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**RESEARCH ARTICLE**

# PERFORMANCE IN REMOVAL OF PHOSPHOR FROM AQUEOUS SOLUTION BY FENTON OXIDATION PROCESS

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**ABSTRACT**

Phosphor is considered among the major pollutants in water environments. Phosphor contamination in surface water and groundwater resources originates mainly from the excessive use of fertilizers and uncontrolled land discharges of untreated wastewater. Discharge of it into the environment causes very health impact. The aim of this study was to investigate the efficiency of Fenton's advanced oxidation process ($H_2O_2/Fe^{+2}$) in phosphor removal from aqueous solutions. This is an experimental study which is carried out in laboratory scale. In this study, effect of the important operational variables including pH, $Fe^{+2}$ dosage, $H_2O_2$ dosage, initial phosphor concentration and contact time were evaluated on the phosphate removal from Aqueous Solution by Fenton has been investigated. The results showed that this method has the ability to remove phosphor from aqueous solutions to less than standard level WHO (≤1 mg/l). pH, ratio $H_2O_2/Fe^{+2}$ and contact time have direct effect and initial phosphor concentration has reverse effect of phosphor removal. The results showed that the Fenton process, can reach respectively 97% phosphor removal. So that optimum condition of the phosphor removal is in the ratio $H_2O_2$ / $Fe^{2+}$ dosage= 2200 /1000 mg/l, contact time of 60 min, pH=3.5 in initial phosphor concentration in 100 mg/L. Statistical test showed that the mean concentration in the before and after doing all process variables, there were significant differences ($P\leq0.05$). As the results showed, the efficient removal of phosphate using Fenton process is desirable in the water treatment and pollution control.



## INTRODUCTION

Phosphorus in domestic wastewater is one of the most important micronutrients for plant and microorganism growth. High discharge values of this nutrient in the acceptor water, increase the growth of algae, resulting in the increase of eutrophication phenomenon and can destruct the balance of water organism and affect the water quality (Lu *et al*., 2009). The algae grow in phosphorus concentrations of less than 0/05mg/l. Thereby reducing the phosphorus concentration in the effluent is necessary to prevent algal blooms (Yue *et al*., 2010). Phosphorus exists in urban wastewater in various forms, such as: total phosphorus, soluble phosphorus and suspended phosphorus. World Health Organization standards for phosphorus in drinking water is 0/2 mg/land Iranian Environmental Protection Agency standards for discharging the surface water is equivalent to 1 mg/l (Ballet *et al*., 2007).

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Phosphorus removal techniques are three physical categories such as electro dialysis, reverse osmosis ,contact filters and ion exchange that is expensive or very inefficient and only remove 10% of the total phosphorus, the biological methods like anaerobic and aerobic digest requiring expertise, high cost, long retention time and exploitation problems. Also the chemical methods include chemical precipitation and adsorption (Yue *et al*., 2010; Ballet *et al*., 2007 and Jeon and Yeom, 2009). Chemical precipitation method using ferric salts and aluminium is the most effective and more durable methods for phosphorus removal (Srivastava *et al*., 2006). However, the costs associated with the use of metal salts and mud and pH change in the chemical methods; reduce the application rate of these methods (Goldstein and Meyersteim, 1993). Recently processes in water and wastewater filtration applied extensively that always because of active hydroxyl radicals production is compatible with the environment and have high potential for radical oxidation of organic combinations have been known as AOP (Advanced Oxidation Processes) (Chang-Jun *et al*., 2007). Advanced oxidation processes that were used in water filtration in recent years, include: ozone and ultraviolet radiation, ozone plus UV, $O_3/H_2O_2$, $H_2O_2$/UV, $UV/O_3$ and

Fenton process. Advanced oxidation processes of iron anion as a catalyst in an acidic environment reacts with the oxidant and produce hydroxyl radicals, this reaction is oxidation - reduction (Jadhav *et al*., 2013). Fenton process is one of the newest advanced oxidation processes in recent years that due to the production and consumption of toxic pollutants and slow resolvable has become more practical in the industry. Fenton for the first time in 1894 in an oxidation investigation used tartaric acid with the mixture of hydrogen peroxide and iron salts. The use of this reaction, recently have been considered in the environmental applications. Compared to other methods were$H_2O_2$ is a nature-friend material in which slowly turn into oxygen and water, in addition $Fe^{+2}$ that is the most common metal used in this reaction, is an abundant substance with low toxicity and easy water filtration (Elmollaa *et al*., 2010 and da Silva *et al*., 2007). Dangerous by product production in Fenton oxidation in comparison with other advanced oxidation methods is considerably low, the simplicity of exploitation, the lack of restriction on mass transfer, consumption of toxic pollutants and slow resolvability are the benefits of this method (Badawy *et al.,* 2009; Barreto-Rodrigues *et al*., 2009 and Huang *et al*., 2009). Many studies on phosphorus removal by electro with iron plates (Srivastava *et al*., 2006), volatile ash (Lu *et al*., 2009) red mud (Yue *et al*., 2010), Nan filtration (Ballet *et al*., 2007), wetland (Li *et al*., 2013) and… have been done, but a study on removal phosphorus by advanced oxidation (AOP) has not been done. The purpose of this study is to evaluate the efficiency of the Fenton oxidation process on phosphorous removal and the effect of determining different parameters (pH, optimum concentration of $H_2O_2$, the optimal concentration of $Fe^{+2}$, contact time, phosphorus initial concentration effect).

## MATERIALS AND METHODS

This experimental study using lab-scale pilot in a closed system (Batch) applied in aqueous handmade solution. In this study, a solution of $H_2O_2$ with the weight percent of 30% mass volume of 1/13Kg/L and ferrous *sulphate* ($FeSo_4$, 7 $H_2O_2$), *sulphuric* acid ($H_2SO_4$), sodium sulphate ($Na_2SO_3$), standard solution of phosphate ($KH_2PO_4$) as sources of phosphorus in 1/5 litter glass beakers covered with aluminium foil were used. To perform the experiments, the volume of 1 litter of pH aqueous synthetic solution (Yue *et al*., 2010; Ballet *et al*., 2007; Jeon and Yeom, 2009; Srivastava *et al*., 2006; Goldstein and Meyersteim, 1993; Chang-jun *et al*., 2007; Jadhav *et al*., 2013; Elmollaa *et al*., 2010 and da Silva *et al*., 2007), the $H_2O_2$ concentration of (300-3000 mg/L), ion concentration of $Fe^{+2}$ (50-2000 mg/L), reaction time (10-100 min) and the initial concentration of phosphorus (200-50 mg/L) were provided (9). In all experiments, samples by magnetic mixer were treated, with speed of 1000 RPM (15); then, the samples were prepared for phosphorus measurement. For measuring residual phosphorus concentration, ascorbic acid method by a spectrophotometer (Shimadzu) UV/VIS with a quartz cell at a wavelength of 880 NM, the test by pH meter (Eutech) were used. Obtained absorbance amount was applied in the phosphorus calibration curve and phosphorus concentration of each sample was calculated. All tests did by a 4500PE method in accordance with test methods of water and wastewater book (APHA /AWWA /WEF, 2003). In all experiments, for measuring the pH effect on phosphorus removal efficiency, Molar $HNO_3$ 0/1 solution and Molar NaOH0/1 solution were used (Deliyanni *et al*., 2007). All used chemical materials were of the Merck German Company. The data were analysed by statistical software of SPSS 17, descriptive-inferential statistics, T-test statistical test at significant level of $P \leq 0/05$ and the related figures were drawn by Excel software. The removal efficiency calculated as follows: R = (input-output)/(input) × 100

## RESULTS

Fenton process 'efficiency to remove a variety of pollutants depends on several important factors such as pH, concentration of $H_2O_2$, iron ion concentration and the initial concentration of pollutant (Jadhav *et al*., 2013). In this study, the effect of pH parameters, concentration of $H_2O_2$, ion concentration of $Fe^{+2}$, reaction time and the initial concentration of phosphorus on phosphorus removal efficiency in the Fenton process was investigated. Figure 1 shows the effect of different pH (Yue *et al*., 2010; Ballet *et al*., 2007; Jeon and Yeom, 2009; Srivastava *et al*., 2006; Goldstein and Meyersteim, 1993; Chang-jun *et al*., 2007; Jadhav *et al*., 2013; Elmollaa *et al*., 2010 and da Silva *et al*., 2007), the initial concentration of phosphorus (200-50 mg/L), hydrogen peroxide, iron ion and oxidation time of 60 min on phosphorus removal efficiency. Patently, the maximum percentage of phosphorus removal is at pH=3/5 and with pH increase, the efficiency amount of phosphorus removal to the=5 has a subtle backdrop but with more pH increase, the removal efficiency reduced linearly.

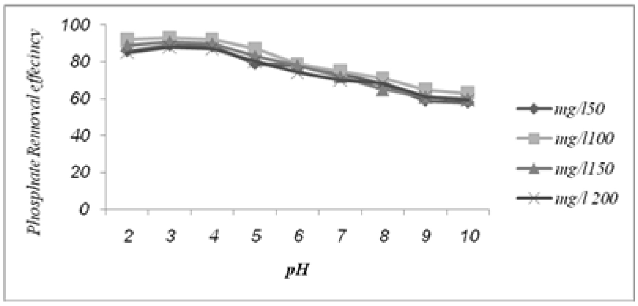


**Fig. 1. Optimum pH determination for the phosphorus removal ($H_2O_2$ =2200 mg/L, $Fe^{+2}$ =1000 mg/L, time = 60 min, initial phosphorus concentration is variable)**

To examine the effect of $H_2O_2$ concentration on $H_2O_2$ efficiency process; different concentrations in the range of 300-3000 mg/L were added to the samples. As shown in Figure 2 with increasing concentration of hydrogen peroxide to mg/L in the presence of $Fe^{+2}$ =1000 mg/L, pH=3/5, time=60 min, the initial phosphorus concentration 50-200 mg/L phosphorus removal efficiency increases its percentile and after this concentration, the elimination remains constant. Statistical test results showed that the concentrations mean of phosphorus removal rate; before and after aqueous solution process has a significant difference ($P \leq 0/05$).

In order to investigate the concentration of iron ions in this process, the $Fe^{+2}$ concentration of 50-2000 mg/L; $H_2O_2$=2200 mg/L, pH=3/5, time=60 min, the initial phosphorus concentration of 50-200 mg/L amount was set. As can be seen in the figure; the constant concentration of hydrogen peroxide with increasing concentrations of ferrous ions is associated with reduced levels of phosphorus removal. The most efficiency of equal phosphorus removal in the iron concentration is mg/L.

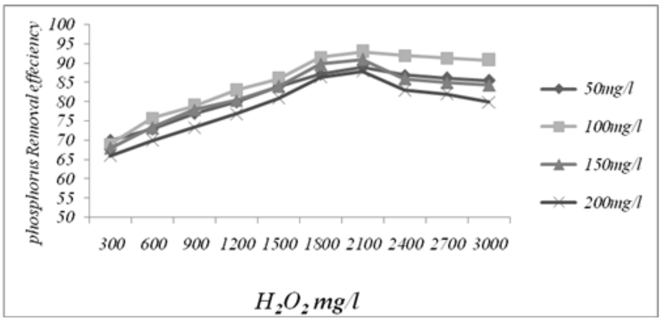


**Figure. 2 Determining the optimal dose of $H_2O_2$ in phosphorus removal ($Fe^{+2}$ =1000 mg/L, pH=3/5, time = 60 min, initial phosphorus concentration is variable)**

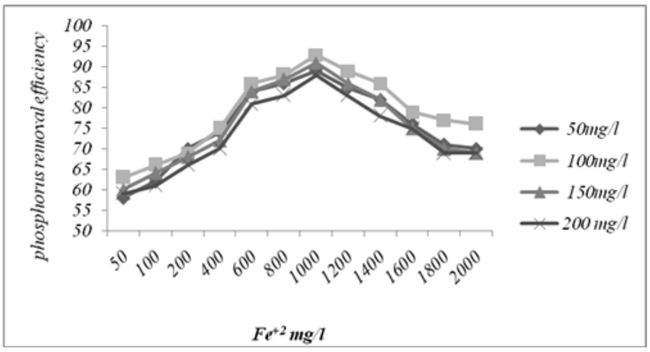


**Figure. 3 Determining the optimal dose of $Fe^{+2}$ in phosphorus removal ($H_2O_2$=2200 mg/L, pH=3/5, time=60 min, initial phosphorus concentration is variable)**

Figure 4 shows the effect of reaction time (10-100 min) to remove phosphorus in $H_2O_2$=2200 mg/L, $Fe^{+2}$ =1000 mg/L, pH=3/5, the initial phosphorus concentration 50-200 mg/L and reviewing this figure shows that over time the amount of phosphorus removal increases and in 60 minutes oxidation the best removal rate obtained and after the reaction of Fenton, the removal rate stays constant.

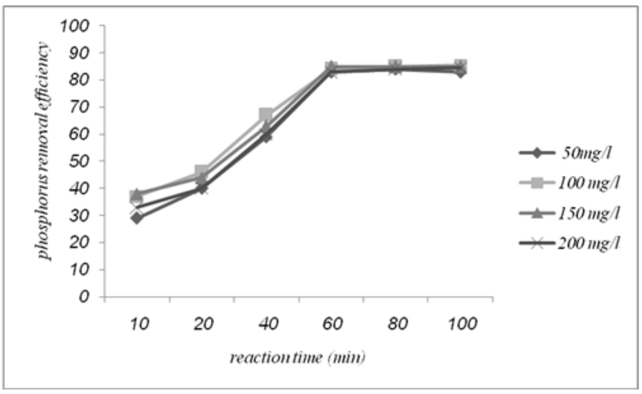


**Figure. 4 The determination of optimum reaction time on phosphorus removal ($H_2O_2$=2200 mg/L, $Fe^{+2}$=1000 mg/L, pH=3/5, initial phosphate concentration is variable)**

## DISCUSSION

### Effect of pH on phosphorus removal efficiency

pH is one of the influencing factors on the efficiency of Fenton process. pH value will affect hydroxyl radicals 'production and thus the oxidation efficiency. OH radical production usually has greater acceptance in acidic pH. At alkaline pH, the $Fe^{+2}$ converted and precipitate as $Fe(OH)_3$ and removed from the catalytic cycle, thus a sufficient catalyst will not remain in the action environment (Feng *et al*., 2010 and Ghosh *et al*., 2011). This issue causes $H_2O_2$ decomposition and process reduction. Studies have also shown that the oxidative potential of OH radicals, decreases when the pH increase. In the above pH due to the instability of iron ions, removal efficiency decreased while pH=3, $Fe(OH)^{+2}$, exist as quite soluble (Lin and Jiang, 2003). In this study, the best results of phosphorus removal (95%) by Fenton in the range of pH=3-4 obtained due to the high stability of $H_2O_2$, $Fe^{+2}$ at low pH. Ferrous ion was also unstable at high pH and is converted easily to ferric ions. Because these ions have high affinity to form hydroxoferric complexes and when the pH increase of more than 5, h2o2is degraded rapidly (Figure 1). The results with the studies by Irdeme *et al.* (2006) on wastewater filtration (Irdeme *et al*., 2006), Naohito *et al.* (2010) in korea On phosphorus removal by aluminium hydroxide (Paola *et al*., 2010), on the phosphorus removal by red mud (Naohito *et al*., 2010) considering the effect of pH on Fenton process have done ranging from 3 to 4 and is consistent with the best range of phosphorus removal.

### Concentration effect of $H_2O_2$

By fixing the iron concentration, pH=3 and 60 minutes reaction time with the initial concentration increase of $H_2O_2$to 2200 mg/L, phosphorus removal percentage increased (Figure 2) and one of the reasons is the increase in the amount of producing hydroxyl radical. In higher concentration, $H_2O_2$ had no effect on the removal of this factor and are due to the $H_2O_2$ degradation to oxygen and water, the combination of hydroxyl radical and preventing the formation of them. Higher concentration of 2200 mg/L of hydrogen peroxide is not suitable due to the expansiveness of water and oxygen, lees active hydroperoxile radical formation and reducing the efficiency of the oxidation process. Oxidation rate clearly depends on the amount of consumed $H_2O_2$. According to laboratory tests it seems necessary to determine the concentration rate of $H_2O_2$ and obtaining optimal rate of hydrogen peroxide to organic material. The most effective method of organic material removal; particular variety of synthetic, is chemical oxidation (Huang *et al*., 2009). The results are consistent with Meric *et al.* (2005), Yetilmezsoy *et al*. (2008) in wastewater filtration by Fenton process.

### Concentration effect of $Fe^{+2}$

As shown in Figure 3,with stabilizing the concentration of $H_2O_2$ 2200 mg/L, pH=3 and reaction time of 60 min with increasing iron concentration up to 1000 mg/L, increase the efficiency of phosphorus removal and increasing over this value will have no effect on the process. The concentration of iron ions has a significant impact on Fenton process efficiency. Without the presence of iron ions, hydroxyl radical will not formed; therefore iron ion concentration also through the production of hydroxyl radical increase and drawing up phenomenon is effective in reducing phosphorus level. By increasing the iron ion concentration of these quantities, phosphorus removal efficiency remains fixed and this issue can be due to the desire of hydroxyl radicals to oxidation-reduction reaction of $Fe^{+2}$ and $H_2O_2$. The excessive increase of iron concentration (II) has an inhibitory effect on the production of hydroxyl radicals and reduces the speed and degradation efficiency of chemical combinations (Lucas and Peres, 2009). The results are consistent with Wang *et al.* (2010) in dyeing industries wastewater filtration (Wang *et al*., 2010).

**Effect of oxidation time**

Oxidation time is one of the parameters that affect the process efficiency. To determine the best time and its effect on the Fenton process, tests were conducted at 10-100 minutes. As is clear from the figure, the highest levels of phosphorus removal were achieved in 60 minutes. In Fenton reaction, high concentrations of free hydroxyl radical formed in the first few minutes of the reaction (Figure 4). With time passing, the amount of the intermediate products of hydrogen peroxide degradation increases and by a mixture in a test environment, increases the chance of iron ion contact with intermediate products of hydrogen peroxide degradation and eventually radical hydroxyl production become more on the environment and the efficiency process increase (Goldstein and Meyersteim, 1993). The results of the study are consistent with Badawy *et al.* (2009), on wastewater filtration (Zhang *et al*., 2006) by Fenton oxidation.

**The effect of initial phosphorus concentration**

Phosphorus removal by Fenton in an aqueous solution containing concentration (50, 100, 150, 200 mg/L) in which was tested at all stages. Based on the obtained results in low concentrations (≥50 mg/L), removal efficiency is relatively low. Increasing the concentration to 100 mg/L, removal efficiency increases. But phosphorus concentration increase (≥100 mg/L) showed no tangible impact on phosphorus removal. Results are consistent with Deliyanni *et al.* (2007) of phosphorus removal (Deliyanni *et al*., 2007), Wang *et al.* (2010) in the dyeing industry wastewater filtration (Wang *et al*., 2010).

**Conclusions**

In this study, the effect of pH parameters, oxidation time, initial concentration of phosphorus, the concentration of hydrogen peroxide and ferrous ion on phosphorus removal from handmade aqueous solution by the Fenton process was investigated. The results showed that the best efficiency of phosphorus removal to 97% in optimal conditions are $H_2O_2$=2200 mg/L, $Fe^{+2}$=1000 mg/L, pH=3/5, time=60 min, the initial phosphorus concentration=100mg/L. With regard to the achieved results it cleared that Fenton process is an effective process in removing organic materials like phosphorus from the water considering the amount of removal efficiency and more economic cost in comparison with other removal process of these pollutants. Also to access more complete and better combination methods; in other studies, removal efficiency promoted by this process with the use of combination with other oxidants like ultraviolet radiation.

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