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Removal of metals and recovery of released nutrients from municipal and industrial sludge using different biosurfactants

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ABSTRACT

This study investigated the release of metals and nutrients from municipal and industrial sludge using plant-derived biosurfactant (saponin) and microbial-derived biosurfactant (rhamnolipid). It also investigated the recovery of nutrients released from municipal sludge by a biosurfactant in the form of struvite. Compared to saponin, metals and nutrients release levels from municipal and industrial sludge were higher for rhamnolipid. The removal efficiencies of Ni, Cr, Fe and Zn from industrial sludge at a 5/1 liquid/solid ratio with 7% rhamnolipid concentration were 55.37%, 15.52%, 9.70%, and 4.20%, respectively. Compared to industrial sludge, less metal was released from municipal sludge with rhamnolipid, whereas the nutrients release was higher. Therefore, hydrolyzed municipal sludge liquid with rhamnolipid was used to the formation of struvite. Optimal conditions for the release of nutrients and metals from municipal sludge were obtained at a liquid/solid ratio of 5/1 and a 10% concentration of rhamnolipid. At these optimal conditions, the concentration of PO_4^{3-} and NH_4^+ released was 1,564 and 1,419 mg/L, respectively. Under these conditions, the struvite produced from hydrolyzed municipal sludge liquid contained 2.24% N, 10.82% Mg, 11.03% P, 5.37% K and 4.11% Na by percentage weight calculated from the results of energy dispersive X-ray spectrometry. The heavy metal contents of the struvite obtained, Pb, Cu, Ni, Cr, Cd, and Hg, were below detection limits. The Zn content of the struvite was only 0.21 mg/kg.

Keywords: Biosurfactant; Industrial sludge; Metal removal; Municipal sludge; Nutrients recovery; Struvite

1. Introduction

The production of sludge from wastewater treatment plants has been increased due to rapid industrialization and urbanization. Metals concentrations in sludge vary from one site to another, depending on the municipal and industrial input into the system. Over the past few decades, many approaches to sludge treatment and disposal have been introduced. These methods include chemical treatment, thermal treatment, bioleaching, electrokinetic treatment and wet oxidation [1]. In particular, the focus of researchers has been on chemical methods rather than other methods due to their simple operational processes, shorter operation times and high removal efficiency of heavy metals from the sludge. Various organic acids, inorganic acids, and chelating agents have been applied to efficiently remove heavy metals from sludge [2,3]. However, while a large dosage of chemical reagent and low pH can produce high removal efficiencies, it results in high processing costs and difficulty in adjusting the pH of the treated sludge. Therefore, it is necessary to find environmentally friendly reagents to take the place of the organic acids, inorganic acids and chelating agents [3].

Biosurfactants are bioavailable surface-active compounds produced mainly by bacteria, fungi, and yeasts [4]. Also, biosurfactants can be extracted from the metabolites

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of plants. Saponins are a kind of biosurfactant produced by various plant parts, such as roots, stems, bark, leaves, seeds, and fruits, and they act as natural non-ionic surfactants [5]. Rhamnolipids are glycolipid biosurfactants produced by various bacterial species including some from *Pseudomonas* sp., and their special structure has an anionic nature [6]. Biosurfactants can form micelles and reduce surface and interfacial tension. Consequently, biosurfactants can effectively solubilize, disperse and desorb both organic and heavy metals [7]. Also, biosurfactants can change the morphology of sludge flocs [8]. A limited number of studies have reported the release of nitrogen and phosphorus using biosurfactants in anaerobic fermentation of waste activated sludge [8,9,10]. Furthermore, to the best of our knowledge, there are no studies on nitrogen and phosphorus release from digested sludge using biosurfactants. Anaerobically digested sludge contains high levels of phosphorus and nitrogen in an insoluble form [11]. Thus, phosphorus and nitrogen are often released from digested sludge by hydrolysis and recovered by the crystallization of struvite ($MgNH_4PO_4$) [12,13]. Global phosphorus resources have been rapidly depleted [14]; therefore, phosphorus recovery from sludge could provide a key solution to the phosphorus shortage. However, there are no studies yet on the recovery of nutrients released from sludge in the form of struvite, by biosurfactants.

The present study was conducted to achieve three goals. Firstly, industrial sludge and municipal sludge were hydrolyzed using rhamnolipids and saponins. The concentrations of released metals and nutrients were determined in the liquid obtained from hydrolysis. The efficiency of metals removal from sludge using biosurfactants was calculated based on the released metals concentrations. The experimental conditions that delivered the greatest nutrients release were also determined. Secondly, the nutrients released from the municipal sludge by rhamnolipids were recovered in the form of struvite, and finally, the chemical composition of the resulting struvite was determined using Fourier-transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) and heavy metal analyses.

2. Materials and methods

2.1. Sludge samples and preparation

Two kinds of sludge samples were used in this study. Digested municipal sludge was obtained from an anaerobic digester effluent in a sewage treatment plant with an anaerobic/anoxic/aerobic process (A/A/O, enhanced biological nutrient removal process) in Antalya, Turkey. Thickened industrial sludge was provided from an organized industry region wastewater treatment plant located in Isparta, Turkey, using chemical and biological treatment processes. The sludge samples were oven-dried at 103°C ± 2°C for 42 h, then finely ground and sieved to a 1 mm mesh size. These samples were used for metals and nutrients measurements, and hydrolysis experiments.

2.2. Characteristics of the sludge samples

The main characteristics of the anaerobically digested municipal sludge were as follows: 36.45 ± 3.46 g/L of total solids (TS), 25.35 ± 3.04 g/L of total volatile solids (TVS), 51.47 ± 3.49 g/L of total chemical oxygen demand (TCOD), 1.29 ± 0.05 g/L of soluble chemical oxygen demand (SCOD), 41.9 ± 1.2 mg/g of total nitrogen (TN), 24.75 ± 0.16 mg/g of total phosphorus (TP) and a pH of 7.64. The digested municipal sludge contained a high content of TN and TP.

The main characteristics of the thickened industrial sludge were as follows: 31.0 ± 0.28 g/L of TS, 24.5 ± 2.83 g/L of TVS, 81.15 ± 20.29 g/L of TCOD, 3.28 ± 0.16 g/L of SCOD, 4.79 ± 0.06 mg/g of TP at and a pH of 6.33.

The elemental composition of the sludge samples is given in Table 1. Industrial sludge contained higher concentrations of Si, Fe, Zn, Cu, Cr, and Ni.

2.3. Rhamnolipid and saponin

Rhamnolipid (R90) was purchased from AGAE Technologies (USA). The raw rhamnolipid – containing 90% pure rhamnolipids – was in solid form, and used without further purification. Rhamnolipid biosurfactants are glycolipids containing L-rhamnose and ß-hydroxyl fatty acids that exhibit amphiphilic properties (with both hydrophilic and hydrophobic parts). This rhamnolipid product had been purified from *Pseudomonas aeruginosa* and contained a mixture of rhamnolipids with fatty acids of varying tail length. They are highly biodegradable, non-toxic and renewable.

Saponin from Quillaja bark was purchased from Sigma-Aldrich (USA) and used without further purification. The maximum sapogenin content was 35%. Quillaja saponin is obtained from the bark of the South American soaptree, Quillaja Saponaria Molina (part of the Rosaceae family).

2.4. Hydrolysis using rhamnolipid and saponin

Hydrolysis by biosurfactant was performed in batch experiments using a Biosan MSH-300i magnetic stirrer at a constant mixing rate (250 rpm) for 4 h at room temperature. Higher levels of metals released by biosurfactants have been reported for longer reaction times [6,15]. Nutrient recovery achieved by the formation of struvite is affected by the presence of metals. Heavy metals may also affect the quality of recovered nutrients to be used as 'clean fertilizer'. Thus, the recovered product may be contaminated with released metals and heavy metals from the sludge [13]. Consequently, the reaction period in this study was not too long, since it was aimed at the recovery of nutrients released through hydrolysis.

The factors investigated in the hydrolysis experiments using the biosurfactant are shown in Table 2. Three rhamnolipid concentrations (4%, 7%, and 10%) and three saponin concentrations (10, 30, and 50 g/L) were selected to determine the effects of the biosurfactant (mL)/sludge (g) ratio on metals and nutrients release. Saponin obtained from Quillaja bark is soluble in water and was purchased from Sigma-Aldrich (USA).The solubility of saponin was tested in 50 mg/mL of deionized water [16]. The solubility in water may be increased by adding small amounts of alkali. For this reason, the solutions were prepared based on the solubility of saponin in water.

Hydrolysis experiments were performed at the original pH value of the prepared biosurfactant solutions. No pH adjustment was carried out using an acid or base. The pH

Table 1
Elemental composition of the sludge samples

Element	Concentration (mg/kg)	
	Digested municipal sludge	Thickened industrial sludge
Ca	17,470 ± 128.0[a]	14,040 ± 118.3
Mg	1,793 ± 30.4	3,505 ± 48.6
K	4,848 ± 41.5	2,988 ± 37.1
Na	663.6 ± 8.7	29,260 ± 171.7
Si	n.d.[b]	122,500
Al	4,827 ± 57.9	2,910 ± 35.3
Fe	6,187 ± 79.4	14,250 ± 120.7
Zn	1,592 ± 13.8	4,017 ± 30.08
Cu	120.60 ± 2.0	261.10 ± 3.8
Cr	39.67 ± 0.06	446.4 ± 5.3
Pb	14.30 ± 0.03	22.54 ± 0.06
Ni	21.07 ± 0.05	380.50 ± 4.8
Cd	b.d.[c]	b.d.
Hg	b.d.	b.d.

[a]Mean ± SD (n = 2).
[b]n.d., not determined.
[c]b.d., below detection limit.

values of the 4%, 7% and 10% rhamnolipid solutions were 9.20, 8.82 and 8.85, respectively. The pH values of the 10, 30 and 50 g/L saponin solutions were 4.37, 4.21 and 4.08, respectively. In parallel, blank experiments without biosurfactants were conducted as a control using deionized water.

At the end of the experiments, the samples were centrifuged (at 9,000 rpm for 20 min) after hydrolysis to precipitate the sludge samples. The hydrolyzed sludge liquid or supernatant was filtered through a 0.45 µm membrane filter, and the concentration of PO_4^{3-} and metals in the solution was analyzed.

2.5. Struvite formation

Hydrolyzed digested municipal sludge liquid from using rhamnolipid was used for struvite formation. The batch chemical precipitation experiment for struvite formation was conducted with a 90 mL volume and continue stirring with a magnetic stirrer at room temperature (stirring speed 250 rpm). The formation of struvite requires Mg^{2+}, NH_4^+ and PO_4^{3-}, with an ideal molar ratio of 1:1:1. Since the formation of struvite is used to recover nutrients from wastewater and sludge, vast quantities of phosphate and magnesium ions are needed to satisfy an equimolar ratio for magnesium, ammonium, and phosphate because the molar concentration of ammonia is generally much higher than these other two components of struvite [13,17]. Thus, $MgCl_2.6H_2O$ and H_3PO_4 were used as additional sources of Mg^{2+} and PO_4^{3-} to simultaneously recover PO_4^{3-} and NH_4^+.

The pH value of the sample was adjusted and maintained at the desired level with a 20% NaOH solution. Samples were stirred for 30 min and then held for 1 h to allow the precipitated solid matter to form. Then, the contents of the beaker were filtered through a coarse filter. The solid matter left on the coarse filter was dried by holding it at room temperature for 48 h.

2.6. Analytical procedure

TS, TVS, and TN were conducted according to the procedure described in the Standard Methods [18]. TCOD and SCOD were determined by the Hach reactor digestion method. PO_4^{3-} and NH_4^+ were determined using the Hach ascorbic acid method and the Hach Nessler method, respectively. To analyze the total metal and TP contents, 1.0 g of sludge sample was weighed, and microwave digestion using HNO_3, HCl and HF were applied. TP, Ca, Mg, K, Na, Si, Al, Fe, Zn, Cu, Cr, Pb, Ni, Cd, and Hg were measured using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer, DV2100) after acidic microwave digestion. SCOD, PO_4^{3-}, and the contents of the metal were determined by filtering the sample through 0.45 µm membrane filters. Metals removal efficiencies (R) were calculated using the following equation (1):

$$R(\%) = \left(\frac{C \times V}{M \times m}\right) \times 100 \quad (1)$$

where C is the metal concentration in the hydrolyzed liquid after biosurfactant hydrolysis (mg/L); V is the volume of the biosurfactant solution (mL); M is the weight of the sludge sample (g), and m is the metal concentration in the sludge sample before biosurfactant hydrolysis (mg/kg).

The pH values of digested sludge were measured using 1:5 water extraction, mechanically stirring for 3 h and subsequent determination using a Hanna HI 221 pH meter. The dry precipitate obtained from struvite crystallization was characterized using an X-ray diffractometer (XRD; Bruker, D8 Advance Twin-Twin), an SEM (FEI, Quanta FEG 250) equipped with EDS, and an FTIR (Perkin Elmer BX, Waltham, MA, USA). FTIR data were collected in the 400 to 4,000 cm^{-1} range. To determine the heavy metal contents of the dry precipitate, microwave digestion was applied by the addition of HNO_3 and HCl to 0.1 g of solid sample in pressure-resistant Teflon tubes [19].

Table 2
Factors investigated in the hydrolysis experiments using the biosurfactant

Sludge sample	Rhamnolipid concentration (M)	Saponin concentration (g/L)	Biosurfactant/sludge ratio (mL/g)
Digested municipal sludge	4%, 7% and 10%	10 g/L, 30 g/L, 50 g/L	5/1 and 10/1
Thickened industrial sludge	4%, 7% and 10%	10 g/L, 30 g/L, 50 g/L	5/1 and 10/1

All experiments were replicated to evaluate the reproducibility of the results, and the mean values are presented.

3. Results and discussion

3.1. Effects of rhamnolipid and saponin on the release of metals from industrial sludge and municipal sludge by hydrolysis

Fe, Ni, Si, Zn and Cr released from industrial sludge using rhamnolipid were significantly higher compared to the blank (Fig. 1a). Based on these release values, metal removal efficiencies were calculated using Eq. (1). The maximum removal efficiency for Ni was 76.72% at a rhamnolipid concentration of 4% and a 10/1 liquid/solid ratio. Cr, Fe and Zn removal efficiencies for a 5/1 liquid/solid ratio and a 7% rhamnolipid concentration were 15.52%, 9.70%, and 4.20%, respectively. Under these experimental conditions, Ni removal efficiency was 55.37%. The Pb, Cu and Al released using rhamnolipid were much lower than other metals (data not shown). It indicated that Pb, Cu, and Al are difficult to extract from the sludge. Hidayeti et al. [20] reported that the Pb, Zn and Cu efficiencies from paper industry sludge using a microbial-derived biosurfactant at the end of 3 d was 14.04%, 6.5%, and 2.01%, respectively.

Compared to rhamnolipid, lower levels of metal release were obtained with industrial sludge using saponin (Fig. 1b). The maximum removal efficiencies for Ni, Cr, and Fe at 30 g/L of saponin and a 10/1 liquid/solid ratio were 76.97%, 6.49%, and 4.22%, respectively. The maximum removal efficiency for Zn was 1.37% at a concentration of 30 g/L and a 10/1 liquid/solid ratio. The Pb, Cu, Al, and Si released using saponin were much lower than other metals (data not shown). Gao et al. [21] reported that the removal efficiencies of Zn, Ni, Mn, Cr, Cu and Fe from electroplating sludge were from 5 to 40% for a saponin concentration of 30 g/L over 24 h. For the metals mentioned, the highest removal efficiencies were obtained for a saponin concentration of 50 g/L [21]. Kiliç et al. [15] investigated the effect of saponin on Cr removal from tannery sludge at pH values of 2, 2.5 and 3 during a 6 h reaction. The Cr removal efficiency was obtained to be 12.6% using a 5% concentration of saponin at a pH of 2.

By comparison with those reported in the literature, this study found higher metal removal efficiency values over a 4 h-reaction period with the original rhamnolipid pH value (with no pH adjustment).

Fe, Ni, Zn and Cr released from digested municipal sludge using rhamnolipid were significantly higher compared to those of the blank experiment (Fig. 2a). The maximum Cr, Zn and Fe removal efficiencies at a 10/1 liquid/solid ratio with 10% rhamnolipid were 68.04%, 7.41%, and 3.52%, respectively. The maximum removal efficiency for Ni was 80.66% at a 4% concentration and a 10/1 liquid/solid ratio. Tang et al. [6] investigated heavy metal removal from dewatered sludge using rhamnolipids, which they received from an urban wastewater treatment plant. The wastewater treatment plant treats both domestic and industrial wastewaters, with domestic wastewater accounting for 60% of the total wastewater. The removal efficiencies of Cu, Zn, Cr, Pb, Ni and Mn from dewatered sludge using rhamnolipids at a concentration of 2 g/L and a 10/1 liquid/solid ratio for 24 h were 16%, 15%, 12%, 5%, 14.01%, and 6.11%, respectively.

As is the case of industrial sludge (Figs. 1a and b), lower levels of metal release from digested municipal sludge were found using saponin, compared to using rhamnolipids (Fig. 2b).

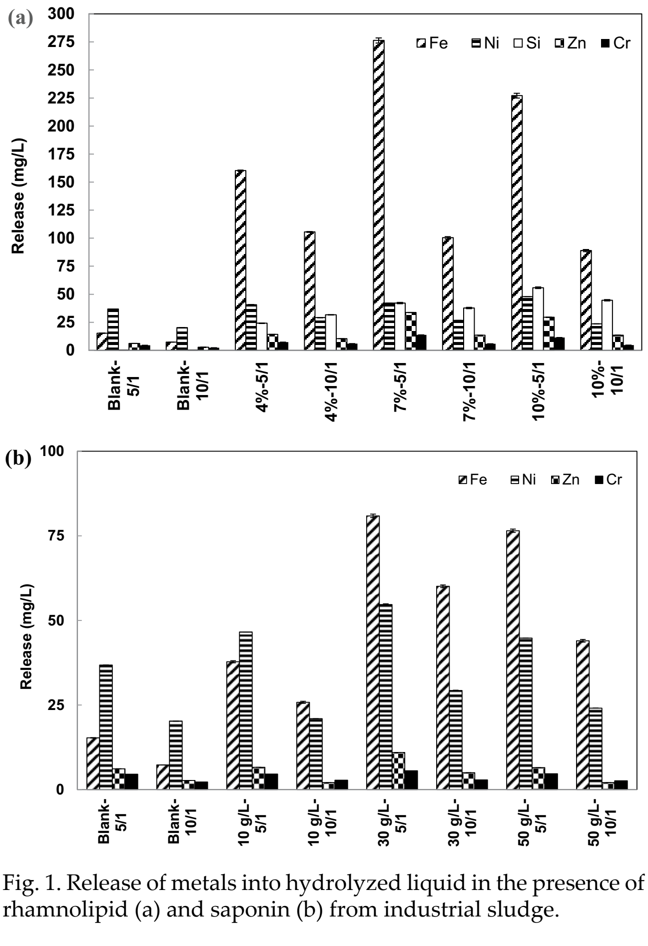


Fig. 1. Release of metals into hydrolyzed liquid in the presence of rhamnolipid (a) and saponin (b) from industrial sludge.

3.2. Effects of rhamnolipid and saponin on the release of nutrients from industrial sludge and municipal sludge by hydrolysis

In addition to the metals released by applying biosurfactants, nutrients release values from industrial sludge were also determined. Compared to the blank and saponin applications, rhamnolipid application significantly increased the PO_4^{3-} release from industrial sludge (Figs. 3a and b). At a 7% rhamnolipid concentration and a 5/1 liquid/solid ratio, the maximum PO_4^{3-} release was 417 ± 50.91 mg/L (Fig. 3a).

High NH_4^+ release values were obtained from industrial sludge using both rhamnolipid and saponin (Figs. 4a and b). NH_4^+ release values increased as the rhamnolipid and saponin concentrations increased. At a 10% rhamnolipid concentration and a 5/1 liquid/solid ratio, the maximum NH_4^+ release was 497.29 ± 24.63 mg/L (Fig. 4a). At a 50 g/L saponin concentration and a 5/1 liquid/solid ratio, the maximum NH_4^+ release was 333.79 ± 9.58 mg/L (Fig. 4b).

A higher dosage of rhamnolipid resulted in more PO_4^{3-} being released from the digested municipal sludge (Fig. 5a). The maximum PO_4^{3-} release value (1564 ± 39.59 mg/L) was obtained at a rhamnolipid concentration of 10% and a

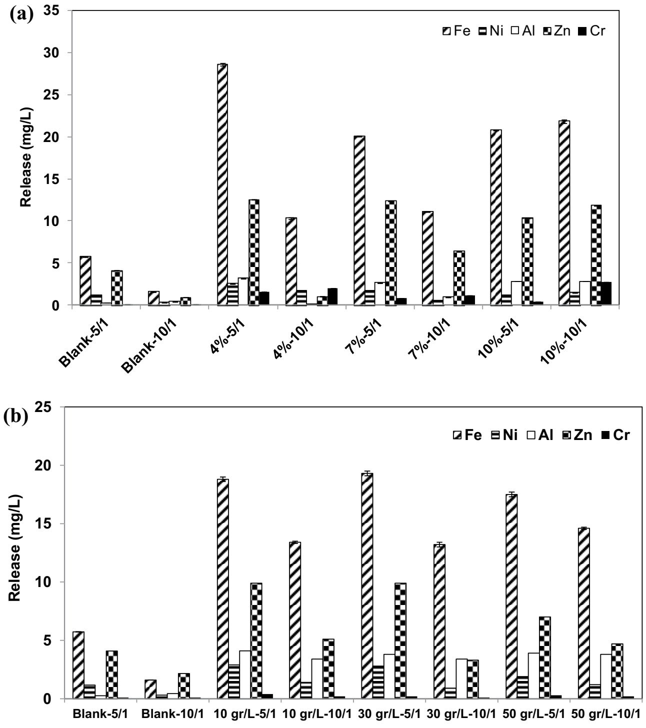


Fig. 2. Release of metals into hydrolyzed liquid in the presence of rhamnolipid (a) and saponin (b) from digested municipal sludge.

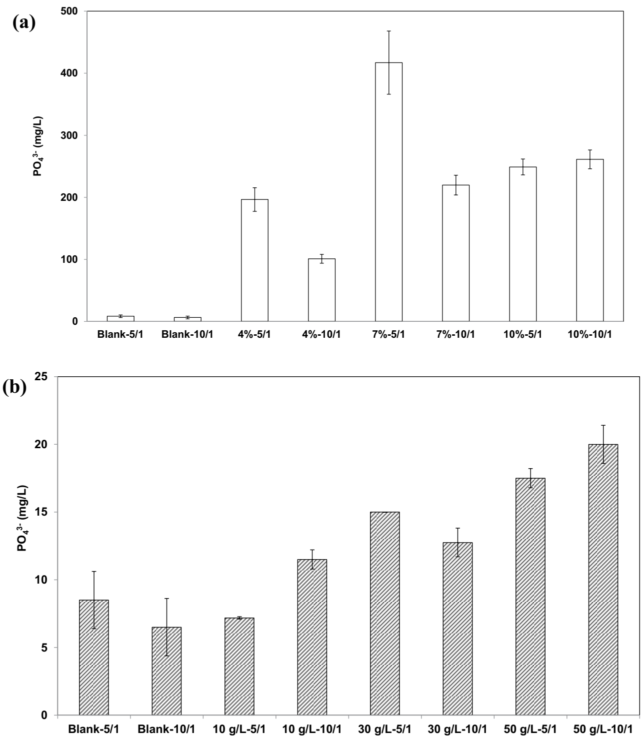


Fig. 3. Release of PO_4^{3-} into hydrolyzed liquid in the presence of rhamnolipid (a) and saponin (b) from industrial sludge.

5/1 liquid/solid ratio. The results indicated that, compared with rhamnolipid, saponin caused relatively less PO_4^{3-} release into the hydrolyzed liquid (Fig. 5b). Huang et al. [10] investigated the effects of surfactin, rhamnolipid and saponin on the anaerobic fermentation of waste activated sludge. In the study, it was reported that nitrogen and phosphorus release values were lower with the use of saponin.

NH_4^+ released from digested municipal sludge increased as the rhamnolipid concentration increased. As in the case of PO_4^{3-} release, the maximum NH_4^+ release (1419 ± 21.89 mg/L) was obtained at a 10% concentration of rhamnolipid and a 5/1 liquid/solid ratio (Fig. 6a). Compared to rhamnolipid, saponin resulted in a higher NH_4^+ release value (Fig. 6b). The maximum NH_4^+ release (1,568.64 ± 29.19 mg/L) was at a saponin concentration of 10 g/L and a 5/1 liquid/solid ratio.

The metals content of the hydrolyzed sludge liquid is an important element that affects the purity of struvite [13]. Compared to industrial sludge, the metals released from the municipal sludge were lower, whereas the nutrient release value was higher. Therefore, it was thought that the municipal sludge was suitable for the recovery of the nutrients released by the biosurfactant. The optimal test conditions for PO_4^{3-} and NH_4^+ release from digested municipal sludge was determined to be a rhamnolipid concentration of 10% and a 5/1 liquid/solid ratio (Figs. 5a and 6a).

3.3. Struvite formation from the hydrolyzed digested municipal sludge liquid using rhamnolipid

The maximum release of PO_4^{3-} and NH_4^+ from digested municipal sludge was obtained at a rhamnolipid concentration of 10% and a 5/1 liquid/solid ratio. Under these conditions, Ni, Cr, and Cu releases were at the minimum levels compared to those in other rhamnolipid applications. Al and Fe release were 2.84 mg/L and 20.75 ± 0.02 mg/L, respectively (Fig. 2a). Therefore, hydrolyzed municipal sludge liquid obtained under these conditions was used for the formation of struvite.

Struvite formation is more favorable when the ratio of Mg:P is 1 to 2.5 [14], and the molar ratio of P:N has to be at least 1:1 [22]. In this study, the Mg^{2+}:NH_4^+: PO_4^{3-} proportions were 1.5:1:1, and the pH was maintained at 9.0. Struvite crystals were then formed. The most common method for phosphorus recovery from sewage sludge is the acid extraction method [13]. However, the pH value of the hydrolyzed sludge liquid under acid extraction is very low. In this case, to bring the liquid phase to a pH range between 8 and 9 for struvite formation, more chemicals will be needed. However, in this study, the pH values for the hydrolyzed digested sludge liquid using rhamnolipids were from 7.37 to 8.51.

The FTIR spectrum of the dry precipitate is shown in Fig. 7. The FTIR spectrum of the dry precipitate also confirms the presence of struvite, with characteristic vibration bands for phosphate (υ_3 PO_4^{3-}, 1,006 cm^{-1}), ammonium (ν_4 NH_4^+, 1,440 cm^{-1}) and water (758 cm^{-1}) [23]. The bands for PO_4^{3-} units were observed at 1,006, 571, and 457 cm^{-1}. A strong band at 1,006 cm^{-1} originated from the components of the υ_3 (PO_4^{3-}) vibration. The peak at 571 cm^{-1} was due to the υ_4 bending modes of the PO_4^{3-} units. The bands seen over the range of 1,621 to 1,440 cm^{-1} were those of the HNH deformation modes of NH_4^+. The band at 2,961 cm^{-1} was due to the antisymmetric stretching vibrations of the NH_4^+ groups. The absorption band at 2,932 cm^{-1} was due to the NH_4^+ ion.

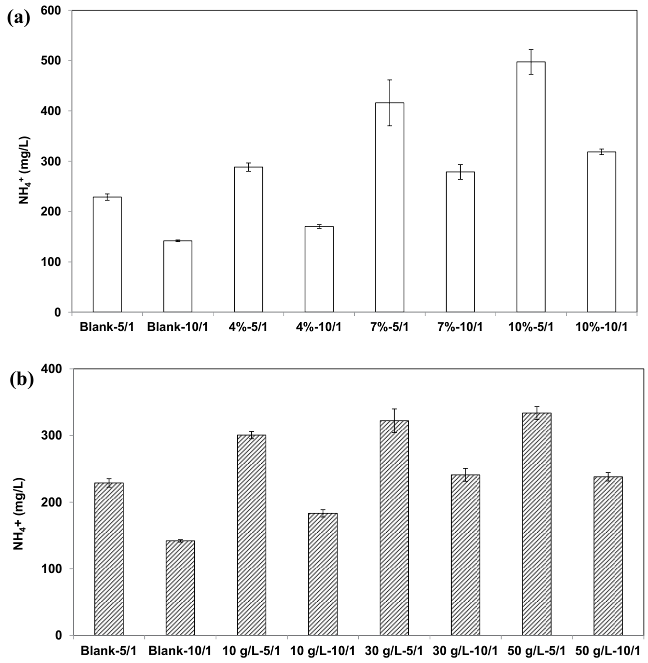


Fig. 4. Release of NH_4^+ into hydrolyzed liquid in the presence of rhamnolipid (a) and saponin (b) from industrial sludge.

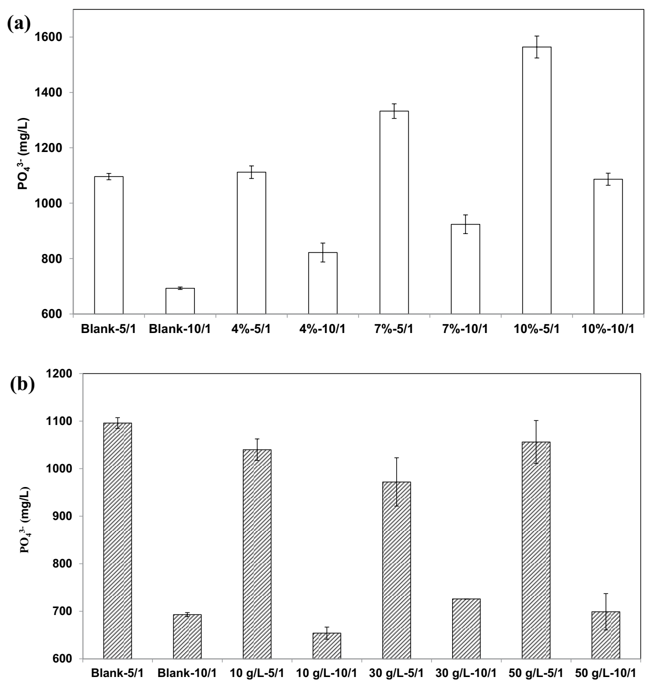


Fig. 5. Release of PO_4^{3-} into hydrolyzed liquid in the presence of rhamnolipid (a) and saponin (b) from digested municipal sludge.

XRD analysis results for the dry precipitate matched the database model given for ammonium magnesium phosphate hydrate ($NH_4MgPO_4·6H_2O$, struvite) in terms of the position and intensity of the peaks. In addition to struvite formation, XRD analysis of the dry precipitate showed iron phosphate

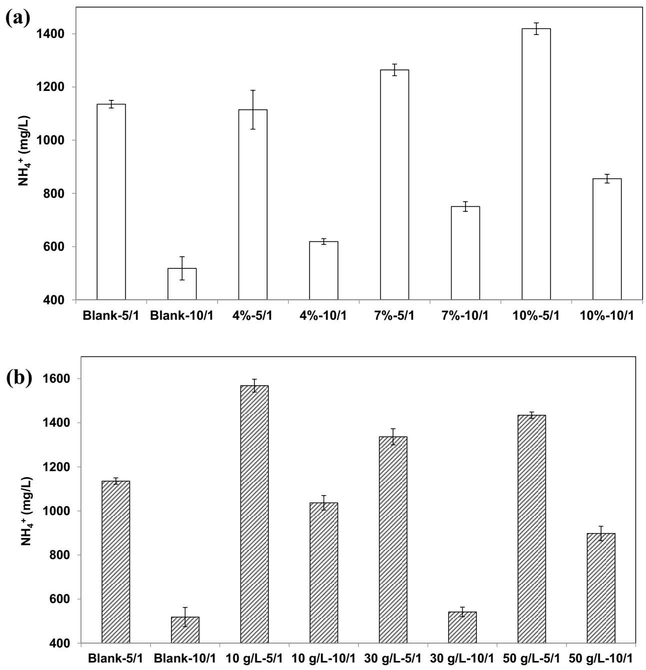


Fig. 6. Release of NH_4^+ into hydrolyzed liquid in the presence of rhamnolipid (a) and saponin (b) from digested municipal sludge.

($FePO_4$) and potassium magnesium phosphate hydrate ($KMgPO_4·6H_2O$, struvite-K) formation (data not shown).

SEM analysis of the dry precipitate showed that struvite crystals developed (Fig. 8a). The chemical properties of the dry precipitate were also analyzed by EDS (Fig. 8b). The EDS results show that high P and Mg contents were present in the dry precipitate. The dry precipitate also contained N, K, Na and other minerals in trace amount as impurities. From the EDS result, the dry precipitate contained 2.24% N, 10.82% Mg, 11.03% P, 5.37% K, and 4.11% Na by percentage weight.

The contents of the heavy metals in the struvite precipitate, Pb, Cu, Ni, Cr, Cd, and Hg, were below the detection limits. The Zn content in the struvite was only 0.21 mg/kg (data not shown).

3.4. Evaluation of the use of biosurfactants in sludge hydrolysis for nutrient recovery

The hydrolysis of sludge using chemical reagents such as inorganic acids and chelating agents results in a lower pH in the hydrolyzed liquid. This makes it difficult to adjust the pH of the treated sludge. Additionally, the chelating agents might create secondary pollution [6]. The use of saponins and rhamnolipids as biosurfactants delivers environmental and economic benefits. They do not cause secondary pollution [15]. Biosurfactants have been successfully employed in sludge hydrolysis [24]; however, some challenges still remain in their application. The large-scale application of biosurfactants is limited owing to the high cost. It has been reported that growth conditions/optimized production using economically feasible renewable substrates and efficient multi-step downstream processing would help to produce more economically feasible and profitable biosurfactants [5,24].

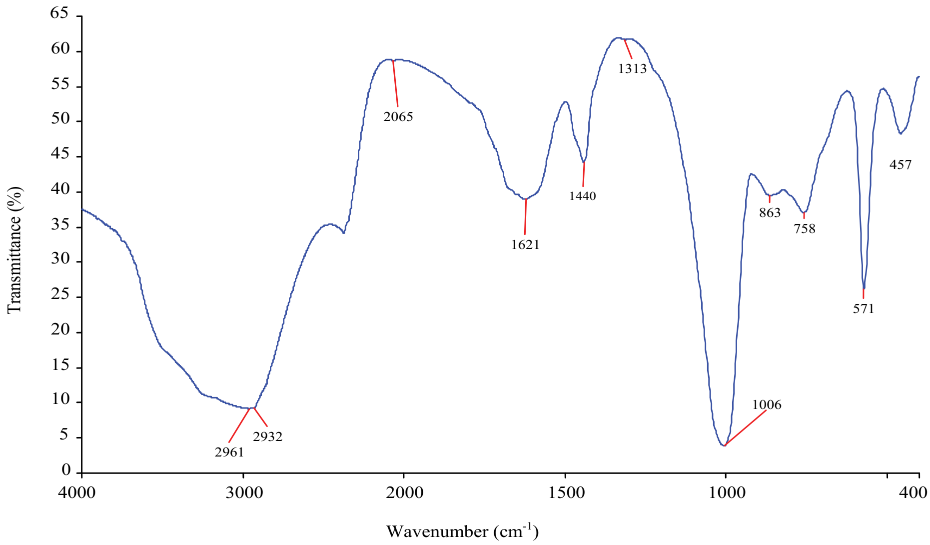
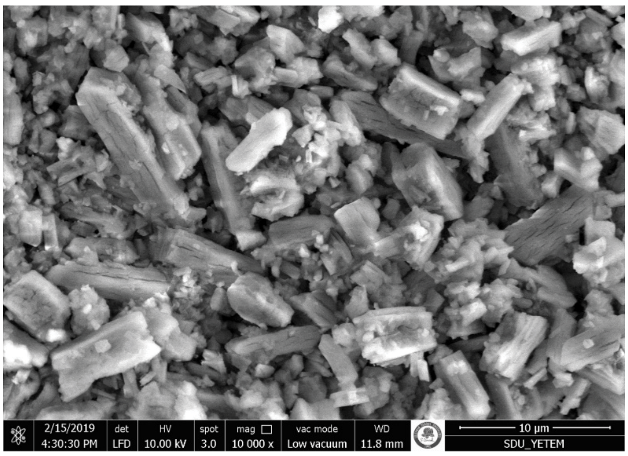


Fig. 7. FTIR spectrum of the dry precipitate obtained from hydrolyzed digested municipal sludge liquid by rhamnolipid.

(a)



(b)

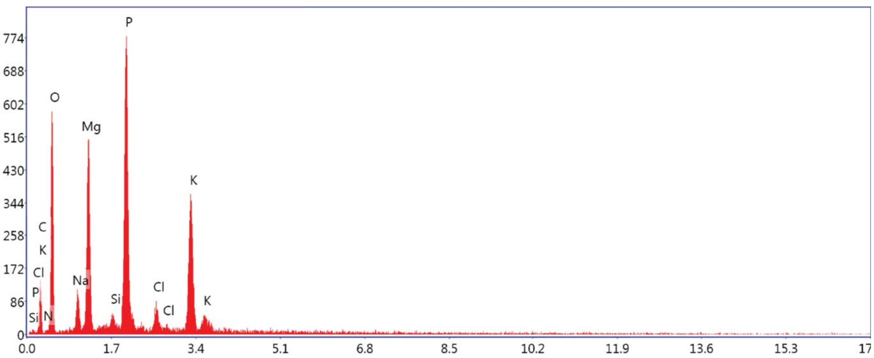


Fig. 8. Morphology and chemical composition of the dry precipitate obtained from hydrolyzed digested municipal sludge liquid using rhamnolipid as analyzed by SEM (a) and EDS (b).

Natural phosphorus deposits will only last for the next 30 to 60 years [22,25]. Sewage sludge is a very promising phosphorus resource because it is the second biggest source of phosphorus found worldwide [22]. Therefore, phosphorus recovery from sludge could provide a key solution to a future phosphorus shortage. Since the formation of struvite is used to recover nutrients from wastewater and sludge, vast quantities of phosphate and magnesium ions are needed to satisfy an equimolar ratio for magnesium, ammonium, and phosphate because the molar concentration of ammonia is generally much higher than these other two components of struvite [13,17]. To overcome this obstacle, efforts have been made to find cost-effective substitute sources of phosphate and magnesium. For inexpensive sources of magnesium, magnesite, brine, seawater, magnesium oxide and the by-products of nanofiltration of seawater have been proposed [17].

In this study, the nutrients released from the municipal sludge by rhamnolipids were recovered in the form of struvite. Struvite is known to be an environmentally friendly fertilizer because of its slow release properties [17]. Moreover, struvite can be used as a raw material for fire-resistant products and binding substances in cement [26]. However, low-cost production of biosurfactants and inexpensive magnesium sources for struvite formation on a large-scale application is required.

4. Conclusions

This study showed that rhamnolipid was an effective compound to release both metals and nutrients from municipal and industrial sludge. The amounts of Fe, Ni, Si, Zn and Cr released from industrial sludge using rhamnolipid were greater than those found using saponin. The maximum Cr, Fe and Zn removal efficiencies from industrial sludge were obtained at a rhamnolipid concentration of 7% and a 5/1 liquid /solid ratio. The amounts of Fe, Ni, Zn and Cr released from digested municipal sludge using rhamnolipid were greater than those found using saponin. The maximum Cr, Fe and Zn removal efficiencies from digested municipal sludge were obtained at a rhamnolipid concentration of 10% and a 10/1 liquid/solid ratio. The maximum nutrients release from digested municipal sludge were obtained at a rhamnolipid concentration of 10% and a 5/1 liquid /solid ratio. PO_4^{3-} and NH_4^+ released from digested municipal sludge using rhamnolipids were recovered by struvite crystallization. The formation of struvite obtained from hydrolyzed digested municipal sludge liquid was confirmed by FTIR, XRD, and SEM-EDS. The EDS results showed that the struvite contained 2.24% N, 10.82% Mg, 11.03% P, 5.37% K, and 4.11% Na by percentage weight.

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