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To cite this article: Ruijuan Ji 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **300** 052002

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Removal of 1-hymxyethylidene-1,1-diphosphonic Acid of Organic Phosphorus Scale Inhibitors in Circulating Water

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Abstract. In order to remove 1-hymxyethylidene-1, 1-diphosphonic acid (HEDP) of organic phosphorus scale inhibitors in circulating water effectively, a chemical precipitation method has been used. The influences of parameter on HEDP removing rate, such as species and dose of chemical precipitation agent, reaction time, are studied, so that the optimal conditions are confirmed. The results show that the HEDP removing rate can be higher than 95% and the relative standard deviation of measured value is less than 1%, when the mass concentration of FeSO_4 is 2 g/L, the dosage of $\text{Ca}(\text{OH})_2$ is 0.052 g, and reaction time is 30 min. This method is simple and rapid, has high precision and good reproducibility, can be used to remove organic phosphorus by factory, with broad application prospect.

Keywords: 1-hymxyethylidene-1,1-diphosphonic Acid; Organic Phosphorus; Chemical Precipitation Method; Ultraviolet Spectrophotometry

1. Introduction

With the continuous recycling of industrial water, the concentration of calcium and magnesium ions gradually increases. It not only affects the normal operation of the cooling water system, but also seriously corrodes the pipeline, thus increasing the maintenance cost [1]. So it is commonly that adding organic phosphorus scale inhibitor to circulating water in industry [2]. 1-hymxyethylidene-1, 1-diphosphonic acid (HEDP), as one of the representatives of organic phosphorus scale inhibitors, can form stable complexes with iron, copper, zinc and other metal ions, and has a good scale inhibition effect [3,4].

However, it brings new environmental problems, which increases the content of organic phosphorus and exceeds the discharge standard. Therefore, organic phosphorus cannot be ignored and it is urgent to take measures [5]. Currently, the commonly used methods for the removal of organic phosphorus include photocatalytic oxidative degradation, ozone oxidative degradation, and microbial degradation, etc. [6-8], which all need to first oxidize and degrade organic phosphorus to inorganic phosphorus, and then remove it with chemical reagents. These methods have many steps, complex equipment, high cost and narrow application range.

In view of the shortcomings of above methods, this study proposes a direct way of removal of organic phosphorus by chemical precipitation, that is, a method of directly adding a chemical reagent to remove the organic phosphorus without oxidation. The optimal parameters for removing organic phosphorus



HEDP are determined experimentally. The method has the advantages of simple steps, convenient operation, low cost and high removal efficiency.

2. Experiment

2.1. Experimental Theory

The circulating water containing organic phosphorus scale inhibitor HEDP was added with calcium hydroxide, iron salt or aluminum salt to produce hydroxide precipitation under alkaline conditions. The organic phosphorus was adsorbed and swept up to precipitate together. The content of HEDP in the supernatant was determined after filtering the precipitate. Excessive oxidant was added to degrade HEDP to orthophosphate. The content of orthophosphate was determined by ultraviolet spectrophotometry at 700nm wavelength. According to the phosphorus standard curve, the actual phosphorus content and the removal rate of organic phosphorus can be calculated.

2.2. Experimental reagents and apparatus

FeSO₄ and Ascorbic acid are produced by Sinopharm group chemical reagent co. LTD; Ca(OH)₂, AlCl₃, Al₂(SO₄)₃, FeCl₃, Na₂S₂O₈, KH₂PO₄, Ammonium molybdate are produced by Tianjin kemeiou chemical reagent co. LTD; HEDP, PAM are produced by Shandong Taihe Water Treatment Co., Ltd.

UV-2450 UV visible spectrophotometer, shimadzu, Japan; FA2004 electronic balance, Shanghai jingke instrument co., LTD. PH-3C pH meter, Shanghai thunder magnetic instrument factory.

2.3. Experimental Methods

2.3.1. Standard Curve Drawing. The phosphorus standard solutions of 0.0, 0.50, 1.00, 3.00, 5.00, 10.0 and 15.0mL were respectively removed into a 25mL colorimetric tube. Then added 1mL ascorbic acid solution and 2mL ammonium molybdate solution and fully mixed. After standing for 15min, deionized water was used as a reference to measure the absorbance. Draw the standard curve. As shown in Figure 1.

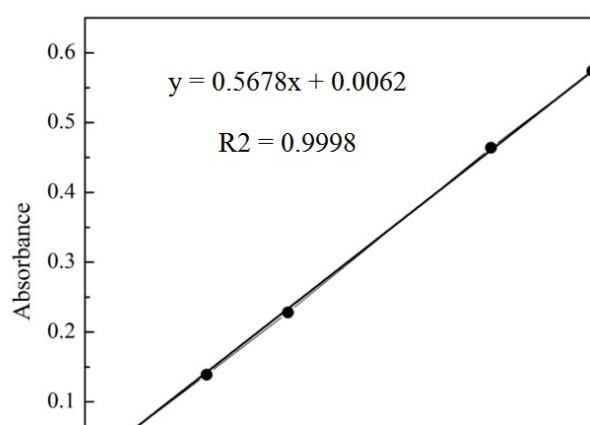


Figure 1. Phosphorus standard curve.

It can be seen from Figure 1 that the linear regression equation of phosphorus mass concentration and absorbance is $y = 0.5678x + 0.0062$, and the correlation coefficient $R^2 = 0.9998$, indicating a good linear relationship between phosphorus mass concentration and absorbance.

2.3.2. Experimental Steps. 100 mL 40 mg/L HEDP were added the quantitative of $\text{Ca}(\text{OH})_2$ until pH reach to 12, then added a certain amount of iron or aluminum salt and 1mL PAM, mixed well. After standing for a period of time, 5 mL solution were moved into 25 mL colorimetric tube, added 4 mL $\text{Na}_2\text{S}_2\text{O}_8$ solution, heated 30 min under high pressure, added 1 mL ascorbic acid solution and 2 mL ammonium molybdate solution, after 15 min, measure the absorbance.

3. Results and discussion

3.1. Selection of phosphorus removal agents

FeSO_4 , FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$ and AlCl_3 were choiced as phosphorus removal agents, which were added into 100 ml 40 mg/L HEDP respectively to investigate the influence of different agents on the removal effect of HEDP, as shown in Table 1.

Table 1. Removal rates of organic phosphorus HEDP by different phosphorus removal agents.

Reaction time /min	Removal rates of HEDP/(%)			
	$\text{Al}_2(\text{SO}_4)_3$	AlCl_3	FeCl_3	FeSO_4
5	45.1	42.4	39.2	37.4
10	76.0	68.5	67.3	72.2
20	93.2	87.3	82.0	90.7
30	96.5	96.2	95.7	96.0
40	96.8	96.0	95.8	96.0
50	96.4	95.9	95.6	95.9

It can be seen from Table 1 that the removal efficiency of HEDP is $\text{Al}_2(\text{SO}_4)_3$, AlCl_3 , FeSO_4 , FeCl_3 from high to low. When the reaction time is 30 min, the HEDP removal rate is over 95%. Among them, $\text{Al}_2(\text{SO}_4)_3$ has the highest removal efficiency with the large dosage and high cost. The HEDP removal rates of AlCl_3 and FeSO_4 are similar, and the effluent concentration is up to standard, but the price of AlCl_3 is much higher than that of FeSO_4 . Therefore, FeSO_4 with low cost is selected as the phosphorus removal agent.

3.2. Determination of the optimal dosage of calcium hydroxide

The solid powder of 0.028, 0.040, 0.052, 0.070, 0.088 and 0.100g calcium hydroxide were added into 100mL 40mg/L HEDP respectively. Under the above experimental conditions, the effect of $\text{Ca}(\text{OH})_2$ on the removal rate of HEDP was investigated to determine the optimal dosage, as shown in Figure 2.

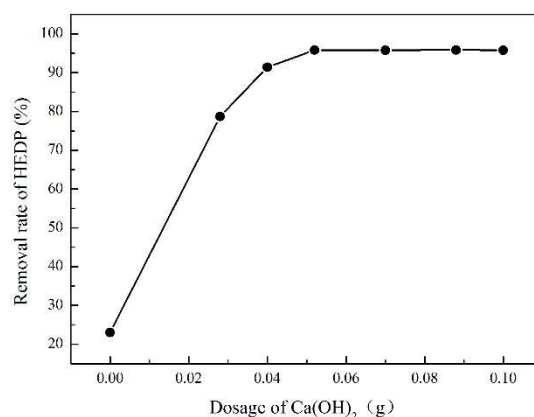


Figure 2. Effect of $\text{Ca}(\text{OH})_2$ on the removal rate of HEDP.

As can be seen from Figure 2, when the dose of $\text{Ca}(\text{OH})_2$ reaches 0.052g, the removal rate of HEDP exceeds 95%, and it no longer rises with the increase of $\text{Ca}(\text{OH})_2$, and basically tends to be stable. Therefore, the optimal dosage of $\text{Ca}(\text{OH})_2$ is 0.052g.

3.3. Determination of the optimal dosage of phosphorus removal agent

FeSO_4 of 0, 0.50, 1.00, 2.00, 4.00, 6.00mL were added into 100mL 40mg/L HEDP respectively which the mass concentrations were 0, 0.5, 1.0, 2.0, 4.0, and 6.0 g/L. Under the above experimental conditions, the effect of FeSO_4 on the removal rate of HEDP was investigated to determine the optimal dosage. The results are shown in Figure 3.

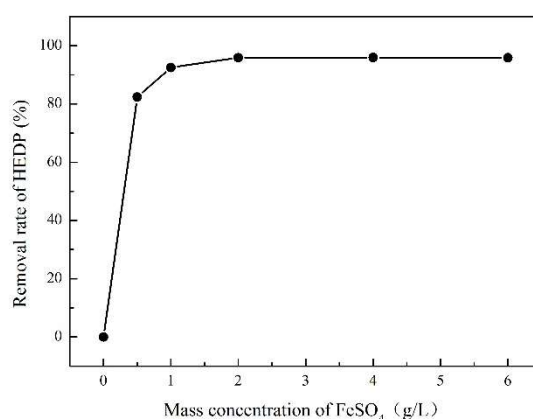


Figure 3. Effect of mass concentration of FeSO_4 on removal rate of HEDP.

As can be seen from Figure 3, the removal rate of HEDP increases with the increase of the mass concentration of FeSO_4 . When the mass concentration is greater than 2.0g/L, the removal rate of HEDP remains basically unchanged. Therefore, the optimal mass concentration of FeSO_4 is 2.0g/L.

3.4. Determination of the optimal reaction time

The influence of reaction time on the removal rate of HEDP was investigated under the condition that the mass concentration of FeSO_4 was 2.0 g/L and the addition of $\text{Ca}(\text{OH})_2$ was 0.052 g. The results are shown in Figure 4.

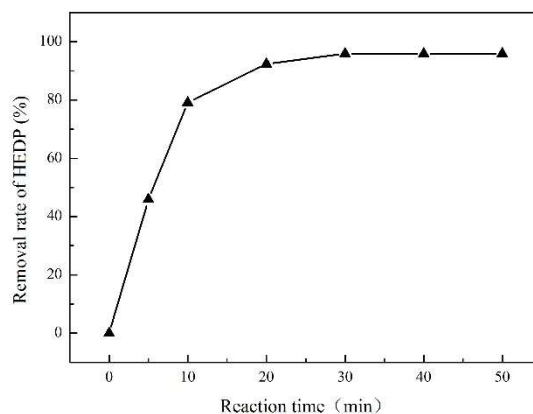


Figure 4. Effect of reaction time on removal rate of HEDP.

It can be seen from Figure 4 that the removal rate of HEDP increases rapidly with the increase of reaction time. When the reaction time is 30min, the removal rate of HEDP reaches more than 95%. after

reacting 30min, there is no significant change in the removal rate, indicating that the reaction is basically balanced. Therefore, the optimal reaction time is 30min.

3.5. Precision experiment

In order to measure the precision of the method for removing organic phosphorus HEDP, different concentrations of HEDP solutions were experimentally prepared to under the optimal experimental conditions, that is, the dosage of calcium hydroxide was 0.052g, and the concentration of FeSO_4 was 2.0g./L, reaction time was 30min. Each concentration gradient was measured in parallel three times, and the experimental results are shown in Table 2.

Table 2. Precision experiment results.

mass concentration of HEDP /(mg·L ⁻¹)	the three-parallel content of HEDP in the supernatant /(mg·L ⁻¹)			average value /(mg·L ⁻¹)	standard deviation /(mg·L ⁻¹)	Relative standard deviation /(%)
5	0.0678	0.0689	0.0682	0.0683	0.0006	0.88
10	0.1186	0.1192	0.1206	0.1195	0.0010	0.84
20	0.2501	0.2533	0.2508	0.2514	0.0017	0.68
30	0.3745	0.3700	0.3715	0.3720	0.0023	0.62
40	0.4890	0.4884	0.4932	0.4902	0.0026	0.53

Table 2 shows that the relative standard deviation of the three parallel determination values with different concentration gradients is less than 1%, indicating that the determination values have good reproducibility and high accuracy. In other words, it is feasible to remove organic phosphorus HEDP by chemical precipitation.

4. Conclusion

In this study, the organic phosphorus HEDP in circulating water was removed by chemical precipitation method. The optimal reaction conditions were determined by repeated experiments on different parameters: FeSO_4 was the best agent and the mass concentration was 2g/L, the dosage of $\text{Ca}(\text{OH})_2$ was 0.052 g, and reaction time was 30 min. Under this condition, the removal rate of HEDP can be higher than 95%, the emission concentration reaches the standard, and the relative standard deviation of experimental measurements is less than 1%, indicating that the chemical precipitation method is feasible for HEDP removal. The method has good reproducibility, high precision, simple process, high treatment efficiency and broad application prospect, which provides a possibility for rapid removal of organic phosphorus HEDP in wastewater.

References

- [1] Liang z y, zhu y, cheng z f, et al. Turbidimetric determination of polyacrylic acid in circulating water [J]. Industrial water treatment, 2014,34 (4) : 76-78.
- [2] Ye x l, liu y. Influence of positive phosphorus content on industrial circulating cooling water system [J]. Science and technology communication, 2012 (14) : 96-98.
- [3] Yuan chun, Jiang zong-kou. Control method of orthophosphate content in the synthesis of hydroxyethyl bisphosphonic acid [J]. Chemical industry journal, 1997,11 (9) : 29-31.
- [4] Ye f. Analysis of phosphoric acid in hydroxyethyl diphosphonic acid products and its relationship with structure [J]. Industrial water treatment, 1991,11 (6) : 28-29.
- [5] Zhang y l, zhao h w, et al. Prediction of impact of scale and corrosion inhibitor degradation of

- organophosphorus on circulating cooling water system [J]. Industrial water treatment, 2015,35 (6) : 10-14.
- [6] Nowack b. Environmental chemistry of phosphonates [J]. Water Research, 2003,37 (11) : 2533-2546.
- [7] Shao kolong, Zhou collen, Lu hong et al. Journal of environmental engineering, 2009,3 (7) : 1259-1262.
- [8] Cui lina, Li ji, Lu xiaomei. Research and development of wastewater phosphorus removal technology [J]. Science of environmental protection, 2011,37 (2) : 10-13.