Removal of phosphorus and nickel from an automobile wastewater by coagulation/flocculation combined with magnetite

Zhimei Liu, Feng Liu*, Shengjun Wu, Xiaoxiao Wang, Yangming Lei
Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences,
Chongqing, 401122, China
liuzhimei@cigit.ac.cn

***Abstract*—The method of coagulation/flocculation combined with magnetite powder was used to remove total phosphorus (TP) and nickel from an automobile wastewater. In the method, magnetite powder, poly-aluminum chloride (PAC) and cationic polyacrylamide (PAM) were added into the wastewater. Through a factorial design evaluation, the dosage of PAC was considered as the main factor influencing the TP removal. With a PAC dosage of 0.5 g/L and initial wastewater pH of 10.03, TP removal efficiency reached 96.6% using the method of coagulation/flocculation. When initial pH of the wastewater was adjusted to 10.03, nickel removal efficiency reached 98.0%. Therefore, coagulation/flocculation in relatively high pH (10.03) could effectively remove phosphorus and nickel synchronously. The sludge settling velocity reduced greatly in the beginning of settlement and reached zero after 17 min with magnetite dosage of 2 g/L. The dosage of magnetite powder could enhance the solid-liquid separation in the coagulation/flocculation method.**

***Keywords*—Total phosphorus (TP), Nickel, Coagulation/flocculation, Magnetite powder (Fe_3O_4), Sludge**

INTRODUCTION

With the development of economy, we have witnessed a rapid development of automobile factories in China, which produced abundant wastewater that contains a variety of pollutants, especially phosphorus and heavy metals. They may cause serious environmental pollution. A large number of phosphorus was discharged into water (e.g. rivers and lakes), resulting in eutrophication. Accumulation of heavy metals in soil and water will also pose significant threats to human health. Therefore, effective measures for solving these pollutions caused by phosphorus and heavy metals from automobile factories should be paid more attention to.

Coagulation/flocculation, having been found to be cost effective, easy to operate alternatives, was widely used for phosphorus treatment in industrial wastewater. At present, coagulants were widely used for phosphorus removal. They mainly include poly aluminum chloride (PAC), poly aluminum ferric chloride (PAFC), ferric chloride ($FeCl_3$), trihydrate ferric sulfate｛$Fe_2(SO_4)_3 \cdot 3H_2O$｝, aluminum sulfate｛$Al_2(SO_4)_3$｝[1]. Compared to other coagulants, poly aluminum chloride (PAC) is considered to be the better coagulant because of its shorter reaction time and lower price. PAC is a partially hydrolyzed aluminum chloride solution that has recently been found to provide stronger and faster settling flocs [2].

The methods used for the removal of heavy metals include chemical precipitation, membrane separation, ion exchange and adsorption [3]. Chemical precipitation has been widely used for removing heavy metals.

Magnetite (Fe_3O_4), a kind of mineral material, is considered as a magnetic seeding which is effectively combined with flocs to further remove pollutions by the mean of magnetic separation. Magnetic seeding combined with magnetic separation technology was used for pollutions removal from wastewater since the 1970s [4].

In this paper, coagulation/flocculation, chemical precipitation and magnetic separation were applied for phosphorus and nickel removals from automobile wastewater. The optimum coagulant dosages (PAC), the variation of initial pH and effects of combination of coagulation/flocculation and magnetite on the removals of TP and Ni were investigated.

MATERIALS AND METHODS

A. Materials

The PAC used in the experiment was obtained from huakang water treatment material co., Ltd, Henan, China. The pH of PAC was 3.73 at solid to solution ration of 100:1(g/L). The sample had the mainly chemical composition by weight with Al_2O_3 (28.0 %-30.0 %), basicity (60.0 %-85.0 %), and water-insoluble matters (1.0 %).

Magnet used in the experiment was made of NdFeB (a strong magnetic material), which has the intensity of 0.7 T magnetic field. Its length is 50mm, width 50mm and thickness 10mm.

Samples of the wastewater were derived from collecting pond of automobile factory that produced the components of automobile and motorcycle (e.g. engines, platforms and etc.). Generated wastewater is mainly composed of electrophoretic wastewater, cleaning wastewater, phosphating wastewater and degreasing wastewater. The average volumes of wastewater generated daily from the factory were 270 m^3. The composition of the wastewater is given in Table 1.

TABLE I. THE ANALYSIS OF WASTEWATER QUALITY

Index	COD (mg/L)	BOD_5 (mg/L)	SS (mg/L)	TP (mg/L)	Ni (mg/L)	pH
Mean	80.20	10.10	20.20	20.00	1.16	6.03

B. Experimental methods

The pH values of 0.6 L wastewater samples were adjusted to 6.03, 8.00, 10.03, respectively, by using 1.25 mol/L sodium hydroxide, then 1.2 g magnetite was added to each of the beakers. A magnet block was placed at the bottom of each of the beakers. After stirring for 2 min at 200 rpm and clarifying, the supernatant was withdrawn to determine Ni [5], the others were used for coagulation experiment.

Coagulation experiments were done as follows: (taking an example of pH 6.03, the rest was done in the same treatment)

The 0.5, 0.8, 1.0, 1.5, 2.0 ml PAC (100 g/L) and 0.2g Fe_3O_4 were added to 100 ml supernatant samples, respectively. Similarly, a magnet block was placed at the bottom of each of the beakers. After rapidly mixing for 2 min at 200 rpm, 0.2 ml PAM (2g/L) was added. After slowly mixing for 2 min, the liquid was clarified for 30 min, and then the supernatant was withdrawn from a point located about 2 cm below the top of the liquid level of the beaker to determine the TP, pH by using standard methods [6]. All chemicals used for the analytical determinations were of analytical reagents and guarantee reagents.

The orthogonal test was similar to above.

RESULTS AND DISCUSSION

A. Effect of coagulant dosages on TP removal efficiency

The effect of different PAC dosages on the removal of TP is shown in Fig.1. When the initial pH of wastewater was adjusted to 6.03 and 8.00, PAC dosage of 0.5g/L made TP concentrations deceased to 3.34 mg/L and 3.10 mg/L, respectively, respectively. Afterward, when PAC dosages were 0.8 g/L, 1.0 g/L and 1.5 g/L, TP concentrations had little variation, all reaching below 0.7 mg/L. However, with PAC dosage of 2.0 g/L, TP concentrations greatly increased to 19.8 mg/L and 8.19 mg/L, respectively.

When the initial pH of wastewater was adjusted to 10.03, TP removal efficiency all reached above 97.6 % under the condition that PAC dosages were between 0.5 g/L and 2.0 g/L, meeting urban wastewater discharge standard (GB18918-2002, ≤0.5 mg/L) .

When PAC dosage was 0.5 g/L, initial pH of wastewater was adjusted to 6.03, 8.00 and 10.03, respectively, TP removal efficiencies were 83.3 %, 84.5 % and 96.6 %.

From the above results, it was shown that PAC dosages and initial pH had great effects on phosphorus removal. pH of inside-liquid affects phosphate existence form. The variation trend of phosphate is $H_3PO_4 \rightarrow H_2PO_4^- \rightarrow HPO_4^{2-} \rightarrow PO_4^{3-}$ with the rise of pH [6]. In the experiment, when initial pH was adjusted to 10.03, TP removal efficiency was higher with the less PAC dosage.

It indicated that PO_4^{3-} may be the dominant form when pH was 10.03 and PAC dosage was 0.5 g/L. A great deal of PO_4^{3-} was effectively combined with aluminum to form the insoluble

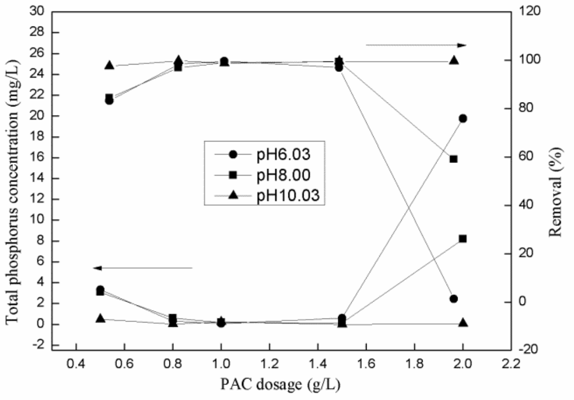

Fig. 1. The effect of coagulant dosages on TP removal efficiency under the condition of the different initial pH

sediments for removing phosphate pollutions. Considering phosphorus removal effect and cost, it is suggested that the optimum coagulant dosage for PAC was 0.5 g/L when the initial pH was 10.03.

B. The variation of pH after reaction

From figure 2 it can be seen that final liquor pH gradually reduced with the increase of PAC dosages after reaction. When the initial pH was 6.03, finial liquor pH decreased from 6.47 to 4.61.When the initial pH was 10.03, finial liquor pH decreased from 8.63 to 6.9. When the initial pH was 8.00, finial liquor pH decreased from 7.39 to 5.72. From these results, it can be seen that if pH is 4.0-5.0, a large number of hydrogen ions compete with PAC hydrolysis polymers, resulting in poor removals of the phosphorus. However, it is also reported by some literatures that high pH value may produce negatively charged organic contaminants on which adsorption will be electro-statically hindered [7]. In the experiment, it is recommended that the optimum pH value is between 6.0 and 8.7, when using PAC in coagulation process.

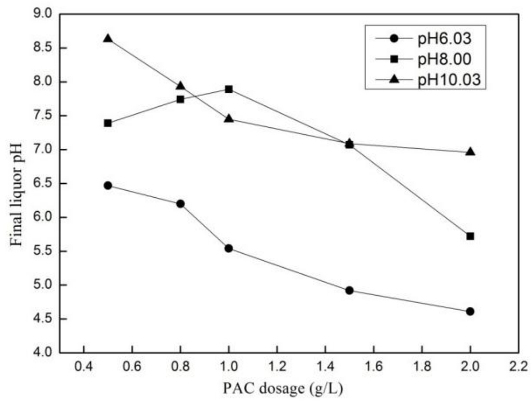

Fig.2.The variation of pH after reaction

C. Factorial design evaluation

To evaluate the effect of initial pH, PAC dosages and magnetite dosages on total phosphorus removal efficiency, an orthogonal experimental was designed. The removal efficiency of TP was considered as a response variable. Initial pH, PAC dosages and magnetite dosages were regarded as three factors. They were expressed by X_1, X_2, X_3, respectively. Each factor was arranged two levels (high level, low level).The Table 2 showed the values of each factor in the experiment. TP was analyzed for each of all experiments as shown in Table 3. A fist–order model was used for describing the experimental result:

$$Y=a+bX_1+cX_2+dX_3. \quad (1)$$

Where Y=removal efficiency of total phosphorus, %, a=intercept, b, c, d = coefficients, X_1=initial pH, X_2=PAC dosages, g/L, X_3=magnetite dosages, g/L. The multiple regression analysis, F-test and T-test were performed using SAS 8.5.

According to the regression Eq.1, the result was shown as follows:

$$Y=50.06+7.56X_1-21.76X_2-6.97X_3. \quad (R^2=0.84, P<0.05) \quad (2)$$

Detail regression results were shown in Table 4.

In the orthogonal experiment, the correlation coefficient is much larger, the effect of the factor is more important, correspondingly. b_2 is the biggest negative correlation coefficient in Eq.2, which showed that the effect of PAC dosages was the most important factor. Increasing the PAC dosages can reduce phosphorus removal efficiency. b_1 is the positive correlation coefficient, revealing the higher TP removal efficiency with the rise of pH. However, Magnetite dosage had smaller effect, which is not similar to Li and Shen's work [8-9]. The reason may be two aspects. Firstly, magnetite used in the experiment is analytical grade Fe_3O_4 which may be different to magnetite nanoparticles of Shen's work [9]. Magnetite nanoparticles can provide more surface area for active absorption site, which is very important in pollutions removal process. Secondly, magnet, being the intensity of 0.7 T the magnetic field, was used in the experiment for magnetic separation which is different to the superconducting magnetic separation of Li's work [8]. Superconducting magnet can provide the intensity of 3.6 T magnetic field. The strong magnetic field may strengthen the combination between the coagulant and magnetite, and finally increase the pollutions removal. However, the lower magnetic field may cause the poor combination between the coagulant and magnetite. Based on the above analysis, magnetite has not played an important role in phosphorus removal in the experiment. Consequently, superconducting magnetic separation and magnetite nanoparticles should be paid more attention to in the future work.

TABLE II. A 2^3 FULL FACTORIAL DESIGN

Factors	Low level	High level
Initial pH (X_1)	6.00	10.03
PAC dosage, g/L (X_2)	0.5	2.0
Magnetite dosage, g/L (X_3)	0.6	2.0

TABLE III. EXPERIMENTAL DESIGN AND REMOVAL EFFICIENCY OF TOTAL PHOSPHORUS

Number	X_1	X_2	X_3	Y
1	6.00	0.5	0.6	81.95
2	10.03	0.5	0.6	98.70
3	6.00	2.0	0.6	39.10
4	10.03	2.0	0.6	97.50
5	6.00	0.5	2.0	83.45
6	10.03	0.5	2.0	98.90
7	6.00	2.0	2.0	32.25
8	10.03	2.0	2.0	63.60

TABLE IV. REGRESSION ANALYSIS FOR TP REMOVAL EFFICIENCY

Source	Df	Sum of square	Mean square	F value	Pr＞F
Model	3	4180.00	1393.33	6.78	0.0478
Error	4	822.60	205.65		
Corrected total	7	5002.60			

D. The effect of removal efficiency of Ni with the variation of pH

The effect of Ni removal efficiency with the pH variation was shown in Fig.3. It was seen that Ni removal efficiency increased from 11.8 % to 98.0 % with the rise of pH. When the pH was adjusted to 10.03, Ni removal efficiency reached 98.0 %, meeting urban wastewater discharge standard (GB18918-200, TP≤ 0.5 mg/L). It was revealed that generated hydroxyl ions in alkaline condition were combined with nickel ions to form precipitates for removing nickel. When the pH of the wastewater was adjusted to 10.03, PAC dosage of 0.5 g/L made TP concentrations decreased to below 0.5 mg/L as shown in Fig.1. Therefore, coagulation/flocculation in relatively high pH (10.03) could effectively remove phosphorus and nickel synchronously.

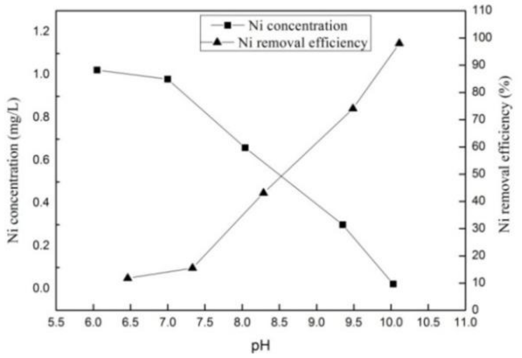

Fig.3.The removal efficiency of Ni with the variation of pH

E. The effect of the settling velocity

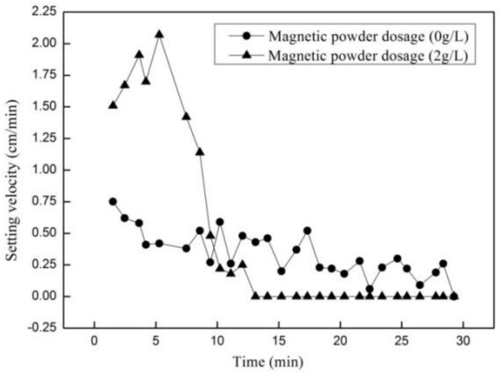

Fig.4.The setting velocity of sludge with the time

The variation of sludge setting velocity with the time was shown in Fig.4. It was shown that sludge settling velocity sharply reduced and basically tended to zero after 17 min (2 g/L of magnetite dosage). However, sludge settling velocity gradually reduced and basically tended to zero after 29 min (0 g/L of magnetite dosage). It was revealed that magnetite powder could accelerate sludge settlement and shorten settlement time. Combining use of coagulant, PAM and magnetite powder resulted in production of relatively low sludge volume. Because of the greater density of magnetite, flock size combined with magnetite powder became more compact, resulting in the quickly settling velocity.

Moreover, when magnet was placed under the beaker, it is found that sludge was fast settled in a few seconds. The reason may be that the flock size combined with magnetite was magnetized by the external magnetic field. The magnetic particles were captured by the external magnetic force. The magnetic force combined gravitation can accelerate the flocs precipitation process. Therefore, sludge was fast settled in a few seconds. Similar report has been presented by Okada et al. [10]. From the view of solid-liquid separation, magnetic separation technology may replace the traditional coagulation and co-precipitation.

CONCLUSIONS

Considering phosphorus removal effect and cost, it is suggested that the optimum dosage for PAC was 0.5g/L when the initial pH was 10.03.

The dosage of PAC was the main factor in phosphorus removal process by factorial design evaluation when using the magnetic field 0.7 T.

When the pH was adjusted to 10.03, the removal efficiency of Ni reached 98.0 %, meeting urban wastewater discharge standard (GB18918-2002, TP≤0.5 mg/L). Therefore, adjusting initial pH combined with coagulation/flocculation could achieve the purpose of removing total phosphorus and nickel.

Magnetite powder accelerated sludge settling velocity. The coagulation/flocculation combined with magnetite powder could enhance the solid-liquid separation.

ACKNOWLEDGMENT

We are grateful for financial support from science and technology research program of Chongqing, China (under grant no.cstc2011ggC20016), a part of which is presented in this study.

REFERENCES

[1] W. S. Guo, H.H. Ngo, S. Vigneswaran, F. Dharmawan, T. T. Nguyen and R. Aryal, “Effect of different flocculants on short-term performance of submerged membrane bioreactor,” Separation and Purification Technology,” Amsterdam, Netherlands, vol.70, pp. 274–279, January 2010.

[2] L. M. Malecki-Brown and J. R. While, “Effect of aluminum containing amendments on phosphorous sequestration of wastewater treatment wetland soil,” Soil Science Society of America Journal. Madison, United States, vol. 73, pp. 852–861, May 2009.

[3] A. Stafiej and K. Pyrzynska, “Adsorption of heavy metal ions with carbon nanotubes,” Separation and Purification Technology,” Amsterdam, Netherlands, vol.58, pp. 49–52, December 2009.

[4] T. Ohara, H. Kumakura and H. Wada, “Magnetic separation using superconducting magnets,” Physica C-superconductivity and its Application. Amsterdam, Netherlands, vol. 357–360, pp. 1272–1280, August 2001.

[5] Chinese Environment Protection Administration (EPA). Water and wastewater monitoring methods. 4th, ed., Chinese Environmental Science Publishing House, 2002, pp.243-238,373.

[6] Y. Zhao, J. Wang, Q. Wang, Z.K. Luan and Z. Liang, “Phosphorus removal from starch wastewater using red mud,” China water &wastewater. Tianjin, Chinese, vol. 25, pp. 20–22, 27, August 2009.

[7] N. Z. Al-Mutairi, M. F. Hamoda and I. Al-Ghusain, “Coagulant selection and sludge conditioning in a slaughterhouse wastewater treatment plant,” Bioresource Technology. Kidlington， England, vol. 95, pp.115–119, November 2004.

[8] Y. R. Li, J. Wang, Y. Zhao and Z. K. Luan, “Research on magnetic seeding flocculation for arsenic removal by superconducting magnetic separation,” Separation and Purification Technology. Amsterdam, Netherlands, vol.73, pp.264–270, June 2010.

[9] Y. F. Shen, J. Tang, Z. H. Nie, Y. D. Wang, Y. Ren and L. Zuo, “Preparation and application of magnetite Fe_3O_4 nanoparticles for wastewater purification,” Separation and Purification Technology. Amsterdam, Netherlands, vol.68, pp.312–319, August 2009.

[10] H. Okada, Y. Kudo, H. Nakazawa, A. Chinba, K. Mitsuhashi, T. Ohara and H. Wada, “Removal system of arsenic from geothermal water by high gradient magnetic separation-HGMS reciprocal filter,” IEEE Transactions on Applied superconductivity. United States, vol. 14, pp. 1576–1579, June 2004 [18th International Conference on Magnet Technology. Applied superconductivity. Piscataway, United States].