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Phosphorus removal and recovery from polytetrahydrofuran wastewater by solventing-out crystallization

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ABSTRACT

Phosphorus recovery through crystallization has been widely recommended for wastewater treatment. Polytetrahydrofuran wastewater was subjected to lab-based solventing-out crystallization to investigate methanol and ethanol as phosphorus recovery extractants. Extractant species, dosage, reaction time, and pH were measured to determine the optimum extractant and parameters for phosphorus recovery. The results show that the phosphorus recovery rates from raw wastewater were 88 and 93% with methanol and ethanol as extractants, respectively, at 30 mg/L extractant dosage, 2 h reaction time, and pH 6.7. Phosphorus recovery rate reached 99% under the following optimum reaction conditions: pH level, 9.0; optimum ethanol dosage, 20 mg/L; and reaction time, 5 min. The crystals were identified as Na_2HPO_4 through X-ray diffraction, and 97% Na_2HPO_4 mass fraction was detected through ion chromatography. Most crystals had no crystal water. Two ethanol recovery cycles were determined via the ethanol recovery experiment on the supernatant after crystallization.

Keywords: Reaction time; Ethanol; Phosphorus recovery; Supersaturation coefficient

1. Introduction

Polytetrahydrofuran (PolyTHF) is a colorless, transparent, and viscous liquid at near room temperature. This compound is soluble in most organic solvents, but insoluble in water. It can be potentially applied for spandex and high-grade polyurethane elastomeric production [1] in textiles, pipes, chemicals, synthetic leather, medical devices, shipbuilding, construction, and military. However, PolyTHF wastewater treatment has always been a problem, which limits the development of PolyTHF for industrial application [2]. Wastewater treatment has been addressed in China and other countries through combustion [3,4], but this process is expensive, causes pollution, and burns valuable phosphorus resources in the wastewater [5]. Phosphorus can be recovered if it is recycled during wastewater treatment, thereby reducing the cost of PolyTHF wastewater treatment. Phosphorus resource availability is considerably limited for human utilization. Thus,

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phosphorus recovery from wastewater has recently attracted more attention from the water industry, phosphorus industry, and policy-makers [6–8].

Phosphorus recovery by crystallization has been widely recommended for wastewater treatment [9–11]. Crystallization methods in previous studies involved the addition of magnesium or calcium salts and increase in pH level to form insoluble magnesium ammonium phosphate (MAP) [12–14] and 2-hydroxylapatite (HAP) [15–17] crystals. Phosphorus was recovered and reused as agricultural fertilizer [18,19]. However, a study has shown that MAP and HAP crystallization methods in PolyTHF wastewater treatment result in very low phosphorus recovery efficiencies. Therefore, a new crystallization method for removing phosphorus from PolyTHF wastewater should be developed.

PolyTHF wastewater from novel furfural production at a Chinese factory was selected. The main constituents of the wastewater were 15,000–18,000 mg/L phosphorus, 1.6 mg/L furfural, 1.2 mg/L furan, 1.8 mg/L tetrahydrofuran, and 5,500–8,000 mg/L chemical oxygen demand (COD). According to the crystallization principles and solvent characteristics, along with preliminary investigations by our group, methanol and ethanol have been found that they can be the extractant for crystallizing phosphate and realizing recycling. Organic solventing-out crystallization is a facile method with high phosphorus recovery efficiency and low running cost. This process has not been previously used for industrial wastewater treatment. In this paper, the extractant species, dosage, reaction time, and pH have been investigated to determine the optimum extractant and recovery parameters for the highest phosphorus recovery efficiency.

2. Materials and methods

2.1. Experiments

PolyTHF wastewater was filtered using a filter paper with 120 μm pore size, and phosphorus content was determined. PolyTHF wastewater was used in batch experiments to study the phosphorus recovery efficiency of the crystallization using methanol and ethanol. The pH value of the raw water was 6.7, and 20 mL wastewater sample was used. For every tested parameter, i.e. solvent dosage, reaction time, and pH level, each sample was stirred with a magnetic stirrer for 30 s at 200 rpm under room temperature (18–20°C).

The other crystallization conditions of the various parameters were as follows:

Reaction time: At pH 6.7, 30 mL of methanol and 30 mL of ethanol were added to 20 mL wastewater sample, respectively, which were reacted for 1–5 h.

Organic solvent dosage: Different dosages of equal volumes of methanol and ethanol (5, 10, 15, 20, 25, 30, and 40 mL) were added to the samples under pH 6.7, and the solutions were reacted for 2 h.

pH level: pH level (5–10) was adjusted by adding Noah (0.1 mol/L) or HCl (0.1 mol/L). Then, 30 mL methanol or 30 mL of ethanol was added to 20 mL wastewater samples, and the solutions were reacted for 2 h.

Wastewater phosphorus content was measured after crystallization, and phosphorus recovery was determined using the ratio of the crystallized phosphorus and phosphorus in raw water. The formed crystals were naturally dried at room temperature [20].

In the analysis of the phosphorus crystallization recovery, the supersaturation coefficient S represents the degree of PolyTHF wastewater phosphorus supersaturation.

$$S = \frac{C}{C_0} \tag{1}$$

where C is the mass fraction of the solute in a solvent at a certain temperature, and C_0 is the saturation mass fraction of the solute in a solvent at the same temperature.

2.2. Reagents and equipment

Phosphorus content was determined through potassium antimony tartrate and ammonium molybdate methods under 450 nm wavelength using a spectrophotometer (722 model, Shanghai Spectrum Instruments Co. Ltd, Shanghai, China). Crystal composition was analyzed through X-ray diffraction (XRD; Shimadzu XRD-6000X, Japan). Crystal water was confirmed in the crystals through thermogravimetric analysis (TGA; Pyris Diamond TG/DTA, PekinElmer, USA) by heating the sample from 30 to 800°C at 10°C/min. The content of HPO_4^{2-} was analyzed by ion chromatography (IC) (881, Metrohm, Switzerland) equipped with a METROSEP A SUPP 4 anion column and conductivity detector. Here, 1.8 mm of sodium carbonate and 0.17 mm of sodium bicarbonate were used as mobile phases, and the detection limit was below 0.05 mg/L. All the reagents in the experiments were analytical reagent grade. The ethanol recovery used a reduced pressure distillation device (Beijing Aerospace Century star Technology Co. Ltd, China). The refractive index of ethanol was measured by Abbe refractometer (WAY-2 W, Precision Instrument Co. Ltd, Shanghai Branch, China).

3. Results and discussion

3.1. Influence of crystallization time

The effects of crystallization time on organic solvent crystallization are shown in Fig. 1. Phosphorus recovery efficiency remarkably increased when the reaction time was increased from 1 to 2 h, whereas the recovery efficiency did not increase further when the reaction time was prolonged. The supersaturation coefficient *S* of phosphorus has been reduced with time, changing the solution from an oversaturated state to equilibrium. However, when the reaction time was extended to 2 h, the solution may have reached a saturation state. Additionally, the results may have been caused by the two-step crystallization process, i.e. the birth of microscopic crystal particles as the core of the crystal, which are called the crystallization core, and gradual growth of the crystal nucleus into macroscopic crystals. In this study, the crystal nucleus rapidly grew such that only 2 h was consumed for the growth of a macroscopic crystal. The phosphorus recovery precipitates no longer grew afterward. Thus, the optimum reaction time is 2 h.

3.2. Influence of organic solvent dosage

The phosphorus recovery efficiency continuously increased with increasing organic solvent dosage, and ethanol provided higher extracting efficiency (Fig. 2). Phosphorus recovery efficiencies significantly increased at low dosage of 5–30 mL, whereas it exhibited a slower increase at higher dosage of 30–40 mL. The phosphorus recovery efficiencies reached 88 and 93% for methanol and ethanol, respectively. With the added organic solvent, the supersaturation coefficient *S* of phosphorus would be lowered and phosphorus would be precipitated. Increasing the amount of organic solvent increased crystallization nuclei, and more nuclei grew into crystals. Phosphorus recovery efficiency almost did not increase further when solvent dosage was further increased from 30 to 40 mL. Thus, 30 mL the organic solvent is appropriate, and the optimum methanol/ethanol-to-wastewater sample volume ratio is 3:2.

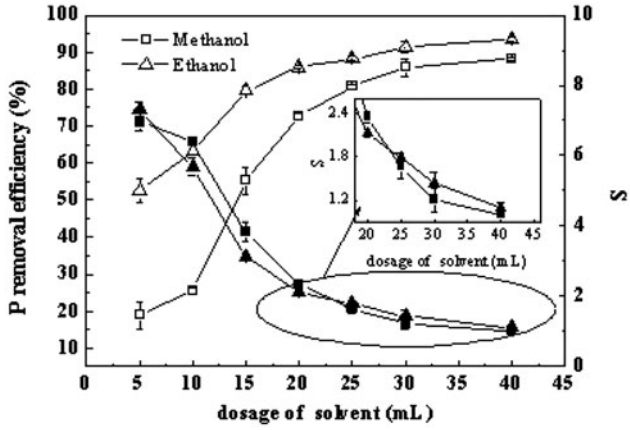

Fig. 2. Effects of dosage of organic solvent on the recovery efficiencies of phosphate and supersaturation coefficients.

3.3. Influence of the pH level

The pH level of a solution is important in the crystallization reaction of organic solvent. Fig. 3 shows that phosphorus recovery efficiencies more

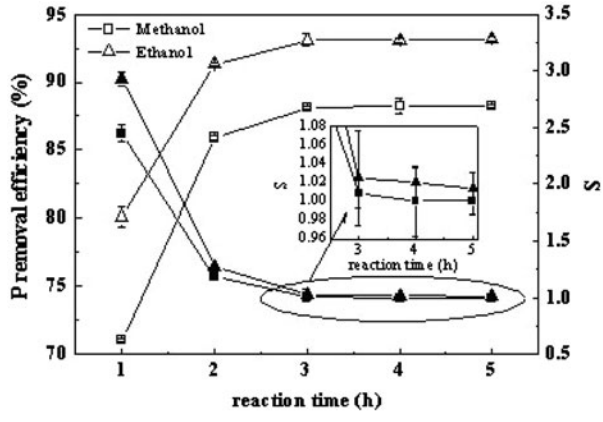

Fig. 1. Effects of reaction time on the recovery efficiencies of phosphate and supersaturation coefficients.

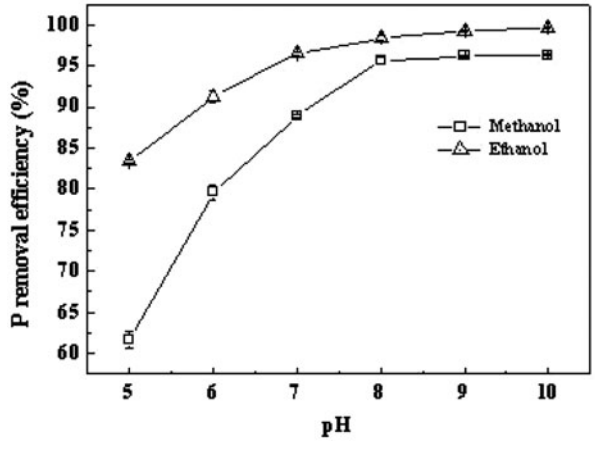

Fig. 3. Effect of pH on the recovery efficiencies of phosphate.

significantly increased at a relatively low pH range of 5.0–9.0, and the phosphorus recovery efficiencies did not considerably increase any further at a higher pH range of 9.0–10.0 because of the following reactions:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad (2)$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \quad (3)$$

The raw wastewater had a pH level of 6.7, in which the phosphate mainly exists as $H_2PO_4^-$. The balance of (2) and (3) shifted to the left when the pH of the wastewater was reduced, in which the main form of phosphate was H_3PO_4, which does not help precipitate crystals. The balance of (2) and (3) shifted to the right when the pH was increased to be weakly alkaline, in which phosphate mainly existed as HPO_4^{2-}. Therefore, the most appropriate pH is 9.0.

3.4. Selection of solvents

The experimental studies show that the phosphorus recovery from the wastewater sample using ethanol is more effective than that using methanol. The theory of similarity and intermiscibility (similar solution dissolved in similar solution) states that crystallizing a salt with strong polarity is much easier to precipitate in ethanol, which has weak polarity. Methanol is also more volatile and toxic, which could be inconvenient in experiments. Hence, ethanol is the optimum organic solvent.

3.5. Determination of optimal parameters

The experiments show that crystal precipitation in wastewater is much faster at pH 9.0 than that at the original pH level of 6.7. This phenomenon suggests that the optimum organic solvent dosage and reaction time change with the pH level. Therefore, a series of orthogonal experiments have been performed under the same condition. Fig. 4 shows that the phosphorus recovery efficiency increased with added ethanol at any reaction time. However, the phosphorus recovery efficiency reached 99% and no longer increased with more ethanol at any reaction time at 20 mL dosage. Fig. 4 also shows that phosphorus crystallization in PolyTHF wastewater was completed under 20 mL solvent and 5 min crystallization time. Therefore, the optimum parameters for PolyTHF wastewater crystallization are 1:1 ethanol-to-wastewater ratio, 5 min precipitation time, and pH 9.0.

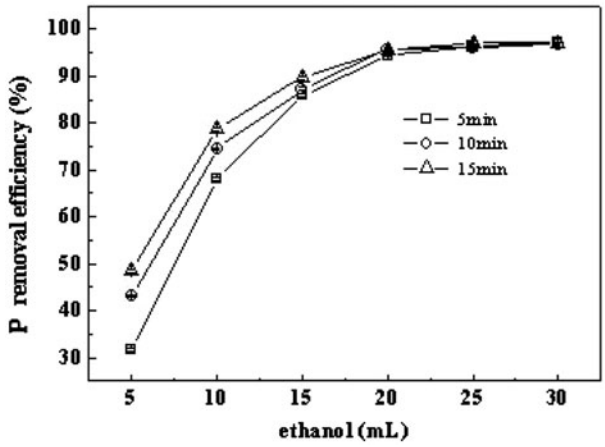

Fig. 4. Effect of pH on the recovery efficiencies of phosphate at different reaction time.

3.6. Analysis of crystal composition

Fig. 5 shows the XRD patterns of the precipitates at the optimum condition of pH 9.0. Line 1 represents the standard XRD pattern of Na_2HPO_4, and line 2 represents the XRD pattern of the phosphate recycled from the wastewater. The characteristic diffraction peaks of the two patterns almost totally coincided, so the precipitate is considered to be mostly Na_2HPO_4. Phosphorus resources are considerably limited for human utilization, for example, as fertilizer.

The presence of crystal water in the Na_2HPO_4 crystals was calculated through TGA, and two significant weight loss regions were observed (Fig. 6). Only 1.5% weight was lost below 60°C in the first region, which shows trace amounts of crystal water in the Na_2HPO_4,

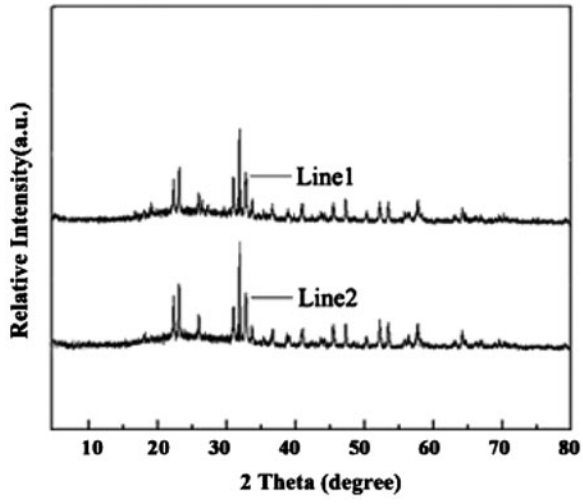

Fig. 5. XRD analysis of the crystals obtained.

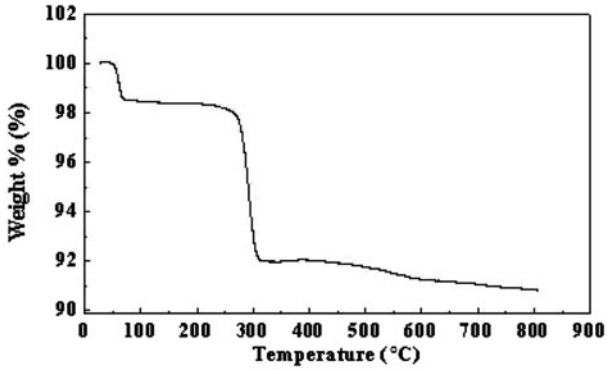

Fig. 6. TGA analysis of the crystals obtained.

but crystal water was not observed in most of the Na_2HPO_4 crystals. The second stage between 240 and 310˚C showed 6.5% weight loss, which could be attributed to further water loss when one mole of $Na_4P_2O_7$ was produced by combining two moles of Na_2HPO_4. The phenomenon is consistent with the properties of Na_2HPO_4. The mass fraction of Na_2HPO_4 in the crystal was determined to be 97% through IC.

3.7. Ethanol recovery cycle

After the crystallization of 100 mL of ethanol mixed with 100 mL of PolyTHF wastewater, the phosphorus recovery was 99%. At 65˚C and 54.45 kPa, the crystallized supernatant was distilled from a reduced pressure distillation device, and the ethanol content in the distillate was up to 78% by Abbe refractometer. After the crystallization of 100 mL of 78% ethanol mixed with an equal volume of PolyTHF wastewater, the phosphorus recovery was measured. After the reduced pressure distillation of the supernatant from a pressure relief device at the same condition, the ethanol content was then measured. This cycle was repeated. The phosphorus recovery and the recovered ethanol content are shown in Fig. 7. The phosphorus recovery and the recovered ethanol content decreased with increasing frequency of ethanol recovery cycle. When the recovered ethanol entered the third cycle, the phosphorus recovery only became 78%, which did not meet the practical phosphorus recovery requirements in practice. Thus, two ethanol recovery cycles were determined, and at this time phosphorus recovery might reach 91%.

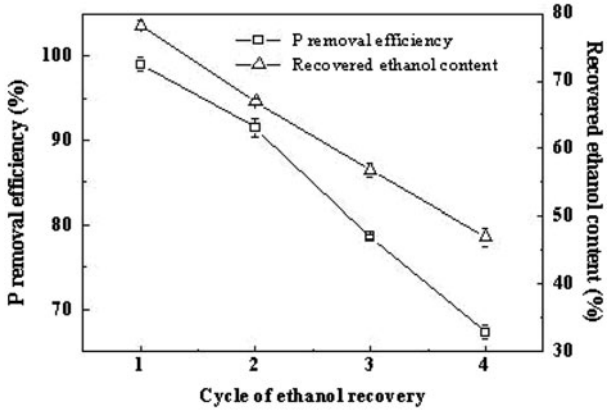

Fig. 7. Effects of ethanol recovery cycle on recovery efficiencies of phosphate and the recovered ethanol content.

4. Conclusions

A simple, low pollution method with high phosphorus recovery rate was achieved through the solventing-out crystallization method.

(1) Efficiency of phosphorus recovery from PolyTHF wastewater sample was determined. Ethanol showed higher phosphorus recovery efficiency than methanol under the same temperature and stirring conditions. Thus, the ethanol is the optimal extractant.
(2) At pH 6.7, 3:2 organic solvent-to-wastewater volume ratio, 200 rpm stirring speed, and 2 h reaction time, phosphorus recovery efficiencies were more than 88 and 93% with methanol and ethanol as extractants, respectively.
(3) Phosphorus recovery efficiency reached 99% at pH 9.0, 1:1 ethanol-to-wastewater volume ratio, 200 rpm stirring speed, and 5 min reaction time.
(4) XRD patterns showed that the crystals were primarily in the Na_2HPO_4 form. TGA analysis showed trace amounts of crystal water in Na_2HPO_4, but crystal water was not found in most of the Na_2HPO_4 crystals. IC results showed that the mass fraction of Na_2HPO_4 in the crystal was 97%.
(5) The result of the ethanol recovery experiment on the supernatant after crystallization shows that phosphorus recovery might reach 91% after two ethanol recovery cycles.

References

[1] G.X. Bai, Advances in production technology for polytetrahydrofuran and consideration about R&D in China, Mod. Chem. Ind. 25(1) (2005) 13–17+19.
[2] J. Liu, W.H. Zhang, Z.F. Cui, D.J. Bian, Experiment research on extraction method by chloroform treatment PolyTHF wastewater, Environ. Sci. Technol. 33 (6E) (2010) 101–105 (in Chinese).

[3] Y. Zuo, J. Liu, D.J. Bian, Z.F. Cui, W.H. Zhang, Study on treatment of wastewater from the production of Poly-THF with Fe–C micro-electrolysis method, in: Environ. Sci. Technol. 33(12F) (2010) 261–264 (in Chinese).
[4] Y.Zuo, S.S. Ai, X. Tian, L.G. Wang, X. Nie, Study on treatment of wastewater from the production of ploy-THF with Fenton method, in: International Conference on Electric Information and Control Engineering Institute of Electrical and Electronics Engineers, Wuhan, China (2011), 6191–6194.
[5] D.J. Bian, Q.K. Ren, S.S. Ai, Y. Zuo, J. Liu, Study on treatment of wastewater from the production of ploy-THF with Adsorption method, in: International Conference on Electric Information and Control Engineering, Institute of Electrical and Electronics Engineers, Wuhan, China (2011), 6191–6194.
[6] J. Driver, D. Lijmbach, I. Steen, Why Recover Phosphorus for Recycling, and How? Environ. Technol. 20(7) (1999) 651–662.
[7] D. Donnert, M. Salecker, Elimination of phosphorus from municipal and industrial wastewater, Water Sci. Technol. 40 (1999) 195–202.
[8] A.K. Søvik, B. Kløve, Phosphorus retention processes in shell sand filter systems treating municipal wastewater, Ecol. Eng. 25(2) (2005) 168–182.
[9] E.H. Kim, D.W. Lee, H.K. Hwang, S. Yim, Recovery of phosphates from wastewater using converter slag: Kinetics analysis of a completely mixed phosphorus crystallization process, Chemosphere 63 (2006) 192–201.
[10] P. Battistoni, A. De Angelis, M. Prisciandaro, R. Boccadoro, D. Bolzonella, P removal from anaerobic supernatants by struvite crystallization: Long term validation and process modeling, Water Res. 36(8) (2002) 1927–1938.
[11] S.A. Parsons, J.D. Doyle, Struvite scale formation and control, Water Sci. Technol. 49(2) (2004) 177–182.
[12] R.D. Schuiling, A. Andrade, Recovery of struvite from calfmanure, Environ. Technol. 20(7) (1999) 765–768.
[13] L. Pastor, D. Mangin, R. Barat, A pilot-scale study of struvite precipitation in a stirred tank reactor: Conditions influencing the process, Bioresource Technol. 99 (14) (2008) 285–6291.
[14] L. Shu, P. Schneider, V. Jegatheesan, J. Johnson, An economic evaluation of phosphorus recovery as struvite from digester supernatant, Bioresource Technol. 97(17) (2006) 2211–2216.
[15] H. Jang, S.H. Kang, Phosphorus removal using cow bone in hydroxyapatite crystallization, Water Res. 36 (5) (2002) 1324–1330.
[16] Y. Song, P.G. Weidler, U. Berg, R. Nüesch, D. Donnert, Calcite-seeded crystallization of calcium phosphate for phosphorus recovery, Chemosphere 63(2) (2006) 236–243.
[17] J.A.M. Van Der Houwen, E. Valsami-Jones, The application of calcium phosphate precipitation chemistry to phosphorus recovery: The influence of organic ligands, Environ. Technol. 22 (2001) 1325–1335.
[18] L.E. de-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), Water Res. 38(19) (2004) 4222–4246.
[19] X.Z. Li, Q.L. Zhao, Recovery of ammonium-nitrogen from landfill leachate as a multi–nutrient fertilizer, Ecol. Eng. 20 (2003) 171–181.
[20] K.S. Le Correa, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Impact of calcium on struvite crystal size, shape and purity, Cryst. Growth 18 (2005) 1020–1024.