Removal of phosphate from secondary effluent with Fe^{2+} enhanced by H_2O_2 at nature pH/neutral pH

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ABSTRACT

Removal of phosphate in secondary effluents was investigated in presence of Fe^{2+}/H_2O_2. The effect of H_2O_2-dose, Fe-dose and initial phosphate concentration were assessed. The results indicated that Fe^{2+}/H_2O_2 could greatly increase the removal of phosphate compared with those achieved by Fe^{2+} alone. For initial phosphate concentration of 0.97–3.75 mg P/L, phosphate removal rates of 50–60% were observed at 1:1 molar addition of Fe(II). However, a 125% excess of Fe-dose was necessary for complete phosphate removal. The experimental data demonstrated that removal of phosphate with Fe^{2+}/H_2O_2 was higher than that observed with ferric coagulation alone. This fact suggested that in situ formed Fe(III) having much affinity for ligand phosphate. Chemical co-precipitation was considered as the dominant mechanism about phosphate removal in presence of Fe^{2+}/H_2O_2. The electron paramagnetic resonance (EPR) spectra tests in secondary effluents showed that Fe^{2+}/H_2O_2 could produce an increasing hydroxyl radical concentration with a decrease in both H_2O_2 dosage and phosphate concentration. Fe^{2+}/H_2O_2 had the potential to be utilized for removal of phosphate due to the lower cost and the higher phosphate removal capability.

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1. Introduction

Eutrophication has long been considered as one of the major water pollution issues in many countries, because it severely deteriorate the water quality in terms of high turbidity, low dissolved oxygen concentration, unpleasant odor, and bad flavor [1]. Phosphorus present in domestic wastewater was an important nutrient, and the discharge of this nutrient into natural waters would lead to impairing the drinking water sources considerably. Some studies have confirmed that phosphorus concentrations in secondary effluents were over sewage standard [2–5]. Therefore, the phosphate must be removed from secondary effluents before their dispersion in the environment.

Most of the soluble phosphate removal was based on chemical immobilization of P by chemical precipitation with di- or trivalent metal salts. Aluminum and iron salts had received considerable interest from environmental chemists due to their applications as coagulants in water treatment [6] and as phosphate removing agents in tertiary sewage treatment [7]. It is well known that Fe(III)- and Al(III)-based coagulants are used to reduce phosphorus and other contaminants in the secondary effluent for reuse [2,5,8–10]. The P chemistry is strongly related to the Fe chemistry due to the strong interaction of P with Fe and Fe-oxyhydroxides [11–13]. Some studies confirmed oxides can incorporate P both in laboratory experiments [14,15] and in field observations [12,13,16]. Other researches had already indicated that Fe(III) was more effective than aluminum in chemical precipitation of phosphorus as indicated by the residual phosphate in solution and the amount of phosphorus removed by 1 mol of coagulant [3,7,17]. Iron oxyhydroxides are capable of incorporating P during growth as a result of oxygenation of anoxic Fe(II)-rich water. Leckie and Stumm found a phenomenon that homogeneous precipitation of phosphate by iron(III) formed in situ by oxidation of iron(II) is more effective than precipitation by added iron(III) salts [18]. Moreover, Fe salts are less of an environmental concern. In addition, ferrous salt was cheaper than ferric salt (http://net.chemnet.com). So, Fe(III) in situ formed from the oxidation of ferrous salt would be an alternative way for phosphate removal based on its cost-effective and strong affinity for phosphate. However, literature about phosphate removal by iron(III) formed in situ by oxidation of iron(II) was less.

This study focuses on the potential contribution of Fe^{2+}/H_2O_2 to the phosphate removal. The present paper deals with the study of phosphate removal in secondary effluents in presence of Fe^{2+}/H_2O_2; in a subsequent paper the results of a similar study in solutions in the presence of Fe^{2+}/H_2O_2 will be presented. These

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Table 1
Characteristics of source water.

Parameters	Ranges
pH	7.0–8.5
Turbidity (NTU)	2.9–6.0
UV_{254} (cm^{-1})	0.108–0.246
COD (mg/L)	35.6–68.9
TOC (mg C/L)	8.40–31.7
NH_4^+–N (mg N/L)	10.2–50.7
Orthophosphate (mg P/L)	0.30–3.11

studies have yielded insight into the reactions between in situ formed ferric and phosphate.

The main objective of this study was to study the phosphate removal by Fe^{2+}/H_2O_2 under natural pH condition. The effect of H_2O_2-dose, Fe-dose and initial phosphate concentration were assessed. Some important parameters such as final phosphate concentrations and final pH values were measured. The second objective was providing insight into the difference between Fe^{2+}/H_2O_2 and ferric coagulation alone with respect to the phosphate removal in secondary effluents.

2. Materials and methods

2.1. Materials and sample preparation

The secondary effluents used in this study were taken from Wenchang sewage treatment plant in city Harbin of China, in which the anaerobic/aerobic (A/O) process was used. The effluent characteristics, as measured during the course of this study, were summarized in Table 1. Orthophosphate concentrations (mg P/L) were ranged in a range of 0.30–3.11, most of which was over 0.50 mg P/L (National Standard of PRC Integrated Sewage Discharge Standard).

All the tests were carried out using a program controlled six paddle stirrer (TA6-4, Wuhan, China). In this study, solid $FeSO_4$ was added to effluents before adding H_2O_2. Then, the reactions were immediately initiated by adding specific amount of H_2O_2. Solid ferric chloride was used in experiments when compared to ferric coagulation alone. After reagents mixing for 5 s at 300 rpm, solutions were under rapid mix at 300 rpm for 1 min followed by slow mix at 60 rpm for 10 min. Then the samples were filtered with 0.45 μm-pore membrane, followed by various analyses. The reagents were of laboratory reagent grade, except for the case mentioned elsewhere.

In the experiment of varying initial phosphate concentration, KH_2PO_4 would be used to adjust the phosphate content of effluents and then followed by adjusting the pH values using 0.01 mol/L NaOH and 0.01 mol/L HCl.

In the experiment about EPR tests, the initial effluents were firstly filtered with 0.45 μm-pore membrane. Then, phosphate content and pH were adjusted and reagents were added to initiate the reaction. Finally, EPR tests were carried out.

2.2. Analytical methods

Before and after adding a known amount of Fe(II) or Fe(III), the phosphate concentration in each experiment was analyzed by spectrophotometric measurement at 700 nm (An UV–visible spectrophotometer UV2550, Shimadzu, Japan) after reaction with molybdate and ascorbic acid in accordance with the standard methods (Water and Wastewater Monitoring and Analysis Method, the Fourth Edition, China, 2002). TOC (dissolved organic carbon) was measured with a TOC analyzer (multi N/C 3100, Analytikjena, Germany).

An EMX EPR spectrometer (A200S-9.5/12, Brucker, Germany) was used to measure the electron paramagnetic resonance sig-
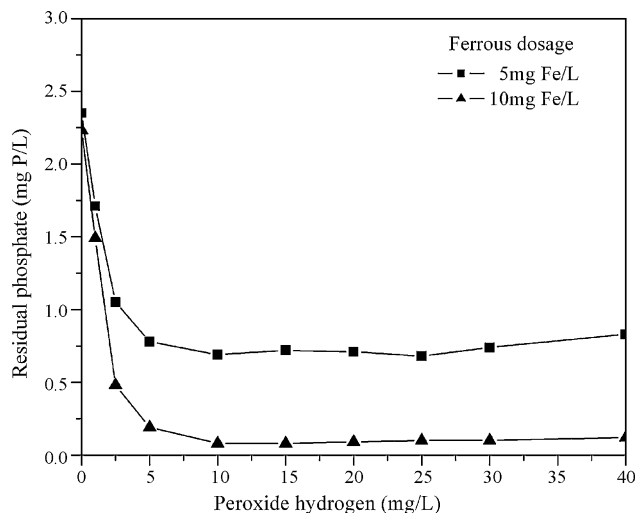

Fig. 1. Effect of H_2O_2 dosage on phosphate removal in presence of Fe^{2+}/H_2O_2. Experimental conditions: $[PO_4^{3-}]_0$: 2.52 mg P/L, initial pH 7.20 and $T = 22\,°C$.

nals with the DMPO (5,5-dimethyl-1-pyroline-N-oxide, Sigma) as the radical adduct. The settings were selected as follows: center field = 3511.940C, sweep width = 100.000G, resolution = 1024 points, frequency = 9.857 GHz and power = 2.301 mW.

3. Results and discussion

3.1. Effect of H_2O_2

The experiments were performed at initial phosphate concentration of 2.52 mg P/L and initial pH 7.20. It was found that Fe^{2+}/H_2O_2 could greatly increase the removal of phosphate compared with those achieved by Fe^{2+} alone. As it appeared in the intercept of the y-axis of Fig. 1, in which H_2O_2 was not added, the residual phosphate in secondary effluent with Fe^{2+} alone was near 100%. The data demonstrated that Fe^{2+} alone was not efficient in removing phosphate (Fig. 1). In evidence, the increase in the phosphate removal was coincident with a conversion of Fe(II) to Fe(III) in presence of H_2O_2.

The phosphate removal was obviously increased by increasing H_2O_2 dosage at $[H_2O_2]_0$ < around 5 mg/L. At $[H_2O_2]_0$ > around 5 mg/L, further increasing H_2O_2 dosage could not improve the
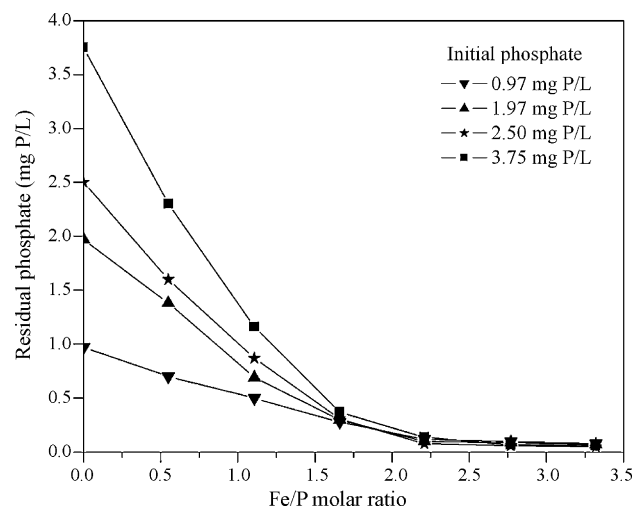

Fig. 2. Effect of mole ratios of Fe/P on phosphate removal in presence of Fe^{2+}/H_2O_2. Experimental conditions: $[H_2O_2]_0$: 5 mg/L, initial pH 7.20 and $T = 22\,°C$.

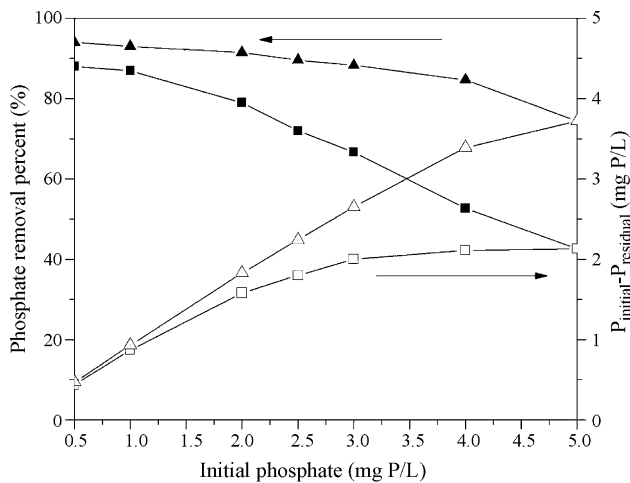**Fig. 3.** Effect of initial phosphate concentration on phosphate removal in presence of Fe^{2+}/H_2O_2. Experimental conditions: $[H_2O_2]_0$: 5 mg/L, $[Fe^{2+}]_0$: 5 mg/L for square and 10 mg/L for triangle, initial pH 7.20 and $T = 22\,°C$.

phosphate removal. The flat part of the curve presented a complete oxidation of Fe(II) which suggested excessive H_2O_2 could not improve the phosphate removal at constant Fe(II) dosage. The mechanism of these reactions with respect to hydrogen peroxide is very complex and may change with conditions of the reaction and the type of catalyst. The dissociation constant of H_2O_2 is equal to 11.62 ($H_2O_{2(aq)} \leftrightarrow H^+_{(aq)} + HO_2^-_{(aq)}$, [19]). In this experiment, the pH values were varied in a range of 6.7–7.2 (Fig. 4), resulting in that H_2O_2 was not under dissociation. However, hydrogen peroxide was rapidly decomposed with increasing pH above 5 [20]. So, at initial pH 7.2, an optimum H_2O_2 dosage of 5–10 mg/L was obtained (H_2O_2/Fe(II) mole ratio = about 1.6:1 to 3.2:1, [21]). Over a reasonable amount, the effect of hydrogen peroxide on the phosphate removal is gradually increased because of increasing transformation of ferrous to ferric in solutions that was consistent with the mechanism about phosphate removal.

3.2. Effect of mole ratios of Fe/P and initial phosphate concentration

The phosphate removal were plotted against the mole ratio of Fe/P in Fig. 2 which showed the residual phosphate concentration was gradually decreased with an increase in the mole ratios of Fe/P, at $[H_2O_2]$ of 5 mg/L. At the mole ratio of Fe/P = 1.0, only the half of the initial phosphate was removed. More than 96% of phosphate was removed at the mole ratio of Fe/P close to 2.2, for the initial phosphate concentrations used in our experiments.

The chemical reactions between phosphate and ferric ions in wastewater were complex and resulted in a larger stoichiometric ratio than that required by precipitation reaction alone. Theoretically, the mole ratio of Fe/P is 1:1 for the P removal using chemical precipitation with coagulants. However, it was indicated that here the ratio is to be higher, such as, the Fe/P mole ratio of 1.7 could reach about 90% P removal at $[PO_4^{3-}]_0 = 0.97$–3.75 mg P/L. Similar deviations from the stoichiometric ratio are found in several previous studies. Arias and coworkers [22] reported an Al/P mole ratio of 3 leading to the P removal of 60–80%, Xie et al. [5] indicated an Al/P mole ratio of 3.02 leading to the P removal of more than 80%. In the study of Wang et al. [3], after the optimization procedure, the maximum P removal efficiency for secondary effluent was reached at a pH of 6.3 and with a dose ratio of 4.13:1 (Al:P) for aluminum sulfate (97.43%), at a pH of 5.4 with a dose ratio of 4.37:1 (Al:P) for polyaluminum chloride (96.36%), at a pH of 7.0 with a dose ratio of 2.95:1 (Fe:P) for ferric sulfate (89.29%). Obviously, many organic and inorganic ligands existing in secondary effluents would take part in coordination with Fe^{3+}.

The largest phosphate removal are associated with the highest values in the Fe:P ratio. These results clearly showed that the mole ratios of Fe/P were the determining factor for phosphate removal using precipitation with iron species. Detailed discussion can be seen in Section 3.3.

Changes in residual phosphate concentration versus initial phosphate concentration are presented in Fig. 3. As seen from Fig. 3, the phosphate removal percentage is decreased with an increase in
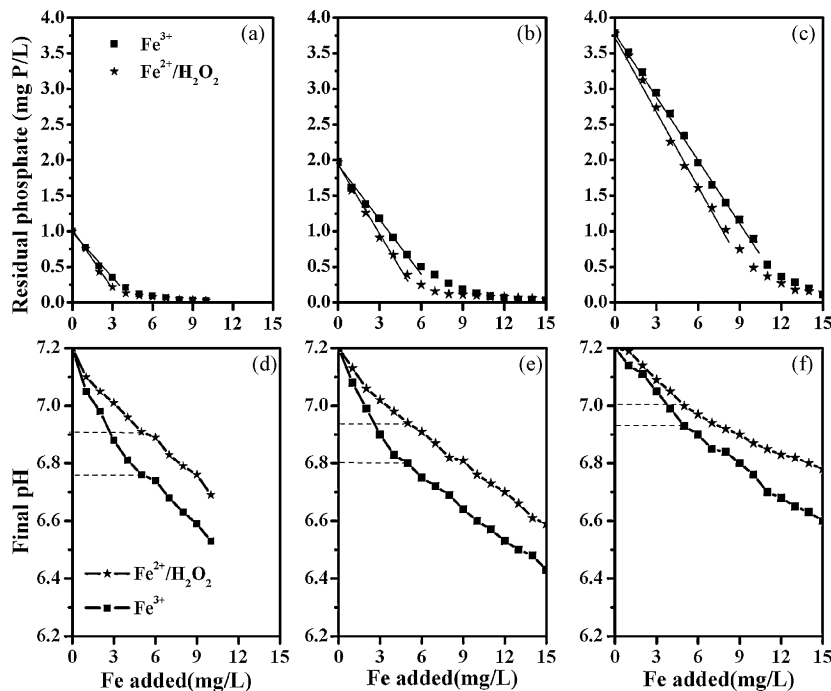

Fig. 4. In comparison with ferric coagulation alone. Experimental conditions: $[H_2O_2]_0$: 5 mg/L, initial pH 7.20 and $T = 22\,°C$.

Table 2
Relationship between iron dosage and removed phosphate in first stage.

$[PO_4^{3-}]_0$ mg P/L	Fe^{3+} coagulation	R^2	Fe^{2+}/H_2O_2	R^2
1.00	$y = 2.48x - 0.0367$	0.9916	$y = 2.06x + 0.0213$	0.9932
1.97	$y = 2.16x - 0.1007$	0.9920	$y = 1.75x - 0.1617$	0.9941
3.78	$y = 1.86x + 0.0579$	0.9982	$y = 1.63x - 0.115$	0.9941

R^2 is the square of correlation coefficient; y (mg Fe/L) is iron dosage; x (mg P/L) is removed phosphate concentration.

Table 3
Stability constants for formation of complexes and solids from metals and ligands [6].

Reaction	Stability constants
$Fe^{3+} + OH^- = [FeOH]^{2+}$	$\log K = 11.8$
$Fe^{3+} + 2OH^- = [Fe(OH)_2]^+$	$\log K = 22.3$
$Fe^{3+} + 4OH^- = [Fe(OH)_4]^-$	$\log K = 34.4$
$Fe^{3+} + 3OH^- = [Fe(OH)_3]^+$ (s)	$\log K = 42.7$
$Fe^{3+} + H_2PO_4^- = [FeH_2PO_4]^{2+}$	$\log K = 23.9$
$Fe^{3+} + HPO_4^- = [FeHPO_4]^+$	$\log K = 22.2$
$Fe^{3+} + nHPO_4^- = [Fe(HPO_4)_n]^{(3-2n)+}$	$\log K = 3.61–9.85$
$Fe^{3+} + PO_4^{3-} = [FePO_4]$ (s)	$\log K = 26.4$
$Fe^{3+} + H_2O + H_2PO_4^- = [Fe(OH)PO_4]^- + 3H^+$	$\log K = 4.33$

initial phosphate concentration, at the iron dosage of both 5 and 10 mg Fe/L.

It should be noted that at initial phosphate concentration >3 mg P/L, $P_{initial} - P_{residual}$ was kept constant of about 2.10 mg P/L and not further increased, at ferrous dosage = 5 mg Fe/L. Clearly, adding ferrous of 5 mg Fe/L resulted in a maximum P removal of 2.10 mg P/L. In contrast, at ferrous dosage = 10 mg Fe/L, $P_{initial} - P_{residual}$ was always increasing and the P removal did not reach maximum.

3.3. Comparison with traditional ferric coagulation alone

Some interested results were illustrated in Fig. 4. The phosphate removal by both Fe^{2+}/H_2O_2 and ferric coagulation alone followed the same general trend (Fig. 4a–c). Two stages can be characterized, for which the first is linear dependent on the iron dosage. The second stage represents the stage when the phosphate removal is slowly increased and finally near to 100%. Although the data are scattered, it can be clearly seen that the higher the iron dosage, the more the phosphate removal. Table 2 listed linear dependency of removed phosphate on the iron dosage. The second stage can clearly be recognized, showing phosphate removal levels off.

The entrance of H_2O_2 caused oxidation of Fe(II) to Fe(III) which resulted in subsequent precipitation due to the insoluble nature of iron(III) oxyhydroxides and phosphates, similar with the results presented in the literature [23]. In addition to precipitation of Fe phases, precipitation of calcium may occur. It is assumed that the potential uptake of phosphate by calcium carbonates is negligible since iron hydroxides precipitation is a fast kinetic process [24,25], whereas calcite precipitation is a slow kinetic process [26]. As well known, adsorption (phosphate was assumed to form inner-sphere complexes with Fe oxides) [27] and precipitation (phosphate was formed complexes with Fe or Fe hydrolysis species) [28] were

considered as the alternative mechanisms for phosphate removal. Other study indicated that the main mechanism of phosphorus removal on addition of ferric chloride and alum involves the precipitation of metal oxyhydroxides and subsequent adsorption of phosphorus by ligand exchange [29]. But, the effective P removal by adsorption took a long time of several hours or several days [30,31]. Lijklema reported that the sorption equilibrium was not reached within 24 h in presence of the fresh precipitate [11]. It is worth noting that in our study, it took about 11 min to effectively remove phosphate. It could be indicated that dominant mechanism for the phosphate removal with Fe^{2+}/H_2O_2 was co-precipitation, similar with those by ferric coagulation alone.

The residual phosphate decreased in a nearly linear fashion with the amount of iron added. Values for removed phosphate were directly proportional to the iron dosage up to removed phosphate = 65 and 80%, with Fe^{2+}/H_2O_2 and Fe^{3+} coagulation alone, respectively. The transition point represented a decrease in effective use of iron. Table 2 showed the relationship that exists between iron dosage and removed phosphate in first stage of Fig. 4. The results showed that at $[PO_4^{3-}]_0$ from 3.78 to 1.00 mg P/L, removal of 1 mol phosphate need an iron dosage from 1.63 to 2.06 mol and from 1.86 to 2.48 mol for Fe^{2+}/H_2O_2 and ferric coagulation alone, respectively. Overall, removing one mole phosphate need to add more than one mole iron. It should be noted that iron dosage for removing one mole P was gradually decreased with an increase in initial phosphate concentration, for both Fe^{2+}/H_2O_2 and ferric coagulation alone.

Phosphate ions could compete with hydroxyl ions for Fe(III) (Table 3). In evidence, Fe^{3+} ions could take part in both complexation-precipitation with phosphate ions and hydrolysis-precipitation with hydroxyl ions, simultaneously. The removal of phosphate by precipitation with iron had been modeled by Fytianos et al. using a model which included a total of 15 chemical reactions and four solid phases with the option of single-phase precipitation or two-phase co-precipitation [28]. The respective chemical equations are as follows:

$$Fe(OH)_3(s) \leftrightarrow Fe^{3+} + 3OH^- \qquad (1)$$

$$Fe_mPO_4(OH)_{3m-3}(s) \leftrightarrow mFe^{3+} + PO_4^{3-} + (3-m)OH^- \qquad (2)$$

where $m > 1$.

These results occurring during removing phosphate process can be explained based on equations above. Increasing initial phosphate concentration would significantly enhance complexation reaction between phosphate and Fe(III) and hydroxyl ions was partially replaced by phosphate, which would result in an increasing binding between phosphate and Fe(III) and then forming some solid hydroxyl phosphate ferric complexes. When $m = 1$, hydrolysis product was formed as solid $FePO_4$ ($\log K_{sp} = -23$). Fytianos and coworkers [28] had already reported some solid hydroxyl phosphate ferric complex as $Fe_{2.5}PO_4(OH)_{4.5}$ ($\log K_{sp} = -97$) and $Fe_{1.6}H_2PO_4(OH)_{3.8}$ ($\log K_{sp} = -67.2$).

The final pH values were recorded in Fig. 4d–f. It is obvious that the final pH values were decreased with an increase in iron dosage, which suggested that Fe(III) had an obvious tendency to hydrolyze in solution with both Fe^{2+}/H_2O_2 and ferric coagulation

Table 4
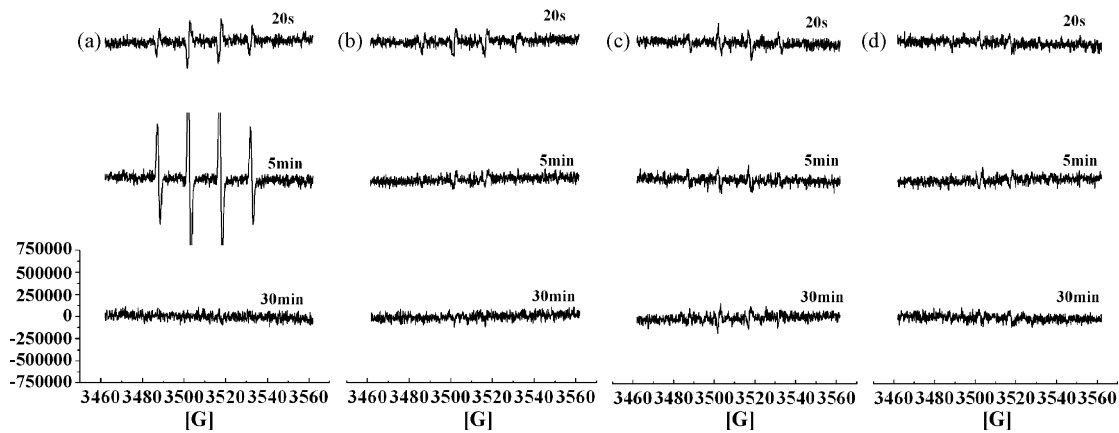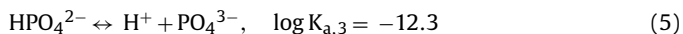Economic comparison.

$[PO_4^{3-}]_0$ (3.78 mg P/L)	Dosage (mg/L)	Residual P (mg P/L)	P removal (%)	Charge (Yuan[a]/t)
Fe^{3+}(FeCl$_3$·6H$_2$O: ~3800/t)[b]	10	0.89	76.5%	0.038
Fe^{2+}(FeSO$_4$·7H$_2$O: ~420/t)[b]	10			
H_2O_2(27.5%H$_2$O$_2$: ~1400/t)[b]	10	0.49	87.1%	0.028

[a] Renminbi.
[b] http://net.chemnet.com.

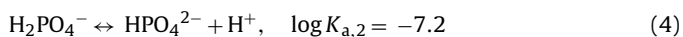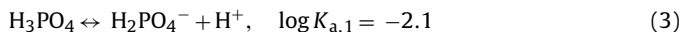**Fig. 5.** EPR spectra characteristics of the $^{\bullet}$OH-radical adduct during phosphate removal with Fe^{2+}/H_2O_2. Experimental conditions: $[H_2O_2]_0 = 10$ mg/L for (a) and (c); 20 mg/L for (b) and (d); $[PO_4^{3-}]_0 = 0.5$ mg/L for (a) and (b); 5.0 mg/L for (c) and (d); $[Fe^{2+}]_0$: 10 mg/L, initial pH 7.20 and $T = 22\,^{\circ}$C.

alone. At initial phosphate concentration from 1.00 to 3.78 mg P/L, the final pH values rose up from 6.91 to 7.00 for Fe^{2+}/H_2O_2 and from 6.76 to 6.93 for ferric coagulation alone, respectively, at iron dosage = 5 mg Fe/L. It was concluded that higher initial phosphate concentrations will lead to higher final pH values in effluents. This suggested that increasing initial phosphate concentration resulted in an decrease in Fe(III) hydrolysis due to the increasing complexation-precipitation of phosphate with Fe(III). As indicated above, complexation of phosphate with Fe(III) was accompanied by Fe(III) hydrolysis and the presence of phosphate inhibited Fe(III) hydrolysis.

It is of particular interest to compare the results when phosphate was removed in presence of Fe^{2+}/H_2O_2 and ferric coagulation alone. As shown in Fig. 4, all further conditions being the same, the only difference is that Fe^{2+}/H_2O_2 resulted in a better phosphate removal during first stage, when compared to ferric coagulation alone. Simultaneously, the final pH with Fe^{2+}/H_2O_2 was slightly higher than those with ferric coagulation alone. The pH values were varied in a range of 6.4–7.2 during phosphate removal in presence of both Fe^{2+}/H_2O_2 and ferric coagulation alone.

$$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+, \quad \log K_{a,1} = -2.1 \tag{3}$$

$$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+, \quad \log K_{a,2} = -7.2 \tag{4}$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}, \quad \log K_{a,3} = -12.3 \tag{5}$$

From the pH-phosphate distribution (Eqs. (3)–(5), [32]), it can be indicated that when $6.4 \leq pH \leq 7.2$, phosphate primarily existed in the form of $H_2PO_4^-$ and HPO_4^{2-} for two systems. In evidence, a little difference in final pH values could not be the main factor resulting in the difference in phosphate removal of both systems. Moreover, further increasing iron dosage would make both systems to get the same phosphate removal, although the difference in final pH remained in both systems. Based on discussions above, the better phosphate removal with Fe^{2+}/H_2O_2 need to be attributed to in situ formed Fe(III) having much affinity for ligand phosphate. This is consistent with the results represented in the literature [11] that reported that the fresh precipitate exhibited the greater binding capacity. Leckie and Stumm also reported that homogeneous precipitation of phosphate by iron(III) formed in situ by oxidation of iron(II) is more effective than precipitation by added iron(III) salts [18]. The phenomena discussed here are significant in situations where iron plays a role in phosphate binding in treatment plants or in the environment.

With adding sufficient iron, difference in the phosphate removal between Fe^{2+}/H_2O_2 and ferric coagulation alone could not be seen. This was possibly because increasing iron dosage could compen-

sate for a little weak phosphate removal with ferric coagulation alone. The detailed mechanism study related to this was not performed deeply in this paper and will be done in the future work.

Economic comparison was presented in Table 4. At $[PO_4^{3-}]_0 = 3.78$ mg P/L, the cost was 0.028 yuan/t for Fe^{2+}/H_2O_2 to reach the P removal of 87.1%, it was 0.038 yuan/t for Fe^{3+} alone to reach the P removal for 76.5%, at the same iron dosage of 10 mg Fe/L. Clearly, using Fe^{2+}/H_2O_2 for phosphate removal in secondary effluent had another advantage of cost effectiveness. At the same iron dosage, Fe^{2+}/H_2O_2 provided higher phosphate removal and required less cost.

3.4. About EPR test

Changes in EPR spectra versus initial phosphate concentration and H_2O_2 dosage were presented in Fig. 5. The signal at low phosphate concentration (Fig. 5a and b) was stronger than those at high phosphate concentration (Fig. 5c and d). Overall, this work indicated that phosphate inhibited free radical formation under near neutral pH condition. This fact was consistent with other's study which reported phosphate suppressed the Fenton system's ability to oxidize dichlorvos at pH 3 [33]. They indicated that the main reason for the suppression of phosphate is that phosphate ions would produce a complex reaction together with ferrous ions and ferric ions, which lowered its ability to catalyze hydrogen peroxide. Obviously, our results under near neutral pH values were similar with those at pH 3. Furthermore, we found that the yield of hydroxyl radical was increasing with the reaction time in earlier time but then reducing at low initial phosphate concentration. This may be due to the formation rate of $^{\bullet}$OH radical was dependent on the ferrous dissolving and oxidation rate. Fe^{2+} was gradually dissolved and oxidized. So, $^{\bullet}$OH radical was formed in the same tendency. However, at high phosphate concentration, dissolved ferrous ions were immediately trapped by phosphate ions, resulting in the inhibition of the formation of hydroxyl radical.

It can be seen that the signal at low H_2O_2 dosage (Fig. 5a and c) was stronger than those at high H_2O_2 dosage (Fig. 5b and d), at given phosphate concentrations. Obviously, H_2O_2 of lightly higher dosage ($[H_2O_2]_0/[Fe^{2+}]_0$ molar ratio = 3.29) could quench hydroxyl radicals formed in secondary effluents at neutral pH, similar with Fenton reaction at excessive H_2O_2 and pH 3 ($HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$, $k = 3.3 \times 10^7$ M^{-1} s^{-1} [34]). However, excessive H_2O_2 could not change the phosphate removal which was in accordance with the mechanism illustrated above.

4. Conclusions

Results obtained from this study have provided valuable information regarding phosphate removal Fe^{2+}/H_2O_2 under nature pH condition. It could be indicated that dominant mechanism for the phosphate removal in presence of Fe^{2+}/H_2O_2 was co-precipitation, similar as those in presence of ferric coagulation alone. The better phosphate removal with Fe^{2+}/H_2O_2 need to be attributed to in situ formed Fe(III) having much affinity for ligand phosphate. EPR spectra tests showed that Fe^{2+}/H_2O_2 could produce an increasing hydroxyl radical concentration with a decrease in H_2O_2 dosage and phosphate concentration in secondary effluent. Fe^{2+}/H_2O_2 had the potential to be utilized for removal of phosphate due to lower cost and higher phosphate removal capability.

Acknowledgments

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