

RESEARCH ARTICLE

Novel Extraction of Phosphorus using Interaction of Tricaprylylmethylammonium Chloride (TOMAC) with Biodegradable Mixture of Vegetable Oils

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Abstract This work addresses the development of green formulation for phosphorus compound removal from aqueous solution via solvent extraction process. Several types of extractants, diluents and stripping agents were experimentally investigated and the best formulation was determined. Additionally, other parameters investigated were extractant and stripping agent concentrations. Results showed that TOMAC, a mixture of palm oil (PO) and sunflower oil (SO) as well as sodium chloride (NaCl) turned out to be the best extractant, diluent and stripping agent, respectively. Almost 100% of 50 ppm of phosphorus were successfully extracted under optimum conditions of 0.3 M TOMAC in a mixture of 50% PO + 50% SO. Fourier-transform infrared spectroscopy (FTIR) analysis confirmed the intermolecular bonding formation between phosphorus, vegetable oils and TOMAC molecules. Meanwhile, almost 96.5% of phosphorus can be recovered using 1.0 M NaCl in two stages of stripping process. Stoichiometric studies showed that about one mole of TOMAC and NaCl were involved during the extraction and stripping reaction of phosphorus, respectively. It can be concluded that the solvent extraction with new green formulation containing TOMAC in interaction with vegetable oils seems to be one of the novel sustainable approaches in removing phosphorus from agricultural wastewater.

Keywords: Phosphorus, solvent extraction, TOMAC, biodegradable oils, wastewater.

Introduction

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Phosphorus is synonymous with agriculture, being essential to crop growth. However, the uncontrolled use of phosphorus as fertilisers can be harmful to the environment due to intensive farming practices and excessive use of fertilisers. These extreme practices result in high volumes of agricultural drainage water that is heavily contaminated with phosphorus. The excess of phosphorus in wastewater has a detrimental effect towards biodiversity of aquatic environments since it accelerates eutrophication, which reduces water supplies and is potentially harmful the human health because of the formation of cyanotoxins [1-2]. Eutrophication occurs when the phosphorus concentration in water bodies rises above 0.02mg/L [3]. Industrial wastewater streams have phosphorus levels higher than 10 mg/L, while municipal wastewater and civic sewage have phosphorus concentrations of 4 to 15 mg/L [4]. Nguyen et al. [5] studied the effect of initial influent phosphorus concentration up to 15.5 mg/L. In order to protect water bodies from this undesired phenomenon, several nations have restricted the standard discharge of effluent for the total phosphorus within the ranges of between 0.5 to 1.0 mg/L [6-7].

A major issue that the world is facing is reducing or eliminating phosphorus from water resources. Basically, a number of techniques have been used to remove phosphorus from wastewater, including



crystallisation, non-aqueous phase extraction, microalgae membrane, adsorption, electrocoagulation, electrochemical, sorption, membrane filtration and reverse osmosis [1-11]. Of these, solvent extraction is considered as an attractive option, owing to its simple operation, low cost as well as potential for phosphorus removal and recovery [12-14]. This technique uses a carrier or extractant that is dependent on the kind of targeted compounds or ions that need to be removed [15-16]. Amongst the common extractants used in solvent extraction include bis (2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302), bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), bis-2-ethylhexyl phosphoric acid (D2EHPA), triethanolamine (TEA), trioctylamine (TOA), TOMAC, octanol, and tributylphosphate (TBP). The abovementioned extractants can be categorised as acidic, basic and solvating or neutral extractants. The acidic extractant has potential to extract the cation via cation exchange mechanism. Meanwhile, the basic extractant can effectively extract the anionic compound through anionic exchange mechanism [17]. Likewise, the stripping agent in solvent extraction also plays an important role in stripping or recovering the extracted targeted compound. Similarly, the acidic and basic stripping agents are preferable for cation and anion compounds, respectively. Another crucial component in the solvent extraction process is the diluent. Several studies claimed that the use of vegetable oil over traditional petroleum-based organic in solute extraction has great potential in reducing chemical consumption and encouraging a greener process [18].

Based on the literatures, very little information has been reported on the solvent extraction of phosphorus. A previous study reported that phosphorus was effectively extracted using primary amine and TBP in kerosene from weakly alkaline solutions. The loaded organic phase was stripped with dilute sodium hydroxide solution [16]. On the other hand, Mu *et al.* [19] addressed the extraction of phosphorus from a sulfuric acid solution using trialkyl phosphine oxides (Cyanex 923) diluted in heptane. Phosphorus could mutually reinforce the extraction by Cyanex 923 in sulfuric media. Throughout these works, it can be inferred that phosphorus has been predominantly extracted using primary amine and solvating extractants (TBP and Cyanex 923). However, the use of vegetables oils as another green substitute in solvent extraction of phosphorus has not been studied yet so far. Likewise, the use of TOMAC, another amine based extractant for phosphorus extraction has not been reported either.

Therefore, the main goal of this study is to address this lack of information by developing a new green formulation for solvent extraction of phosphorus using TOMAC-vegetable oils system from aqueous solution. Several variables, namely extractant types and concentrations, composition of vegetable oils, as well as stripping agent types and concentrations were evaluated to find the optimum conditions for phosphorus extraction.

Materials and Methods

Materials

Potassium dihydrogen phosphate (KH₂PO₄) as feed phase was obtained from Merck. Extractants investigated were Cyanex 272 (90% purity, Fluka), D2EHPA (≥95% purity, Sigma), TEA (99% purity, Sigma), TOA (99% purity, Sigma), TOMAC (99% purity, Sigma), octanol (99% purity, Sigma), and TBP (99% purity, Sigma). Kerosene as organic diluent was acquired from Sigma. Meanwhile, cooking PO (Buruh) was supplied by Lam Soon Edible Oils and SO was purchased from Yee Lee Edible Oils. Next, stripping agents inspected were NaCl (99% purity, Bendosen), potassium chloride (KCl) (99% purity, Bendosen), and sodium hydroxide (NaOH) (99% purity, Merck). Then, reagents used for molybdenum blue method for phosphorus analysis were antimony potassium tartrate (99% purity, Sigma), ammonium molybdate (99% purity, Acros), ascorbic acid (99% purity, Merck) and sulfuric acid (98% purity, Merck). All abovementioned chemicals and reagents are analytical grades that do not require further purifications. Subsequently, equipment used in this work include a pH Meter (Horiba model) for pH measurement of the aqueous solutions, a mechanical shaker (IKA, Germany) for the equilibrium experiments as well as UV-Vis Spectrophotometer (Spectrum lab 750 PRO) for the analysis of the phosphorus concentration. Meanwhile, FTIR was used for analysis of organic phases before and after extraction to confirm the reaction mechanism that occurred during the extraction process.

Solvent Extraction of Phosphorus

Solvent extraction of phosphorus was conducted by equilibrating equal volumes (10 mL) of 50 ppm simulated phosphorus aqueous solution (pH 5.63) and organic phase (TOMAC in kerosene) in stoppered 250 mL conical flask for 18 h by means of a mechanical shaker at 320 rpm agitation speed. Thereafter, this homogenous mixture solution was then carefully poured into a separating funnel and left for 30 min for phase separation. As a result, both aqueous and organic phases were obtained. The organic phase was loaded with phosphorus extracted from the aqueous phase whereas the aqueous phase may



contain untreated phosphorus. The phosphate concentration in aqueous phase was analysed by UV-Vis spectrophotometer (wavelength: 880 nm) using molybdenum blue method [20-21]. Similarly, the extraction procedures were repeated for other types of extractants (D2EHPA, Cyanex 272, octanol, TBP, TOA, and TEA), extractant concentrations (0.05 to 1.0M) as well as diluents (PO and SO, mixture of PO and SO). Then, the organic phase (extractant in diluent) with the highest extraction of phosphorus was used in the next stripping process. Throughout stripping process, equal volumes (10 mL) of the phosphorus-loaded organic phase (from extraction part) and aqueous 0.3M NaCl solution were equilibrated at 320 rpm agitation speed for a duration of 18 h using a mechanical shaker. After the phase separation process, the aqueous part was analysed for phosphorus concentration using UV-Vis spectrophotometer. The stripping procedures were repeated for other types of stripping agents (KCI and NaOH) and concentrations (0.3 to 3.0M). All of the samples were measured in duplicate and were implemented at room temperature (25±1°C). On the other hand, in order to study the extraction mechanism among the phosphorus, vegetable oils and extractant complexes, the organic phases before and after extraction were analysed using FTIR.

Data Analysis

In the solvent extraction process, the analysis was carried out in duplicate for each run with standard error requirement of less than 1%. The percentage of extraction and stripping of phosphorus were calculated using Eqs. (1) and (2). Meanwhile, and distribution ratio was determined as Eq. (3).

Extraction (%)
$$= \frac{C_i - C_{aq}}{C} \times 100$$
 (1)

Extraction (%)
$$= \frac{C_i - C_{aq}}{C_i} \times 100$$
 (1) Stripping (%)
$$= \frac{C_s}{C_{org}} \times 100$$
 (2)

Distribution ratio,
$$D = \frac{C_{org}}{C_{aq}}$$
 (3)

where C_i is the initial phosphorus concentration in aqueous feed phase (ppm), C_{aq} is the phosphorus concentration in aqueous feed phase after extraction (ppm), C_s is the phosphorus concentration in aqueous stripping phase after extraction (ppm), and C_{org} is the phosphorus concentration in organic phase after extraction (ppm).

Results and Discussion

Effect of Extractants Types Towards Phosphorus Extraction

The effect of different types of extractants towards phosphorus extraction were investigated as depicted in Table 1. It can be perceived that all types of extractants except TOMAC showed almost negligible effect towards phosphorus extraction. Throughout this study, the acidic extractants used were D2EHPA and Cyanex 272 which are phosphoric and phosphinic acids, respectively. These acidic extractants are pH dependent which would predominantly extract the cationic compounds in highly acidic aqueous solution [22]. Hence, it is not suitable for phosphorus extraction which is only slightly acidic (pH:5.63) and exist in anionic compound in aqueous media solution. As for solvating extractants which are weakly basic in nature, they can extract either neutral metal complexes or acids via solvation [12]. Likewise, some basic extractants showed insignificant effect towards phosphorus extraction. This could be explained by the fact that the amine based extractants such as TOA and TEA are more suitable for the extraction of anion complexes from basic solutions via anion exchange process [23].

On the other hand, TOMAC showed the highest magnitude of efficiency towards phosphorus extraction (92%). TOMAC (NR₄Cl) is also known as ionic liquid comprising of organic cations combined with ions of organic or inorganic nature [24]. Ammonium structure (NR_4^4) in TOMAC has a permanent positive charge which can form salt with anionic compounds [19]. Meanwhile, several anionic phosphorus species predominantly exist in the acidic, neutral and alkaline mediums which are dihydrogen phosphate $(H_2PO_4^-)$, hydrogen phosphate (HPO_4^{2-}) and phosphate (PO_4^{3-}) , respectively [25]. In this work, $H_2PO_4^$ seems to be dominant in slightly acidic solution. By reaction mechanism, both $H_2PO_4^-$ and TOMAC are hard bases, hence there is no electrostatic interaction attraction between them [19, 26]. Thus, the feasible reaction mechanism of $H_2PO_4^-$ extraction by NR_4Cl in the aqueous feed/organic interphase could be controlled by ion exchange with chloride, Cl⁻ [26]. Based on the maximum extraction efficiency of phosphorus, TOMAC was employed as an extractant for further experiment.



Table 1. Effect of different types of extractants towards phosphorus extraction (Experimental conditions: [Phosphorus]: 50 mg/L; pH: 5.63; [Extractant]: 1.0M; diluent: kerosene; aqueous waste volume: 10 mL; organic volume: 10 mL; temperature: 25±1°C; duration: 18 hours; agitation speed: 320 rpm).

| List of extractants | Туре | Extraction(%) |
|---------------------|-----------|---------------|
| D2EHPA | Acidic | 6 |
| Cyanex 272 | Acidic | 0 |
| Octanol | Solvating | 2 |
| TBP | Solvating | 0 |
| TOA | Basic | 0 |
| TEA | Basic | 0 |
| TOMAC | Basic | 92 |

Effect of Diluent Types Towards Phosphorus Extraction

The viability of using vegetable oil as a diluent in phosphorus extraction is another focus of this work. Figure 1 illustrates the effect that different types of diluent such as kerosene, PO, SO, as well as the mixture of PO and SO have on phosphorus extraction. The viscosity data for these diluents is tabulated in Table 2. Results indicate that using 100% PO and SO individually as diluents provided 74 and 87% of phosphorus extraction, respectively. PO provided quite low extraction compared to other types of diluent, perhaps due to one of its features which is being rich in unsaturated triglycerides, hence promoting high viscosity (p=83.06 cP) [27]. This is in line with the research done by Siddique et al. [28] who claimed that viscosity increases with high saturation and polymerisation. Such feature allows the oil to be accumulated more easily in the aqueous feed/organic interphase, thus limiting the complexation between the phosphorus and extractant [1]. On the other hand, SO has higher unsaturated fat with lower viscosity compared to PO (p = 44.02 cP). An observation by Kim et al. [29] suggest that the loosely packed structure of oils with more double bonds or unsaturated fat made them appear to have lower viscosity. This allows them to easily dilute the extractant as well as increase the number of ionic extractant for complexation with phosphorus at the organic/aqueous feed interphase. However, upon mixing of PO and SO by 50%, the extraction of phosphorus significantly increased up to 93%. According to Noraini et al. [30], the amount of palmitic acid in PO significantly decreased with high amount of SO (above 30%) through the blended mixture of SO and PO. Such mixture reduces the viscosity (p=62.45 cP) of the diluent as well as offers high degree of unsaturation for palm oil which promotes more ionic extractant for complexation with phosphorus. As observed, the extraction result using mixture of vegetable oils as diluent (94%) was comparable to the extraction result using kerosene (94%). Kerosene is a petroleumbased diluent which is frequently hazardous, non-renewable, non-biodegradable, combustible, and volatile in nature [27]. The vegetable oil with favourable characteristics of being biodegradable, nontoxic, inflammable, and renewable is the best substitute for the conventional kerosene in phosphorus extraction. Thus, mixture of SO and PO by 50% was used as diluent for subsequent experiments.

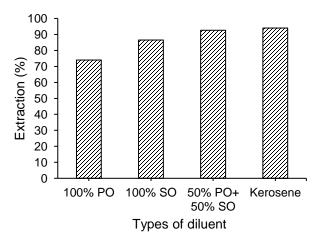


Figure 1. Effect of diluent types towards phosphorus extraction (Experimental conditions: [Phosphorus]: 50 mg/L; pH: 5.63; [TOMAC]: 1.0 M; diluent: vegetable oils and kerosene; aqueous waste volume: 10 mL; organic volume: 10 mL; temperature: 25 ± 1°C; duration: 18 hours; agitation speed: 320 rpm)



Table 2. Viscosity data for the different types of diluent

| Types of diluents | Viscosity (cP) |
|-------------------|----------------|
| kerosene | 1.64 |
| 100% PO | 83.06 |
| 100% SO | 44.02 |
| 50% PO + 50% SO | 62.45 |

Effect of Stripping Agent Type Towards Phosphorus Stripping

The recovery part is just as important as the extraction part in order to strip out or recover the targeted solute in the solvent extraction process. Therefore, the selection of suitable stripping agent is key to the high recovery or stripping the targeted solute from the loaded organic phase. Since the phosphorus appears as an inorganic anion in the aqueous media, the neutral and basic solutions have potential as stripping agents. It has been reported that aqueous NaOH solutions which is a strong Lewis base are effective recovery agents for phosphorus compounds [21, 31]. Besides, it has been found that NaCl is not only efficient in phosphorus recovery but is also cost-friendly [32]. Thus, throughout this study, several potential stripping agents were evaluated, namely NaOH, NaCl and KCl as exhibited in Figure 2. Notably, NaCl appeared as the best stripping agent, generating high stripping percentage of phosphorus compound (59%). Referring to the hard soft acid base theory (HSAB), hard-hard interaction between hard acid and hard base offers strong ionic bonding [19-20]. Phosphorus and alkali metal ion (such as Na, K) are hard base and hard acid, respectively, hence forming strong ionic bonding among each other. Sodium ion, Na^+ with smaller radii compared to potassium ion, K^+ provides high hardness a well as forming strong ionic interaction with phosphorus compound at the organic/aqueous stripping interphase [33]. Conversely, KCI showed low stripping percentage because the ionic radius increases with increasing period, hence K^+ is a softer acid compared to Na^+ . Such feature weakens the ionic interaction between K^+ and the phosphorus in the organic/aqueous stripping interphase. Likewise, NaOH also offered low stripping percentage which was almost half (33%) of that achieved by NaCl (59%). This could be explained by the fact that hydroxide ion, OH^- is a harder base compared to phosphorus, hence its interaction with Na^+ is more dominant compared to the interaction between phosphorus and Na^+ . Such competition lowers the interaction among phosphorus and Na^+ , thus lowering the stripping performance (33%) [33]. Clearly, NaCl is preferable as the best stripping agent for phosphorus in this experiment.

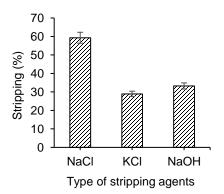


Figure 2. Effect of stripping agent types towards phosphorus extraction (Experimental conditions: [Phosphorus]: 50 mg/L; pH: 5.63; [TOMAC]: 1.0 M; diluent: mixture of vegetable oils; aqueous waste volume: 10 mL; organic volume: 10 mL; temperature: 25 ± 1°C; duration: 18 hours; agitation speed: 320 rpm)

Effect of TOMAC Concentrations Towards Phosphorus Extraction

Figure 3 depicts the effect of various TOMAC concentrations towards phosphorus extraction from 0.05 to 1.0M. Upon increasing the TOMAC concentration from 0.05 to 0.3M, the phosphorus extraction increased from 26 to 100%, respectively. Beyond 0.3M, the extraction provided insignificant change, showing that the extraction was reaching a plateau stage. Obviously, 0.3M of TOMAC is sufficient for the complexation with 50 ppm phosphorus from the aqueous phase.



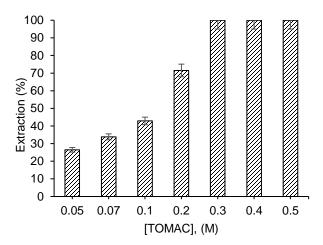


Figure 3. Effect of different TOMAC concentrations towards phosphorus extraction (Experimental conditions: [Phosphorus]: 50 mg/L; pH: 5.63; diluent: mixture of vegetable oils; aqueous waste volume: 10 mL; organic volume: 10 mL; temperature: $25 \pm 1^{\circ}$ C; duration: 18 hours; agitation speed: 320 rpm)

Subsequently, a stoichiometry study was performed to determine the number of moles of TOMAC that was involved in the phosphorus extraction. Assuming that a single complex is formed between 1 mol of phosphorus and n mol TOMAC, the extraction mechanism of phosphorus can be designated by Eq. (4):

$$H_2PO_4^-(aq) + nNR_4Cl(org) \rightarrow (NR_4)n H_2PO_4(org) + nCl^-(aq)$$
 (4)

where nNR_4Cl is TOMAC in organic phase, $(NR_4)n\,H_2PO_4(org)$ is phosphorus-TOMAC complex in organic phase, and n is the number of moles of TOMAC involved during extraction reaction. The equilibrium constant, K_{eq} in the form of equilibrium concentrations, can be expressed as Eq. (5):

$$K_{eq} = \frac{\overline{[(NR_4)^n H_2 P O_4]} \overline{[Cl^-]^n}}{[H_2 P O_4^-] \overline{[NR_4 Cl]}^n}$$
(5)

The amount of phosphorus extracted was evaluated by the distribution ratio, D of the phosphorus, in the aqueous and organic phases, as abovementioned in Eq. (3). Then, the relationship between the distribution ratio and the extraction constant, K_{eq} is as shown in Eq. (6)

$$log D = n log[NR_4Cl] + log \left[\frac{K_{eq}}{[Cl^-]}\right]$$
 (6)

Using these equilibrium conditions and the distribution ratio, the stoichiometry of the phosphorus-TOMAC during extraction reaction can be obtained. The stoichiometry study was performed to determine the n of TOMAC involved in the phosphorus extraction by plotting log D vs. log $[NR_4Cl]$ as shown in Figure 4. It was observed that the graph gives a straight line with a slope, n of 1.4, indicating that about one mole of TOMAC complex was involved in the phosphorus-TOMAC reaction. The reaction equation of phosphorus extraction with TOMAC is illustrated in Eq. (7).

$$H_2PO_4^-(aq) + NR_4Cl(org) \to (NR_4)H_2PO_4(org) + Cl^-(aq)$$
 (7)



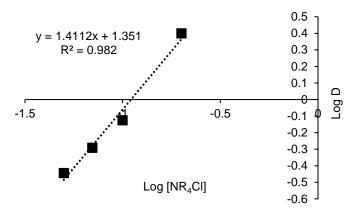


Figure 4. Stoichiometric plot for the equilibrium extraction of phosphorus using TOMAC as extractant

FTIR Analysis

FTIR analysis was done for both organic phases before and after the extraction of phosphorus to support the extraction mechanism as portrayed in Figure 5. Meanwhile, the structures of TOMAC, HPO_4^{2-} and vegetable oils are shown in Figure 6. As observed, the IR spectra of organic phase after the extraction slightly differs with the one before the extraction in the range of 4000-650 cm⁻¹, suggesting the formation of phosphorus-TOMAC complex after the extraction. Figure 5(A) illustrates the IR spectra of TOMAC, vegetables oil and interaction of TOMAC and vegetable oils. As can be seen in Figure 5(A), a strong band at 721.89 cm⁻¹ corresponds to the C-H bond of monosubstituted R groups (C-H₃) for alkane in TOMAC molecules. The band of 967.18 cm⁻¹ signifies the C=C bending of unsaturated bond (alkene) in vegetable oils molecules. Meanwhile, the strong band of 1161.00 cm⁻¹ signifies strong C-O stretching for ester in SO. The medium bands at 1098.26, 1118.29 and 1235.60 cm⁻¹ correspond to C-N stretching in TOMAC molecules. The weak band of 1376.96 cm⁻¹ signifies the O-H bending of alcohol group in vegetable oils molecules. Then, the strong band at 1461.89 cm⁻¹ refers to the C-H bending of methylene group (-CH₂-) in alkane for TOMAC and vegetable oil molecules [34]. The strong band of 1744.18 cm⁻ denotes the C=O stretching for ester in SO molecule. The weak band of 3008.27 cm⁻¹ represents the intramolecular bonded of O-H stretching in alcohol group of vegetable oil molecules. Meanwhile, the broad band of 3389.82 cm⁻¹ specifies the O-H stretching from vegetable oils for intermolecular hydrogen bonded with nitrogen from TOMAC molecules. Likewise, the strong bands at 2854.08 and 2923.12 cm⁻¹ ¹ represent the intermolecular bonding of N-H stretching from TOMAC, suggesting hydrogen bonded with vegetables oils. Referring to Figure 5(B), it can be observed the abovementioned band indicating intermolecular TOMAC/vegetable oil molecules (3389.82 cm⁻¹) has shifted to the broad band and higher intensity at 3415 cm⁻¹ after the extraction, signifying their intermolecular bonding formation between phosphorus molecules.



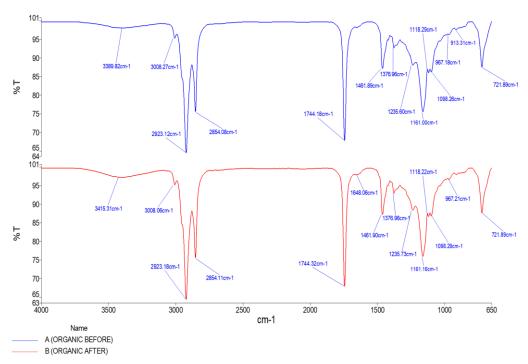


Figure 5. FTIR spectra of the organic phases before (A) and after (B) extraction with phosphorus using TOMAC in vegetable oils system

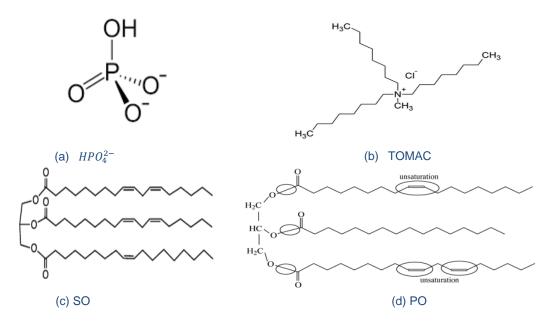


Figure 6. Structures of HPO_4^{2-} , TOMAC, SO and PO [19,35]



Effect of Different Stripping Agent Concentrations

Figure 7 portrays the effect of various NaCl concentrations on phosphorus stripping performances from 0.3 to 3.0M. The stripping performance of anionic phosphorus compound increased from 38 to 59% when the NaCl concentration was increased from 0.3 to 1.0M, respectively. Further increase up to 1.5M shows that the stripping behaviour offers almost insignificant change, showing that the stripping was reaching a plateau stage. However, when increasing the NaCl concentration further to 3.0M, the stripping performance considerably decreased to 26%. Such situation may be due to the interference from a high number of chloride ions (Cl^-) in the aqueous stripping phase. The presence of these ions which are also categorised as hard base are competitive towards phosphorus compound from the organic/aqueous interphase, thus reducing the striping efficiency of phosphorus [33]. Evidently, 1.0 M of NaCl seems to be sufficient for the complexation with 50 ppm anionic phosphorus from the loaded organic phase.

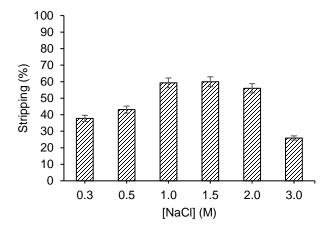


Figure 7. Effect of NaCl concentration towards phosphorus stripping (Experimental conditions: [Phosphorus]: 50 mg/L; pH: 5.63; diluent: mixture of vegetable oils; aqueous waste volume: 10 mL; organic volume: 10 mL; temperature: 25 ± 1°C; duration: 18 hours; agitation speed: 320 rpm)

Next, the stoichiometry study was performed to determine the n of NaCl involved in the phosphorus stripping. The complexes stripping reaction can be represented by Eq. (8):

$$(NR_4) H_2 PO_4(org) + pNaCl(aq) \rightarrow (Na)p H_2 PO_4(aq) + NR_4 Cl(aq)$$
 (8)

The relationship between D and K_{eq} for stripping reaction can be described as Eq. (9):

$$log D = p log[NaCl] + log \left[\frac{K_{eq}}{|NR_aCl|} \right]$$
 (9)

The stoichiometry study was performed to determine the number of moles of NaCl that was involved in the phosphorus stripping by plotting $log\ D$ vs. $log\ [NaCl]$ as presented in Figure 8. It was observed that the graph gives a straight line with a slope, n of 0.7 which is close to 1.0. This indicates that a 1:1 of mole ratio occurred during complexation between phosphorus-TOMAC complexes and NaCl for the stripping process. The phosphorus compound reacts with NaCl, producing sodium dihydrogen phosphate or monosodium phosphate, $(Na)\ H_2PO_4$ in the aqueous stripping phase. The mechanism of complexation in the stripping reaction is shown in Eq. (10):

$$(NR_4) H_2 PO_4(org) + NaCl(aq) \rightarrow (Na) H_2 PO_4(aq) + NR_4 Cl(aq)$$
 (10)



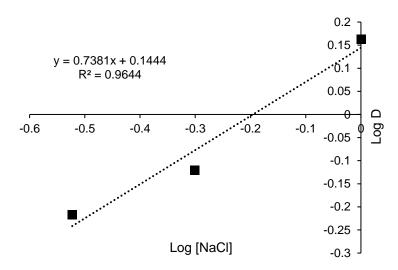


Figure 8. Stoichiometric plot for the equilibrium stripping of phosphorus system.

Some studies recommended performing the stripping process stage by stage as another approach to improve stripping performance of the targeted solute [16, 36-37]. Therefore, two steps of the stripping process were carried out throughout this study, utilising the aforementioned optimum concentration of the stripping agent (1.0M), and the results are displayed in Table 3. After the first stripping stage, about 59% of phosphorus was successfully stripped out from the loaded organic phase. Thereafter, almost 90% of the remaining phosphorus from the loaded organic phase was successfully stripped out through the second stage of stripping. Hence, the total of 96.5% of phosphorus can be recovered after two stages of stripping process.

Table 3. Stage efficiency for phosphorus stripping

| Stage of stripping | Stripping (%) |
|--------------------|---------------|
| 1 st | 59 |
| 2 nd | 90 |

Conclusions

It can be concluded that a new formulation containing TOMAC in a mixture of PO and SO is capable of extracting almost 100% of 50 ppm phosphorus from a slightly acidic aqueous solution. The optimum conditions obtained for the phosphorus extraction were 0.3M TOMAC in 50% PO+ 50 % SO. Next, 1.0M NaCl appears to be the best stripping agent for the two stages back extraction of phosphorus from the phosphorus loaded organic phase (96.5%). Meanwhile, stoichiometry studies for the phosphorus extraction and stripping show that about one mole of TOMAC and NaCl were involved in the extraction and stripping reaction of phosphorus, respectively. The aforementioned findings show the potential of this method as another alternative for the treatment of the wastewater contaminated with the excessive phosphorus concentration especially coming from chemical and agricultural industries. It can be a practical method for testing in a pilot plant focusing on a sustainable approach for future perspective.

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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