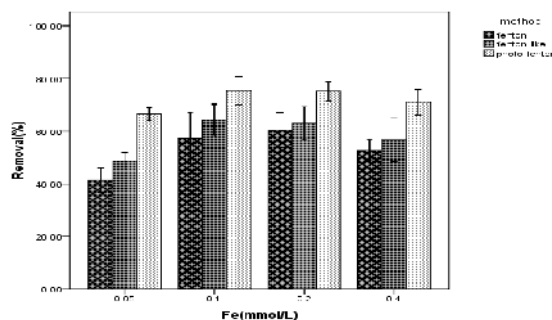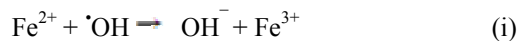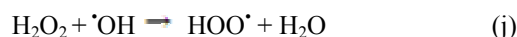
$$Fe^{2+} + ^{\bullet}OH \rightarrow OH^- + Fe^{3+} \qquad (i)$$

Fig. 2:   removal percent of phenol based on Fe concentration (t= 60 min, pH= 3).

In low portion Fe/ H_2O_2 react hydroxyl radicals with more amounts of H_2O_2 and produces $HOO^{\bullet}$ which has less activation than hydroxyl radicals. [26] According to the following equation:

$$H_2O_2 + ^{\bullet}OH \rightarrow HOO^{\bullet} + H_2O \qquad (j)$$

In photo Fenton process, UV lamp provides photons which activate ion ferrous reproduction through prompt reduction of Fe^{3+} ions to Fe^{2+} and cause mineralization promotion process. [27] In this process, adding more than optimum iron salts cause their colors to be black browned which prevent UV light be absorbed and cause $^{\bullet}OH$ to be recombined. [28] Optimizing iron concentration is not only considered according to improving system efficiency, but also is necessary according to ferric production in

industry at a vast scale. In fact, optimum amount provide necessary catalyst for hydrogen peroxide and produces hydroxyl radicals sufficiently.

Effect of pH

pH is an important parameter factor for separating iron samples in aquatic solution as well as a necessary for producing hydroxyl radicals in Fenton, Fenton-like and Photo-Fenton processes. In order to survey the effect of pH on phenol removal, experiments were examined in 4 different pH (Fig. 3-6). Based on our observations in performing experiments, the highest efficiency was obtained in pH 3 during the three processes (Fig.4). Removal efficiency in pH=2 (Fig.3) compared to other pH had less amount that may be due to generated oxonium ion $[H_3O_2]^+$ [29] In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes important at a very low pH . [30] According to the following equation:
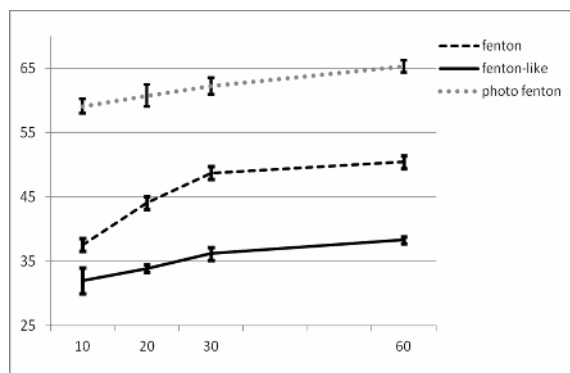
$$OH + H^+ + e \rightleftharpoons H_2O \qquad (k)$$

Fig. 3:   removal percent of phenol in pH=2.
(H_2O_2=3 mM , Fe^{2+}=0.2 mM , Fe^{3+} =0.1 mM).
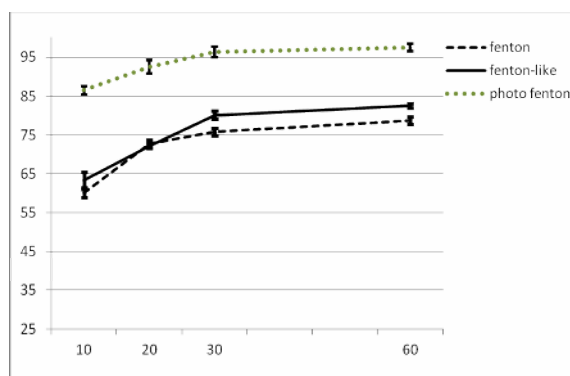

Fig. 4:   removal percent of phenol in pH=3.
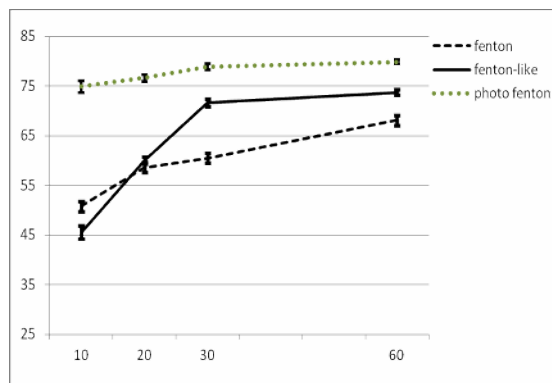(H_2O_2=3 mM , Fe^{2+}=0.2 mM, Fe^{3+} =0.1 mM).

Fig. 5:   removal percent of phenol in pH=4
(H_2O_2=3 mM , Fe^{2+}=0.2 mM , Fe^{3+} =0.1 mM)
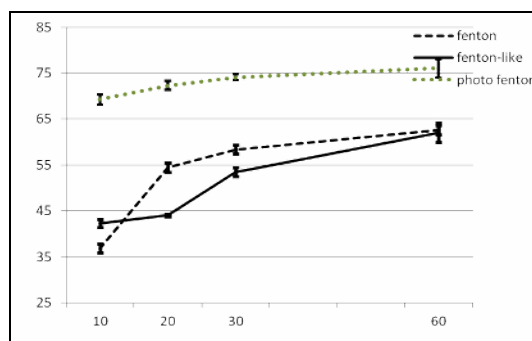

Fig. 6:   Removal percent of phenol in pH=5
(H_2O_2=3 mM, Fe^{2+}=0.2 mM , Fe^{3+} =0.1 mM)

The less efficiency below pH 3.0 in Fenton system may be due to the formation of $[Fe(II)(H_2O)_6]^{2+}$ complex, which reacts more slowly with H_2O_2 than $Fe(II)(OH)(H_2O)^5]^+$, and therefore produces fewer ˙OH. While in Fenton-like system, at a low pH, the reaction of Fe^{3+} with H_2O_2 is inhibited. But at higher pH values iron ion precipitates, therefore the concentration of dissolved Fe^{2+} or Fe^{3+} is decreasing. [16] In pH> 3, a significant fraction of Fe^{3+} precipitates as $Fe(OH)_3$, hindering the reaction between Fe^{3+} and H_2O_2, and therefore the regeneration of Fe^{2+} . Also in high pH, H_2O_2 is rapidly degraded to H_2O and O_2, thus their concentration are decreased at solution. [16, 17]

Effect of Reaction Time

In order to examine the effect of reaction time on phenol degradation, experiments were carried out in 4 reaction times (10, 20, 30 and 60 min). As shown in reaction of (a) and (b), since the reaction rate of reaction of (b) is much slower than that of reaction of (a), the ferrous ion is quickly consumed, but slowly regenerated. But in Fenton-like system,

Fe^{2+} is slowly generated through the reduction of Fe^{3+} by H_2O_2 (reaction of (b)) and Fenton reaction is initiated. Therefore, the degradation of contaminant in Fenton-like process is slow. But it was interesting that the degradation of phenol compounds was greatly improved after an initiation period. These results are in agreement with other studies. [31-33] Since reaction time has a direct effect on the aimed treatment and costs (energy and chemical consumption) determining optimum time is necessary.

Conclusion

Study of Fenton, Fenton like and Photo Fenton advanced oxidation processes to removal of phenol from aqueous solution indicated that they can efficiently remove phenol from the solution. In mentioned process, oxidation concentration, catalyst, pH and reaction time are considered as the most efficient factors. Also at optimal conditions, photo Fenton process with removal efficiency of 97.5% has high efficiency compared to other two processes, then, Fenton like process with 82.5% efficiency stands at the second rank and Fenton process with 78.7% at third. In the recent survey, optimal conditions were pH=3 and the ratio of Fe/ H_2O_2 in Fenton was 0.06 and in Fenton like and Photo Fenton was 0.03 which indicates completing of phenol degradation in the processes with 50% ion ferrous catalyst at Fenton process.

Acknowledgements

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