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Optimization of phosphorus removal from secondary effluent using simplex method in Tianjin, China

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Abstract

Enhanced concentrations of phosphorus entering the aquatic systems have been linked with eutrophication and its associated problems. Jar tests were applied to a secondary effluent in order to determine optimal conditions for coagulation. The coagulants studied were ferric sulfate [$Fe_2(SO_4)_3$], aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$] and polyaluminum chloride (PAC). The experiments were carried out using simplex research technique to determine the optimum conditions of these coagulants for phosphorus removal. For each coagulant examined, 18–25 experiments were carried out until a maximum removal was observed through the experimental procession. Increases of greater than 30% were found for the removal efficiencies of these three coagulants over the course of the experiments. Good removal efficiencies averaging at least 87.25% were obtained through the simplex procession. The orthophosphate removal efficiency was higher than that of total phosphorus for each coagulant. The maximum removal efficiency of total phosphorus obtained from the optimization procedures for ferric sulfate, aluminum sulfate and polyaluminum chloride was 87.3, 95.6 and 94.0%, respectively, and the minimum total phosphorus residual was 0.35, 0.12 and 0.16 mg/L, respectively.

Keywords: Phosphorus removal; Coagulation; Flocculation; Simplex; Water reuse

1. Introduction

The presence of phosphorus in wastewater is usually considered to be the limiting nutrient with respect to the eutrophication of water bodies. Removal of phosphorus from wastewater can, therefore, be an effective method for the control of eutrophication in lakes and similar water bodies. Physical–chemical treatment processes of coagulation–flocculation with aluminum or iron salts are most commonly used for removal of phosphorus compounds in raw sewage. several studies have been performed to determine the effectiveness of chemical coagulation, flocculation and precipitation in raw wastewater treatment [1–5].

Due to water resource shortage and socio-economic development, China faces serious problems of water supply and water pollution. The dominant non-potable uses of freshwater include irrigation, industrial use, surface water replenishment, and groundwater recharge, all of which could be augmented or replaced by reclaimed water with the appropriate level of treatment. In the future, reclaimed municipal wastewater can be an important water resource but its use must be carefully planned and regulated to prevent adverse effects [6–8]. Because activated sludge plants have been relatively successful in removing nutrients biologically, coagulation of secondary effluent is usually the first step in the wastewater reclamation process intended for reuse. Coagulants are used to reduce phosphorus and other contaminants in the secondary effluent intended for reuse [9–12]. Clark and Stephenson [12] provided guidance on the optimum conditions for removal of phosphorus compounds in secondary effluent by using factorial design and simplex design.

There are many factors affecting the phosphorus removal performance, such as pH, alkalinity, coagulant dose, speed

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of flash mixing and other interfering substances. The effect of some of these factors on coagulation were already studied in several works [5,12,13]. Ebeling et al. [5] indicated that flocculation and mixing speed played only a minor role in the removal efficiencies for both orthophosphates and suspended solids. Recent research had identified chemical type, chemical quantity added and pH as important factors in coagulation–flocculation process [12]. Before a real comparison among coagulants can be made, the pH and coagulant dose need to be optimized. Therefore, an experimental design methodology can be used to determine the optimum conditions for each coagulant precipitation. The sequential simplex method is a strategy that rapidly and efficiently locates the region of the optimum by varying all variables simultaneously [12,14–17]. The simplex method uses a logical algorithm of reflection, expansion, and contraction rules to find the optimum with a small number of experiments [14].

The following investigation was aimed at determining the optimum conditions of several coagulants for phosphorus removal in a secondary effluent. A simplex design was used to optimize the experimental parameters.

2. Materials and methods

The secondary effluent used in this study was taken from Jizhuangzi sewage treatment plant in Tianjin, which is a typical sewage treatment plant in northern China. It consists of three commonly used main treatment steps: preliminary and final clarification and an aerator tank. The effluent characteristics, as measured during the course of this study, are summarized in Table 1.

The coagulants selected for the experiment were: ferric sulfate [$Fe_2(SO_4)_3$], aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$] and polyaluminum chloride (PAC, 28% Al_2O_3), products which have been used traditionally in coagulation–flocculation processes applied to wastewaters.

2.1. Experimental procedure and analysis

The studies of coagulation–flocculation were undertaken on a laboratory scale. Jar test coagulation procedure was carried out, using a six paddle stirrer. In each of the tests, 400 mL of secondary effluent was poured into the jar, and the coagulant was added under stirring. Rapid mix took place for 1 min at a speed of 200 rpm, followed by slow mix for 30 min at 30 rpm. The settling period lasted for 30 min. Samples were then taken and analyzed for orthophosphate concentration and total phosphorus concentration. For each set of tests, a test consisting of secondary effluent without coagulant addition was used. The pH was adjusted to the desirable level with the addition of 0.1 mol/L solutions of HCl or NaOH.

Orthophosphate and total phosphorus were analyzed in accordance with the Standard Methods [18]. Orthophosphate was determined by spectrophotometric measurement after reaction with molybdate and sacorbic acid. Total phosphorus was converted to orthophosphate by digestion with sulfuric acid and potassium persulfate. All chemicals used in the study were analytical grade reagents.

Table 1
Characteristics of secondary effluent

Parameter	Range
pH	6.80–7.45
Turbidity (NTU)	2.1–6.0
Total phosphorus (mg/L)	2.07–4.87
Orthophosphate (mg/L)	1.21–3.46
Ammonium nitrogen (mg/L)	26.6–52.3
Total nitrogen (mg/L)	41.6–113.2
COD (mg/L)	33.3–65.4

2.2. Simplex methodology

In this study, the experiments were carried out using modified simplex method [14] to reach progressively the optimum response of a system within few experiments. A modified simplex method [14,19] allows the simplex to converge more rapidly toward an optimum by expansion or contraction along the line of reflection. Due to this improvement, the required number of experiments can be decreased distinctly [16,20,21]. The optimization was carried out for two parameters ($n = 2$), pH and amount of coagulant added. We have defined a domain between 1 and 5 for the dose ratio of coagulants, and between 5 and 9 for pH to avoid undesirable conditions. When an experiment design is outside of the boundary, a very poor response is assigned to the design. The simplex then will calculate another experiment that will be within the allowable range of conditions.

3. Results and discussion

Two important parameters of the process (pH and the coagulant dose) were chosen for the optimization step using simplex methodology. The simplex plots of optimization procedures for ferric sulfate, aluminum sulfate and polyaluminum chloride had been shown in Fig. 1, respectively. For each coagulant examined, 18–25 experiments were carried out until a maximum removal was observed through the experimental procession.

The simplex method, with a small number of experiments (18–25), determined the optimum conditions of ferric sulfate, aluminum sulfate and polyaluminum chloride for the removal of phosphorus in secondary effluent. The evolution of the response during the experiments had been shown in Figs. 2 and 3. The removal efficiencies of orthophosphate and total phosphorus generally increased significantly over the course of the experiments. Increases of greater than 30% were seen for each of these three coagulants. The orthophos-

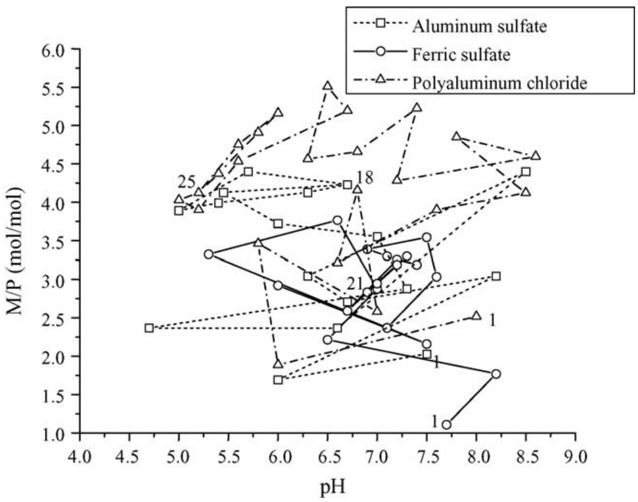

Fig. 1. Plots of simplex methodology.

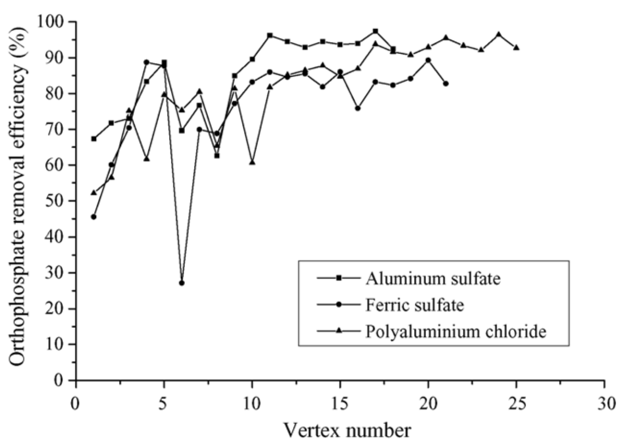

Fig. 2. Evolution of the response of orthophosphate removal efficiencies.

phate removal efficiencies of ferric sulfate, aluminum sulfate and polyaluminum chloride were increased from 45.53 to 89.29, 67.31 to 97.43 and 52.12 to 96.36%, respectively (Fig. 2).

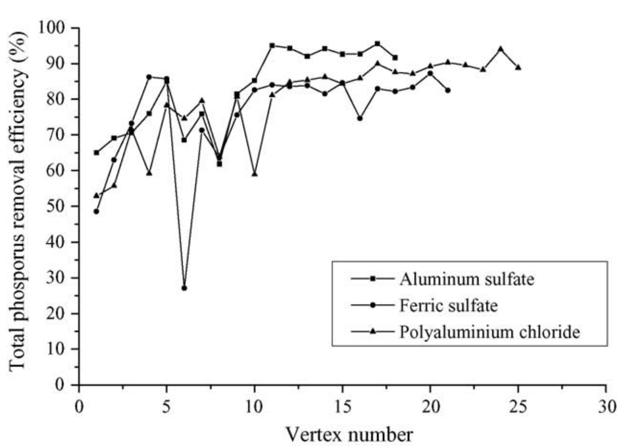

Fig. 3. Evolution of the response of total phosphorus removal efficiencies.

As is shown in Fig. 3, the greatest improvement was obtained with polyaluminum chloride, which started with a total phosphorus removal efficiency of 52.90% and finished with removal efficiency of 93.97%. The removal efficiencies of total phosphorus increased from 48.58 to 87.25% for ferric sulfate, and from 64.99 to 95.60% for aluminum sulfate.

In comparison between Figs. 2 and 3, it is showed that the orthophosphate removal efficiency was higher than the removal efficiency of total phosphorus for each coagulant. The result showed that the coagulants mainly removed the orthophosphate fraction of the phosphorus present in the secondary effluent. This is in agreement with similar results reported in the literature [2,4], and can be explained that the phosphorus in form of orthophosphate is removed by precipitation of phosphate with the metal ion, while the total phosphorus is removed by a complicated combination of interaction and adsorption with the flocculated particles.

The optimum conditions of each coagulant were presented in Table 2. Good removal efficiencies of total phosphorus averaging at least 89.29% were obtained through the simplex procession. The maximum removal efficiency was reached at a pH of 6.3 and at the dose ratio of aluminum sulfate was 4.13:1 (Al:P). Maximum removal efficiency observed on the experimental domain was 97.43% for orthophosphate and 95.60% for total phosphorus. The best results were obtained for polyaluminum chloride (96.36% for orthophosphate and 93.97% for total phosphorus) at a dose ratio of 4.37:1 (Al:P) and a pH of 5.4. The minimum total phosphorus residual of aluminum sulfate and polyaluminum chloride was 0.12 and 0.16 mg/L. In accordance with previous findings [10], aluminum sulfate appeared to have given slightly higher removals as opposed to polyaluminum chloride.

After the optimization procedure, the removal efficiency of ferric sulfate increased to 89.29% for orthophosphate and 87.25% for total phosphorus, with a dose ratio of 2.95:1 (Fe:P) and a pH of 7.0. A comparison of these coagulants indicated that the optimum dose of ferric sulfate was lower than the other two aluminum coagulants. Other research studies had indicated that Fe(III) was more effective than aluminum in precipitation of phosphorus as indicated by the residual phosphate in solution and the amount of phosphorus removed per mol of coagulant [1].

The optimum pH obtained from the simplex methodology for aluminum sulfate, polyaluminum chloride and ferric sulfate were 6.3, 5.4 and 7.0, respectively, which were not in agreement with the findings of previous research [12]. Clark and Stephenson [12] examined the effect of pH separately because the pH levels had not changed significantly during the optimization procedure, and they indicated that the natural pH of the secondary effluents (pH = 7.4) was optimum for phosphorus removal with Fe(III) and Al(III). These findings were not in accordance with other research studies [2,4,9]. It is clear from the results detailed above that there remains some problems about the optimization procedure and this needs to be investigated further.

Table 2
Optimum operating variables for maximum phosphorus removal

Coagulant	pH (range 5–9)	Coagulant addition (mol:mol) (range 1–5)	Orthophosphate removal (%)	Total phosphorus removal (%)	Residual phosphorus (mg/L)
Aluminum sulfate	6.3	4.13	97.43	95.60	0.12
Polyaluminum chloride	5.4	4.37	96.36	93.97	0.16
Ferric sulfate	7.0	2.95	89.29	87.25	0.35

4. Conclusions

Based on the results of the experiments in this study, the following conclusion can be drawn:

- Coagulation with aluminum or iron salts is a highly effective method for the removal of phosphorus from secondary effluent. The minimum total phosphorus residual of ferric sulfate, aluminum sulfate and polyaluminum chloride was 0.35, 0.12 and 0.16 mg/L, respectively.
- As a general conclusion, the simplex method, with a small number of experiments (18–25), determined the optimum conditions of these coagulants for phosphorus removal. The simplex method was able to improve phosphorus removal efficiencies by at least 30% for each of these three coagulants.
- The orthophosphate removal efficiency was higher than the removal efficiency of total phosphorus for each coagulant. The result showed that the coagulants mainly removed the orthophosphate fraction of the phosphorus present in the secondary effluent.
- The maximum removal efficiency of total phosphorus obtained from the optimization procedures of ferric sulfate, aluminum sulfate and polyaluminum chloride was 87.25, 95.60 and 93.97%, respectively.

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References

[1] P.H. Hsu, Comparison of iron(III) and aluminum in precipitation of phosphate from solution, Water Res. 10 (1976) 903–907.
[2] P.R. Thomas, D. Allen, D.L. McGregor, Evaluation of combined chemical and biological nutrient removal, Water Sci. Technol. 34 (1/2) (1996) 285–292.
[3] E. Galarneau, R. Gehr, Phosphorus removal from wastewaters: experimental and theoretical support for alternative mechanisms, Water Res. 31 (1997) 328–338.
[4] M.I. Aguilar, J. Sáez, M. Lloréns, A. Soler, J.F. Ortuòo, Nutrient removal and sludge production in the coagulation–flocculation process, Water Res. 36 (2002) 2910–2919.
[5] J.M. Ebeling, P.L. Sibrell, S.R. Ogden, S.T. Summerfelt, Evaluation of chemical coagulation–flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge, Aquacult. Eng. 29 (2003) 23–42.
[6] A. Levine, T. Shiasano, Recovering sustainable water from wastewater, Environ. Sci. Technol. 38 (2004) 201a–208a.
[7] H. Pinjing, L. Phan, G. Guowei, G. Hervouet, Reclaimed municipal wastewater—a potential water resource in China, Water Sci. Technol. 43 (10) (2001) 51–58.
[8] J. Pelley, Neglected forms of phosphorus play important role, Environ. Sci. Technol. 38 (2004) 383a–384a.
[9] J.F. Ferguson, T. King, A model for aluminum phosphate precipitation, J. WPCF 49 (1977) 646–657.
[10] E. Diamadopoulos, C. Vlachos, Coagulation–filtration of a secondary effluent by means of pre-hydrolyzed coagulants, Water Sci. Technol. 33 (10/11) (1996) 193–201.
[11] M. Ei-Hoz, L.W. Apperley, Removal of phosphorus from secondary effluent by a matrix filter, Desalination 106 (1996) 247–253.
[12] T. Clark, T. Stephenson, Development of a jar testing protocol for chemical phosphorus removal in activated sludge using statistical experimental design, Water Res. 33 (7) (1999) 1730–1734.
[13] J.P. Szpak, D.R. Woods, K. Bouchard, Critique of jar testing for the design of coagulation–flocculation systems, Water Qual. Res. J. Can. 31 (1) (1996) 51–64.
[14] J.A. Nelder, R. Mead, A simplex method for function minimization, Comput. J. 7 (1965) 308–312.
[15] P. Ricou-Hoeffer, I. Lecuyer, P.L. Cloirec, Experimental design methodology applied to adsorption of metallic ions onto fly ash, Water Res. 35 (4) (2001) 965–976.
[16] R.J. Stolzberg, Optimizing signal-to-noise ratio in flame atomic absorption spectrophotometry using sequential simplex optimization, J. Chem. Educ. 76 (6) (1999) 834–838.
[17] S. Srijaranai, R. Burakham, R.L. Deming, T. Khammeng, Simplex optimization of ion-pair reversed-phase high performance liquid chromatographic analysis of some heavy metals, Talanta 56 (2002) 655–661.
[18] APHA/AWWA/WPCF, Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association, Washington, DC, 1989.
[19] S.N. Deming, S.L. Morgan, Simplex optimization of variables in analytical chemistry, Anal. Chem. 45 (3) (1973) 278a–282a.
[20] P.B. Ryan, R.L. Barr, H.D. Todd, Simplex techniques for nonlinear optimization, Anal. Chem. 52 (9) (1980) 1460–1467.
[21] J.W. Elling, J. Leo, L.J. Koning, F.A. Pinkse, N.M.M. Nibbering, Computer-controlled simplex optimization on a Fourier transform ion cyclotron resonance mass spectrometer, Anal. Chem. 61 (4) (1989) 330–334.