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Phosphorus Recovery by Liquid–Liquid Extraction

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Abstract: It is acknowledged that phosphorus removal is more crucial in comparison with nitrogen removal for preventing algae glooming and eutrophication. Chemical and biological methods are common methods for the P removal. Excessive sludge production and difficulties of recovering phosphorus are concerns in terms of sustainable waste management. A liquid-liquid extraction (LLE) process is thus considered for the study aiming at recovering phosphorus from wastewater in a sustainable way. The results revealed that the best extractant is a mixture of kerosene and benzyl-di-methyl-amine (BDMA) at a volume ratio of 2:1. Under the study conditions, one part of extractant can react with four parts of wastewater to transfer >97% of P to the organic phase. In addition, in the stripping step, a 1:1 ratio of extract to recycled acid can result in 96% recovered P, implying an overall 93% phosphorus recovery efficiency can be achieved by the LLE process. Most importantly, the extractant can be recycled and reused at least 5 times if the residual P concentration should be less than 4 mg/L vs. the original P concentration of 21 mg/L. A complexion between amine groups in BDMA and phosphates and the positive charge of the micelles surface when the extractant (composed of kerosene and BDMA) mixed with P containing wastewater would contribute to the P recovery and this is a novel approach to recover P from wastewater.

Keywords: Eutrophication control, liquid–liquid extraction, nutrient management, phosphorus recovery, wastewater treatment

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INTRODUCTION

The presence of excess phosphate in the domestic sewage and industrial effluents discharged to natural water has long been viewed as the cause of algae blooms and eutrophication. The average molar ratio of nitrogen, phosphorus, and carbon in algae protoplasm is approximately 15:1:105 (1) and if any of these components is less than this ratio, it will limit the algae growth. In general that a minimal amount of phosphorus can cause substantial algae growth and its removal is more crucial in comparison with nitrogen removal for preventing algae glooming and eutrophi cation.

The typical phosphate concentration in crude sewage ranges between 5 and 30 mg/L (2). European Union (EU) legislation makes phosphate removal from sewage compulsory. The EU Urban Waste Water Treatment Directive (3) introduced requirements for the control of phosphorus (P) and nitrogen (N) concentrations in the effluent, which was taken into force in England and Wales (4) and Scotland (5) in November 1994, whereby a significant reduction of P and N was required if the effluent is to be discharged in a given area that is sensitive to eutrophication. The total P concentration should not exceed 2 mg/L in the final effluent in an area with a population equivalent (p.e.) of between 10000 and 100000 and not exceed to 1 mg/L when the p.e. is greater than 100000.

Chemical and biological methods have been used for the P removal. It is a common treatment approach to use iron, aluminium, or calcium salts to precipitate P and form sludge which is then separated by sedimentation or filtration from wastewater (6). The crystallization process has also been tested to recover P (7), whereby crystallized hydroxyapathyte $Ca_5(OH)(PO_4)_3$ is obtained as the P-containing product. P removal by biological treatment processes has been attributed to both stoichiometric P consumption in the biomass growth and enhanced P storage in the biomass as polyphosphate. The prerequisite for biological P removal is the exposure of the micro-organisms to alter anaerobic and aerobic conditions so that their uptake of P is above normal metabolic requirements (8).

Liquid-liquid extraction (LLE) is a common separation process, whereby a small quantity of an organic extractant is dissolved in a diluent to form an organic phase. During extraction the desired solute in the aqueous phase (normal water) transfers into organic phase until the equilibrium of the solute in two immiscible phases to be achieved. The second half of the LLE operation is called stripping, which is to recover the desired solute from the organic phase into the aqueous phase (normal an acid phase), and the extractant could be recycled and reused.

The LLE method has been used in nuclear and ore processing and the chemical manufacturing and processing industries. Recovering metals

by the LLE from water treatment sludge and effluents has been reported (9,10). However, it has not been investigated to use LLE to recover or remove phosphorus (P) from wastewater. In this work, the bench-scale experiments were conducted to explore the possibilities of using LLE for the recover of phosphorus. Especially, this study was to select the optimum extractant and to determine distribution ratios of P between the extractant and the wastewater in order to establish the optimum operating conditions. The actual wastewater samples were also used in order to validate the efficiency of the LLE method.

EXPERIMENTAL METHODS

All chemical reagents used were analytical grade and supplied by the VWR, UK. Analysis of phosphate concentration was followed by an established method using the Ascorbic Acid Method (11). The model water was prepared using a phosphate standard solution (1000 mg/L). The phosphate concentration was made in the range of between 1 and 30 mg/L by mixing different volumes of standard solution with deionized water. The wastewater sample was collected from a full-scale wastewater treatment of Southern Water, UK. The sample was taken after the pre-sedimentation stage and its characteristics can be seen in Table 1. A batch study set up was used for both the extraction and the stripping experiments and the operation was performed at room temperature ($22 \pm 1^{\circ}C$). The extractant and the wastewater samples were mixed and thoroughly shaken using a shaker (KS125, Merck Ltd, England). The mixture was then transferred to separate funnels for the separation of the aqueous phase from the organic phase. The organic phase (extract) generated after the extraction step was subjected to the stripping process. A given amount of the extract was mixed with 125 mL of 6 M sulphuric acid and the mixture was thoroughly shaken for 4 hrs at a speed of 250 rpm. Subsequently, the mixture was transferred to funnels and allowed to be separated for 2 hours. The amount of phosphates recovered

Table 1. Wastewater quality parameters

Quality parameters	Values
pH	7.4
Suspended Solids (mg/L)	36.0
Total P (mg/L)	22.9
Soluble P (mg/L)	21.3
Turbidity (NTU)	52.2

was determined by examining the phosphate concentrations in the acid aqueous phase. The distribution ratios (D) of the P between the organic and aqueous phases were calculated by

$$D = [P]_{org}/[P]_{aq},$$

and this resulted in the extraction efficiency (E) to be calculated by

$$E = \{D/(D + 1)\} \times 100\%$$

RESULTS AND DISCUSSION

The extracting agent consisted of two parts, namely the extractant and the diluent. Many parameters that are important in ion-exchange resin production are also important in extractant and diluent selection, and this can be summarized as:

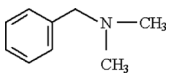
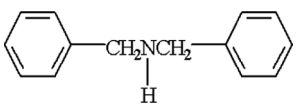
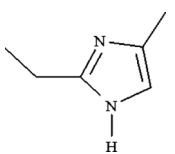
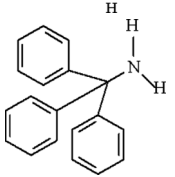
a. stability,
b. density difference to water,
c. low aqueous solubility, and
d. affinity to the phosphorus.

In this study, kerosene was selected as the solvent due to its stability, lower density, and insolubility in water. In addition to these, the use of kerosene was due to its availability, comparatively low cost, and relative safety in handling. The primary extractant is to be selected based on the reactivity and affinity to phosphorus and lowest solubility in water which is essential to ensure minimal loss of the extractant and to prevent the contamination of the treated effluent. Due to the nature of insoluble property in the aqueous phase, both kerosene and the selected extractant will not result in pollution in the treated effluent.

Preliminary studies were performed in selecting a suitable extractant. A range of cationic surfactants was considered based on their solubility in both water and kerosene and the comparative affinity to P and the cost. The study results can be seen in Table 2 and benzyl-dimethyl-amine (BDMA) was selected as the extractant for further studies in terms of the set standards.

The results demonstrated a high affinity of BDMA to phosphates; this could be attributed to the complexion between amines and phosphates. The extractant composed of kerosene and BDMA can form micelles after mixing with wastewater, which possess a positive charge

Table 2. Properties of studied extractants

Extractant	Structure	Characteristics	Comments
Benzyl-dimethyl-amine (BDMA)		Benzyl attached to a dimethylamine, which undergoes quaternization.	Preliminary tests showed that it was soluble in kerosene but insoluble in water. Relative high affinity to P and low cost.
Di-methylbenzyl-amine		In the family of aromatic amines	Similar to benzyl-dimethylamine in terms of solubility in water and kerosene. Low affinity to P and high cost.
2-Ethyl-4-methyl-imidazole		A heterocyclic compound of five di-unsaturated ring structure. An imidazole ring belongs to amino acid groups.	High solubility in water then ruled out as a potential candidate for the experiment.
Triphenylmethyl-amine		In the family of aromatic amines	Similar to benzyldimethylamine and dimethylbenzyl-amine in terms of solubility in water and kerosene. Low affinity to P.

on their surface. Phosphate can be bound on these micelles by electrostatic interaction, enabling the micelle-pollutants complex to be removed effectively from the wastewater effluent.

Preliminary equilibrium studies revealed that in the extraction step, the optimum mixing and separation time was 6 h and 2 h, respectively, while in the stripping step, the optimum mixing and separation time was 4 h and 2 h, respectively.

Figure 1 shows the effects of the ratios of organic to aqueous phases and kerosene to BDMA on the distribution ratio, D, and on the extraction efficiency, E. For a range of starting P concentrations (0–30 mg/L) and other operating conditions, the ratios of 1:4 as organic to aqueous phases and 2:1 of kerosene to surfactant (BDMA) gave the optimum D and E values, i.e., the optimum P extraction efficiency.

For the mixing and separation conditions stated previously, sulphuric acid and hydrochloric acid with various concentrations were studied for their stripping efficiency in respect to the ratio of organic to acid phase. Figure 2 demonstrates that an increase in stripping efficiency with a low ratio of organic to acid phase (i.e., increasing in the acid volume) for each acid and concentration. The greater the ratio of the organic to the acid phase, the less the amount of acid required and therefore, the

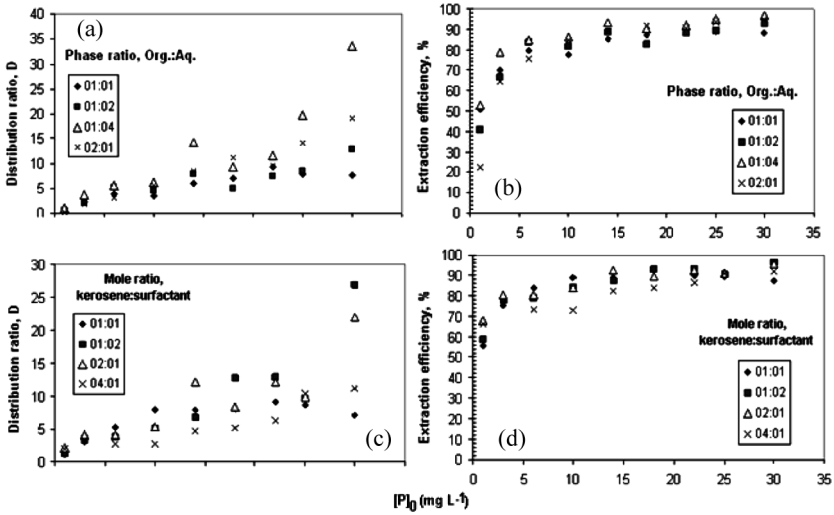


Figure 1. Relationships among starting P concentrations, the distribution ratios (D) and extraction efficiencies (E), (a) the phase ratios vs. D; (b) the phase ratios vs. E; (c) the ratios of kerosene to surfactant vs. D and (d) the ratios of kerosene to surfactant vs. E.

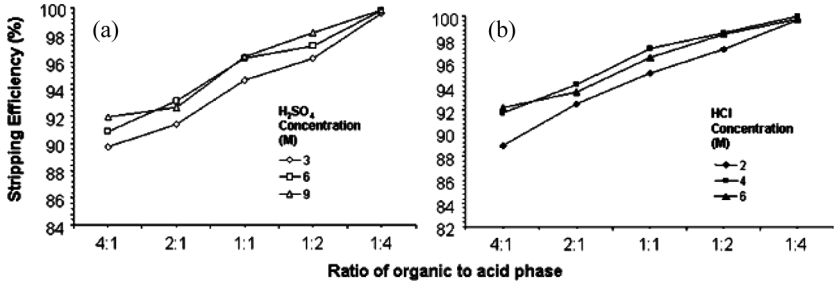


Figure 2. The effects of the type and concentrations of acid and the ratio of organic to acid phase on the stripping efficiency, (a) sulphuric acid and (b) hydrochloric acid.

higher the cost effectiveness. If >96% could be taken as a practical acceptable stripping efficiency, a ratio of 1:1 of the organic to the acid phase can then be used for sulphuric acid at a concentration of either 6 or 9 M and hydrochloric acid at 4 or 6 M. Since sulphuric acid is relatively cheaper than hydrochloric acid, 6 M sulphuric acid and a 1:1 phase ratio were selected for the further study under the same mixing and the separation conditions.

The stripping process is a reverse reaction to the extraction process. The type and concentration of the stripping agent required depend on the solubility of the phosphate and the extractant (BDMA) in the selected stripping agent. A high solubility of phosphate and a low solubility of the amines' group of BDMA in a strong acidic solution (9) would let most phosphates transfer from the extractant into the acid phase and this has been validated through this study. Consequently, the extractant can be reused. The regeneration and reuse studies were performed using the established extraction and stripping conditions and a real sewage sample (Table 1). Three ratios of fresh to recycled extractants (1:1, 1:2 and 1:4) were pre-investigated. There was a general decrease in the extraction efficiency with respect to the increase in the recycled portion of the extractant. The 1:2 ratio of the fresh to the recycled extractant was found to be the optimum in terms of the maintenance of good extraction efficiency. As shown in Fig. 3, under the stated operating conditions, the recycled extractant could be reused for 5 times in order to maintain the E value above 80%. Corresponding to each reuse of the recycled extractant, the E value gradually decreased, from 90 to 80%, and the residual P concentration increased up to 4 mg/L for 5 runs. However, 2/3 of the extractant in each run was the recycled one and this represents the cost-effectiveness of using the LLE method to recover P from waste water.

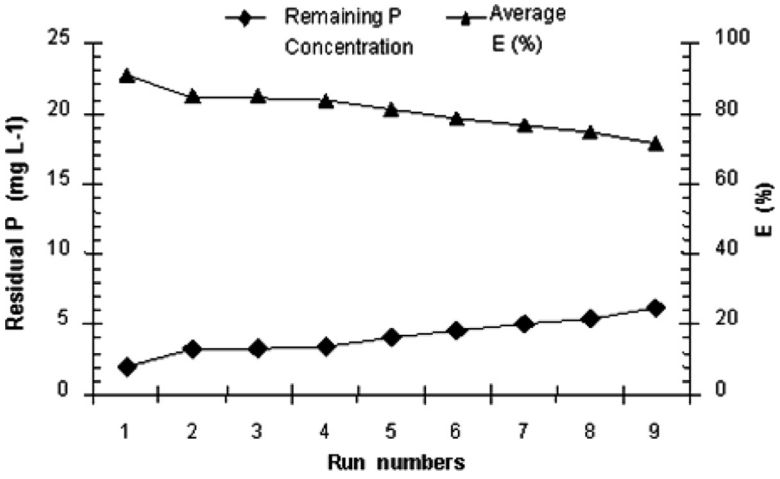


Figure 3. The effect of extractant recycle run numbers on the remaining P concentration and the extraction efficiency, E (P concentration in sewage sample was 21 mg/L, ratio of fresh to recycled extractant = 1:2).

CONCLUSION

In a LLE process, complexion between the amine groups in BDMA and phosphates and the positive charge of the micelles surface formed in mixing the extractant (composed of kerosene and BDMA) with P containing waste water would contribute to the P recovery. It is a new approach to recover P from wastewater by the LLE method while it is commonly used to recover a cationic element (e.g., metals). Under study conditions, one part of the extractant can react with four parts of wastewater to transfer >97% of P. In addition, in the stripping step, a 1:1 ratio of the extract to the recycled acid can result in 96% recovery of P, implying that an overall 96% phosphorus recovery efficiency can be achieved through the LLE process. Most importantly, the extractant can be recycled and reused at least 5 times if the residual P concentration should be less than 4 mg/L vs. the original P concentration of 21 mg/L. A pilot scale study, however, should be carried out in order to validate the laboratory results and to comprehensively evaluate the cost-effectiveness.

REFERENCES

1. Redfield, A.C. (1958) The biological control of chemical factors in the environment. *American Scientist*, *46* (3): 205–221.

2. Strickland, J. (1998) The development and application of phosphorus removal from wastewater using biological and metal precipitation techniques. *J. CIWEM*, *12* (2): 30–37.
3. UWWTD, The Urban Wastewater Treatment Directive (91/271/EEC) (1991). Council of the European Communities. *Official Journal*, L135/40.
4. UWWTR, The Urban Waste Water Treatment Regulations (England and Wales) (1994) *Statutory Instrument*, No. 2841.
5. UWWTR, The Urban Waste Water Treatment Regulations (Scotland) (1994) *Statutory Instrument*, No. 2842.
6. Jiang, J.Q.; Graham, N. (1998) Pre-polymerised inorganic coagulants and phosphorus removal by coagulation. *Water SA*, *24*: 237–244.
7. Berg, U.; Shaum, C. (2005) *Recovery of Phosphorus from Sewage Sludge and Sludge Ashes*; Izmirs, Turkey.
8. Tchobanoglous, G.; Burton, F.L. (2003) *Wastewater Engineering—Treatment, Disposal and Reuse*, Metcalf; Eddy, eds.; McGraw Hill: New York.
9. Ritcey, G.M.; Ashbrook, A.W. (1979) *Solvent Extraction – Principles and Applications to Process Metallurgy Part II*; Elsevier Scientific: New York.
10. Jiang, J.Q.; Panagoulopoulos, A.; Zhang, Y. (2002) *Management of Wastes from Drinking Water Treatments*; Miles, J.; Smith, D.; Owen, P., eds.; Terence Dalton: London, 181–188.
11. Amer. Public Health Assoc; Amer. Wat. Works Assoc; Wat. Environ. Feder., (1995) *Standard Methods for the Examination of Water and Wastewater,* 19th Ed.; APHA Publ. House: Washington, DC.