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Removal of heavy metals in the presence of the biodegradable biosurfactant of sophorolipid from the municipal dewatered sludge

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ABSTRACT

The biodegradable biosurfactant sophorolipid was applied to extract heavy metals from the dewatered sludge. The extraction of Cu, Zn, Cr, Pb, Ni and Mn from the sludge with the presence of sophorolipid was investigated under the different conditions such as sophorolipid concentrations, pH values, contact times and liquid to solid ratios. Heavy metals fractions distribution before and after extraction with sophorolipid was also investigated. At the optimal sophorolipid concentration, extraction efficiencies of Cu, Zn, Cr, Pb, Ni and Mn were 35.90% ± 2.45%, 48.90% ± 3.14%, 65.42% ± 4.12%, 32.07% ± 2.15%, 65.34% ± 5.30% and 17.89% ± 2.14%, respectively. The extracted Zn, Ni and Cr mainly existed exchangeable fractions, reducible and oxidizable fractions, and Cu, Pb and Mn mainly existed exchangeable and oxidizable fractions, oxidizable and residual fractions, and exchangeable and residual fractions. This research indicated that the biodegradable biosurfactant sophorolipid enhance heavy metals extraction from the sludge and preserve nutrient elements in the treated sludge. Sophorolipid offer a particular insight in the effective extraction of heavy metals from dewatered sludge.

Keywords: Heavy metals; Extraction; Fraction; Distribution; Sludge

1. Introduction

Wastewater treatment plants (WWTPs) usually produce millions of tons sludge every year in the word [1]. Sludge contains high contents of the major plants nutrients, such as phosphorus, and organic matters, its land application has been considered as a best way for recycling this plant nutrients and organic matters [1,2]. The use of sludge in agricultural land has many advantages, which include providing the nitrogen, phosphorus and potassium for crops growth [3,4]. Meanwhile, the organic matters can ameliorate the soil's biophysical properties, increase the beneficial organisms community and reduce the synthetic fertilizers and pesticides [5]. However, the increasing trend toward combing municipal and industrial wastewater for treatment in WWTPs, which causes the high contents of heavy metal in sludge. In this sludge, the retained heavy metals may pose a secondary pollution or environmental risk to the ecosystem, and consequently destroyed human health through the food chain, heavy metals are non-biodegradable and accumulated in the environment, which restricts significantly the reuse of sludge [5,6]. It is important to find way for solving the problem is to reduce the heavy metals from dewatered sludge. Therefore, over the past few decades, many methods such as bioleaching methods, electrokinetic methods, chemical extraction, ion-exchange methods, thermal treatments, ultrasound-assisted nitric acid methods have been researched by many researchers [3,5,7–12]. Among them, chemical extraction of heavy metals has received extensive attention, due to its simple operation processes, the short operation times, and high removal efficiency for heavy metals in the sludge [3,11].

Chemical extraction mainly used the chemical reagents to reduce the contents of heavy metals for treatment. Previous studies have demonstrated that heavy metals extraction efficiency mainly depends on contact time, chemical reagent type, high temperature, low pH and long contact time could remove heavy metal extraction [3,13]. The chemical reagents

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can be inorganic acids (H_2SO_4, HNO_3 and HCl), organic acids (critic acid) and chelating agents (EDTA and NTA) [11]. These chemical reagents have been applied to extract heavy metals from the sludge efficiently. However, high removal efficiency demands a large number of dosages, which causes the difficulty in pH adjustment and high processing costs. In addition, these chemical reagents may pose secondary pollution through the groundwater and soil, due to their refractory nature. Therefore, it is vital to find an environmentally friendly biosurfactants to replace the inorganic acids, organic acids, and chelating agent.

Biosurfactants are biological surfactants that are produced by bacteria, fungi or marine microorganisms [14]. Biosurfactant is closely related to its ability to increase solubility, reduce surface tension, its good wetting, complex foaming capacity and detergency properties [14,15]. In comparison with the synthetic surfactants, biosurfactants have the following advantages: higher biodegradability and lower biological toxicity; better environmental compatibility; higher selectivity for organic compounds and metal ions; effectiveness at accelerating biodegradation and solubilization of low-solubility compounds; and less expensive and higher foaming. In addition, biosurfactants are less sensitive to salt, pH and temperature variations [16,17]. Due to the high binding capacity with heavy metal ions, the biosurfactants were applied to extract heavy metals from contaminated soils.

Sophorolipids are generated by the yeast *Torulopsis bombicola* [18]. High yields of the sophorolipid can be achieved from soybean oil and glucose (0.35 g/g substrate). Sophorolipids can reduce the surface tension to 33 mN/m and applied to release bitumen from tar sands [19]. Also, previous studies have demonstrated that sophorolipids can extract heavy metals from contaminated soils and sediments. Previous studies mainly focused on contaminated soils and sediments treatment [18–20]. However, to the best of our knowledge, few literatures reported the sophorolipids extract heavy metals from sludge. It is important to concern the heavy metals content and fractions distribution in the sludge when considering the utilization of sludge as agricultural land in the future.

In this study, sophorolipid has been used as an environmentally friendly chelating reagent to extract heavy metals from dewatered sludge. The extraction performances were evaluated by the removal of Cu, Zn, Cr, Pb and Mn from dewatered sludge, where the effects of sophorolipid concentration, contact time, pH value and liquid to solid ratio on the removal efficiency in the presence of sophorolipid were demonstrated. The extraction experiments were implemented under controllable conditions requiring additional treatments subject to environmental regulations of China. Moreover, all the tested heavy metals distribution in the dewatered sludge before and after the extraction with the aid of sophorolipid was evaluated using the modified BCR sequential extraction procedure.

2. Materials and methods

2.1. Source of dewatered sludge

Sewage sludge sample was collected from the Qun Li Urban Wastewater Treatment Plant (UWWTP), Harbin, China. The WWTP treats both industrial and domestic wastewater with domestic wastewater accounting for 60% of total wastewater. A total of 15 surface samples were collected from five sites in the study area. In each site, three samples were collected from the surface horizon (0–5 cm), and all the samples mixed for obtaining one sample in the waste treatment plant. Dewatered sludge sample was dried in an oven at 105°C for 24 h, followed by grinding and sieving to a size less than 74 μm, then the treated sludge sample was collected and stored in desiccators at room temperature.

2.2. Sophorolipid characteristics

Sophorolipid was purchased from Shandong Jin Mei Biotechnology Co., Ltd., Shandong, China. Sophorolipid is yellow liquid and purity is 52.00%. The critical micelle concentration and minimal surface tension of sophorolipid were 56.21 ± 50.35 mg/L and 34.23 ± 3.23 mN/m by the ring method at room temperature. The sophorolipid chemical structure was shown in Fig. 1 [19].

2.3. Extraction experiments

Heavy metals extraction experiments were conducted in 50 mL polyethylene centrifuge tubes. Different concentrations of sophorolipid were 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g/L, different contact times (0, 0.5, 1, 3, 5, 7, 9, 11, 15, 17, 19, 21, 23, 28, 33, 48, 60 and 72 h), different pH parameters (natural pH (5.25), 4.0, 7.0 and 10.0) and different liquid to solid ratios washing solution (*V*/*m* = 10, 25, 50, 75 and 100).

For each batch test, 0.5 g of sludge sample was suspended in the sophorolipid solution and the contact time was fixed at 24 h except for the effect of contact time experiments. Batch heavy metals extraction experiments were carried out in the designed ratios. Sophorolipid concentration was fixed at the optimum condition aside from the effect of different concentrations. The samples were shaken in a mechanical

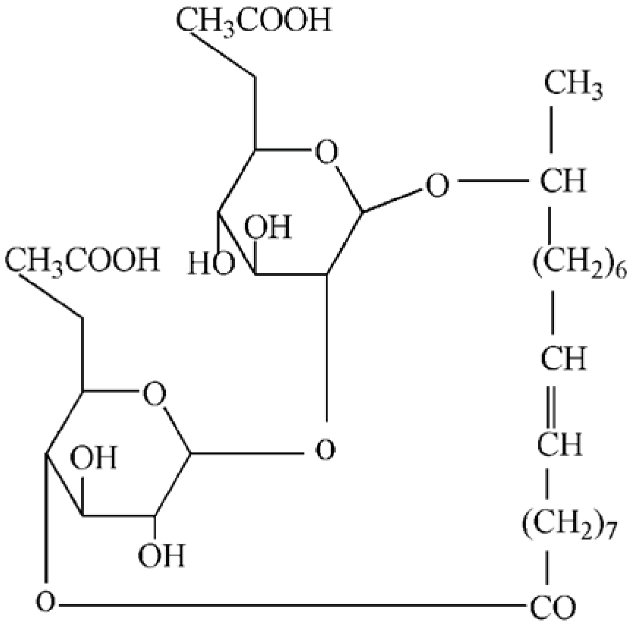

Fig. 1. Structure of sophorolipid.

shaker at 200 rpm at room temperature (25°C ± 2°C). At the end of the extraction experiments, the suspensions were centrifuged at 8,000 rpm for 15 min at 4°C and the supernatants filtered and analyzed the total heavy metals concentrations. The sludge residues were analyzed chemical fractions of heavy metals.

2.4. Sequential extraction experiments

To understand the effect of the process on the heavy metals chemical fractions in the dewatered sludge, sequential extraction was performed using the modified BCR (Community Bureau of Reference) method [13]. The four-step procedure was used as follows [13,21]:

Step 1: 20 mL of CH_3COOH 0.11 M was added to 0.5 g dry sludge and shaken overnight at a temperature of 25°C. The extraction mixture was centrifuged to separate the extract from the residue.
Step 2: 20 mL of 0.5 M $NH_2OH.HCl$ (adjusted to pH = 2.0 with nitric acid) was added to the residue and extracted overnight. Then, the same procedure as step 1 was followed.
Step 3: 5 mL of 8.8 M H_2O_2 was added to twice the residue from step 2, evaporated to near dryness, and then 25 mL of 1.0 M CH_3COONH_4 was added (adjusted to pH = 2 with HNO_3) at a temperature of 25°C. Then, the same procedure as step 1 was followed.
Step 4: The remaining residue at the end of the BCR procedure was digested by 7 mL HNO_3 + 2 mL HF + 1 mL $HClO_4$.

At each extraction step, the mixed suspensions were centrifuged at 8,000g for 15 min at 4°C and the supernatant samples were then filtered by a cellulose membrane with a pore size of 0.45 μm filter. The obtained residue was rinsed by deionized water and the filtrate was collected for the next step. The start of the next step in the extraction process was marked by adding the extraction agent into the sludge residue. At each step nitric acid was added to the filtrate 50 mL before analysis.

2.5. Analytical methods

The sludge pH value was measured by the pHS-3C pH meter (Shanghai, China). 0.5 g of dried sludge sample was pretreated by a SH230N heavy metals digestion instrument (Jinan, China) with strong acid digestion ($HCl–HNO_3–HClO_4$) mixture at 180°C–200°C. After finishing and cooling, the solutions were filtered through the filter into 50 mL glass tube and filled to the mark with dilute nitric acid. Heavy metals concentrations were analyzed using an Optima 5300DV inductively coupled plasma mass spectrometry (PerkinElmer, USA).

The removal efficiency (*R*) was calculate according to the following equation:

$$R = (C \times V)/(M \times m) \times 100\% \tag{1}$$

where *C* is the concentration of the heavy metals dissolved in the extraction solution (mg/L), *V* is the volume of the extraction solution (mL), *M* is the mass of the sludge sample (g) and *m* is the concentration of the heavy metals in the sludge sample (mg/kg). All the tests were performed in triplicates to evaluate the reproducibility of the results, and the average results were reported.

2.6. Statistical analysis

All the tests were performed in triplicates to evaluate the reproducibility of the results; all results were expressed as mean ± standard deviation of the means. The SPSS software (IBM SPSS, version 17) was used for statistical analysis of data.

3. Results and discussion

3.1. Sludge properties

Table 1 indicated the heavy metals contents in dewatered sludge sample, analytical values were reported on a dry weight basis. Cu, Zn, Cr, Pb, Ni and Mn concentrations were 1,261.11 ± 11.21, 681.51 ± 8.98, 212.52 ± 3.25, 67.50 ± 4.32, 126.11 ± 1.12 and 923.33 ± 21.22 mg/kg, respectively. Cu and Zn concentrations exceed the control standards for pollutants in sludge for agricultural use (500 and 250 mg/kg for acid soil where pH < 6.5, 1,000 and 500 mg/kg for alkaline soil where pH ≥ 6.5 for Zn and Cu, respectively). Use this sludge for agricultural land, it would lead to serious heavy metal contamination without treatment. Therefore, these heavy metals were investigated.

Table 1
Heavy metals contents in the sludge compared with Chinese legal standard

Parameters (unit)	Value	Acid soil (pH < 6.5)[a]	Alkaline soil (pH ≥ 6.5)[a]
Water content (%)	81.14 ± 2.16		
pH	7.15 ± 1.21		
Cu (mg/kg)	1,261.11 ± 11.21	250	500
Zn (mg/kg)	681.51 ± 8.98	500	1,000
Cr (mg/kg)	212.52 ± 3.25	600	1,000
Pb (mg/kg)	67.50 ± 4.32	300	1,000
Ni (mg/kg)	126.11 ± 1.12	100	200
Mn (mg/kg)	923.33 ± 21.22	–	–

Note: "–", not mentioned.
[a]National Standard of the People's Republic of China GB 4284-84: control standards for pollutants in sludges from agricultural use.

3.2. Effect of sophorolipid concentrations on the heavy metals extraction

The effect of sophorolipid concentrations on heavy metal extraction efficiency was shown in Fig. 2. As can be observed, the extraction efficiencies increased significantly with the increase of sophorolipid concentration from 0.0 to 2.0 g/L. This proves that the addition of sophorolipid as washing solution is an effective way to enhance the heavy metals removal from sludge. With the sophorolipid concentrations increased, heavy metals removal efficiencies decreased or slightly increased. Whereas, the difficulty of pH adjustment for sludge composting and the augment processing costs had to be considered. Therefore, the optimal sophorolipid concentration was 2.0 g/L.

Washing sludge with sophorolipid was effective for the extraction of all the tested heavy metals. At the optimal concentration, the highest extraction efficiency was observed for Cr (65.42% ± 4.12%). The lowest extraction efficiency was observed for Mn (17.89% ± 2.14%). The extraction efficiencies for heavy metals decreased in the order of Cr(65.42% ± 4.12%) > Ni(65.34% ± 5.30%) > Zn(48.90% ± 3.14%) > Cu(35.90% ± 2.45%) > Pb(32.07% ± 2.15%) > Mn(17.89% ± 2.14%). According to the results of Fig. 2, the extraction efficiencies for the heavy metals increased significantly with increasing sophorolipid up to 2.0 g/L. However, further increases in sophorolipid concentration from 2.0 to 3.0 g/L led to only a slight increase in the removal of heavy metals, due to heavy metals exchangeable and reducible fractions in the sludge were easily extracted and sophorolipid can partly extract the oxidizable and residual fractions.

Especially, Cu is mainly associated with the organic matter, the greatest removal efficiency is obtained in the oxidizable fraction of the sludge, due to the organic matter had a closer affinity with this type of element and formed stable complexes [22,23]. Zn indicated the greatest level of bioavailability due to the high content of metal mobilized in the exchangeable and reducible fractions. Pb and Mn were mainly associated with residual fractions in the sludge. Cr and Ni were mainly associated with oxidizable and residual fractions in the sludge. In this study, Cr and Ni obtained the higher extraction efficiencies than other heavy metals, due to sophorolipid extract the oxidizable and residual fractions. In this work, between heavy metals and mineral bond dissolution followed by the diffusion of the heavy metals in the sophorolipid washing liquid as an emulsion, complex or suspension represent the processes that control the removal of heavy metals from the sludge [19,24,25].

3.3. Effect of pH on the heavy metal extraction efficiency

The comparison study on the heavy metals extraction efficiencies at different pH values. As can be observed in Fig. 3, heavy metals extraction efficiencies decreased fast as pH value increases in the presence of sophorolipid. Without pH adjustment, Cu, Zn, Cr, Pb, Ni and Mn extraction efficiencies were 36.90% ± 1.90%, 45.91% ± 2.50%, 64.42% ± 6.45%, 31.07% ± 2.31%, 66.34% ± 5.67% and 19.89% ± 2.34%, respectively. It implied that the sophorolipid can extract heavy metals from the sludge effectively. At the pH = 4.0, heavy metals extraction efficiencies obtained the highest for Cu, Zn, Cr, Pb, Ni and Mn were 45.26% ± 3.90%, 50.19% ± 4.43%, 70.63% ± 3.21%, 35.83% ± 4.32%, 70.23% ± 3.43% and 25.23% ± 3.43%, respectively. According to Fig. 3, the tested heavy metals extraction efficiencies decreased fastly with the pH increased from 4.0 to 10.0.

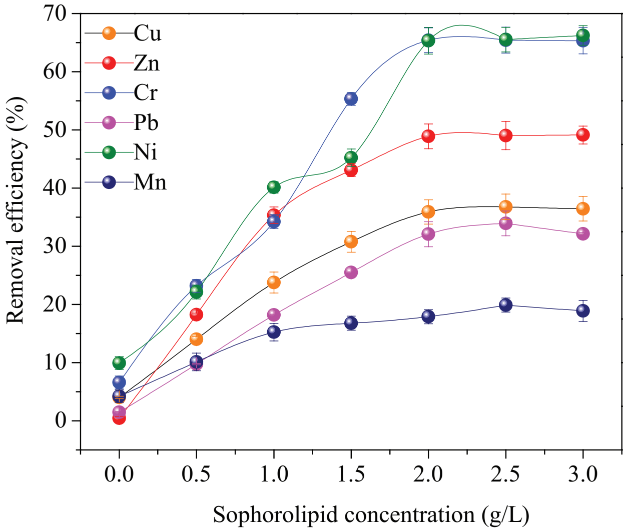

Fig. 2. Influence of sophorolipid concentrations on extraction of heavy metals (without pH adjustment, liquid to solid ratio = 50, contact time = 24 h).

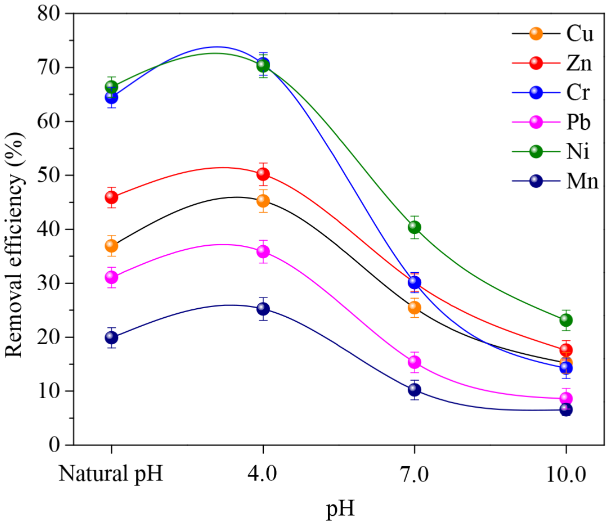

Fig. 3. Effect of the different pH values on heavy metals extraction efficiencies (sophorolipid concentrations = 2.0 g/L, liquid to solid ratio = 50, contact time = 24 h).

These results demonstrated that the pH values could enhance a significant effect on the extraction efficiency, where the acidic conditions with the sophorolipid enhance heavy metals extraction. Especially, Ni and Cr extraction efficiencies were significantly affected by the addition of sophorolipid. At pH = 4.0, Ni and Cr obtained the highest extraction efficiencies which were 70.23% ± 3.43% and 70.63% ± 3.21%, respectively. The removal of heavy metals was promoted in acidic conditions, due to the large amount of H^+ increases the solubility of sludge minerals, as well as the ion-exchange reaction between the solution and the sludge [16,17,26]. Also, the solution pH strongly affected the extraction of other heavy metals from sludge.

Under the natural pH (5.25), the heavy metal obtained a better extraction efficiency in the sophorolipid solution. These results indicated that sophorolipid enhanced heavy metals desorption from the sludge into the solution. Heavy metals extracted from the sludge via biosurfactant-associated complexation and ionic exchange; sophorolipid could form micelles and increase the negative zeta potential of the matrix; the lower surface tension and the ability to change heavy metals into liquid phase via the formation of complexes or micelles. Heavy metals mobilization processes in the sludge, including acidification, chelate effect of metal ions by other ligands, dissolution of sludge oxidative and reductive characteristics and targeted adsorption of other metal ions or anions. Metal ion hydroxide could be replaced easily, due to the hydrogen ions can improve oxide dissolution under the low pH value. Hydrogen ions are inferior competitive cations which can interchange the adsorptive heavy metals via the cation exchange mechanism, and with the hydrogen ion concentration increasing, the sludge particles surface generally obtain positive charge and becomes increasingly protonated to promote desorption of heavy metals which clarified heavy metals removal efficiencies were high at lower pH values [17,27].

3.4. Effect of contact time on the extraction of heavy metals

In order to obtain the optimum extraction performance of heavy metals, the effect of contact time on the removal efficiency was investigated. According to Fig. 4, the results show the kinetics of Cu, Zn, Cr, Pb, Ni and Mn extraction from the sludge sample using sophorolipid (2.0 g/L) with a contact time of 72 h. Fig. 4 indicated that heavy metals removal efficiencies increased with increasing of contact time within 24 h, however, only slow increase was observed after 24 h. The results indicated that Ni and Cr extraction efficiencies were much faster than other heavy metals. Mn extraction efficiency was the lowest in the heavy metals. Cu, Zn, Cr, Pb, Ni and Mn extraction efficiencies were 35.00% ± 2.12%, 50.00% ± 3.21%, 65.00% ± 3.90%, 36.00% ± 2.40%, 65.00% ± 2.65% and 18.00% ± 1.78%, respectively. The results demonstrated that Ni and Cr extraction efficiencies were much higher than Cu, Zn, Pb and Mn in the all contact time, due to the soluble fractions and the weaker chemical binding existed in sludge [28]. Heavy metals extraction efficiencies reached the equilibrium point at 24 h, and then kept constant from 24 to 72 h. Due to heavy metals precipitated or adsorbed inside the sludge, which could be either desorped or dissolved in the extraction process. After that, the heavy metals spread from the sludge matrix into the liquid. When heavy metals diffusion and adsorption reach the equilibrium point, it led to extraction efficiencies kept constant. Hence, heavy metals removal efficiencies kept constant when the contact time ranged from 24 to 72 h. The predominant mechanisms that were ion exchange, exchangeable H^+ cations and dissolution of carbonates, as the sophorolipid which contains, heavy metals extraction from the sludge with increasing H^+ concentration proceeds from an exchange process, which mainly involving protonation of oxide surface sites of sludge or exchange with absorbed heavy metals on the charge sites of sludge surface [18,19,24,25]. Therefore, the 24 h was selected as the optimum contact time for the experiments, the result was also similar with other reports regarding the contact time. This result can be elucidated the fact that the extraction efficiency was not changed with the increase of contact time once the reacting process reaches equilibrium.

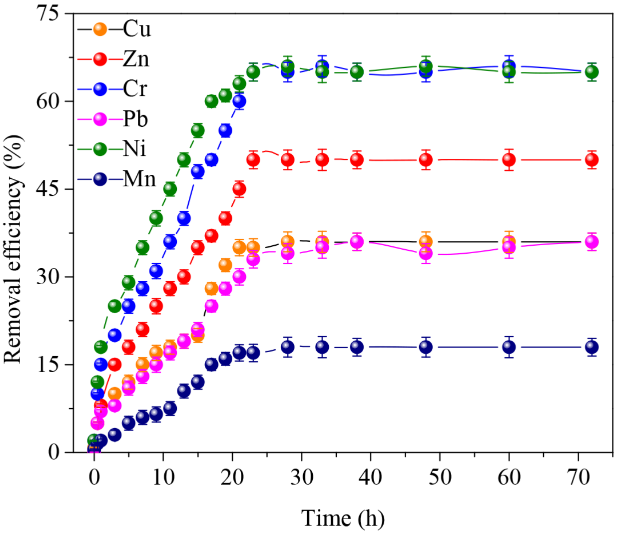

Fig. 4. Effect of contact time on the heavy metals extraction efficiencies (without pH adjustment, liquid to solid ratio = 50, temperature = 25°C, sophorolipid solution = 2.0 g/L).

3.5. Effect of liquid to solid ratio on heavy metals extraction

To understand heavy metals removal efficiencies affected by the liquid to solid ratio. The liquid to solid ratio range was 10–100 (Fig. 5). According to the results of Fig. 5, the heavy metal extraction efficiency increased significantly with increasing liquid to solid ratios from 10 to 50. However, further increases in liquid to solid ratios from 50 to 100 led to only a slight increase in the extraction of heavy metals. When the liquid to solid ratio is 10, Cu, Zn, Cr, Pb, Ni and Mn extraction efficiencies were 13.90% ± 2.11%, 25.90% ± 2.43%, 45.42% ± 2.11%, 11.07% ± 1.01%, 46.34% ± 1.23% and 10.89% ± 1.34%, respectively. At liquid to solid ratio = 25, the Cu, Zn, Cr, Pb, Ni and Mn extraction efficiencies were 25.46% ± 2.12%, 33.45% ± 1.89%, 52.43% ± 3.90%, 21.11% ± 2.93%, 55.43% ± 4.92% and 12.35% ± 2.11%, respectively. The liquid to solid ratio is 50, Cu, Zn, Cr, Pb, Ni and Mn migration efficiencies were 36.90% ± 2.89%, 45.90% ± 2.12%, 66.42% ± 2.11%, 31.07% ± 2.11%, 66.34% ± 4.32% and 19.89% ± 3.21%, respectively. The liquid to solid ratio is 75, the heavy metal obtained the highest extraction efficiency, and Cu, Zn, Cr, Pb, Ni and Mn extraction efficiencies were 37.45% ± 1.32%, 46.75% ± 2.12%, 65.34% ± 3.43%, 33.12% ± 2.56%, 60.34% ± 4.32% and 21.12% ± 4.32%, respectively. The liquid to solid ratios range were from 10 to 50. Heavy metals migrated or mobilized into the liquid phase, due to the heavy metals desorption and solubilization. At this stage, exchangeable and reducible fractions were easily dissolved into the solution. Liquid to solid ratio

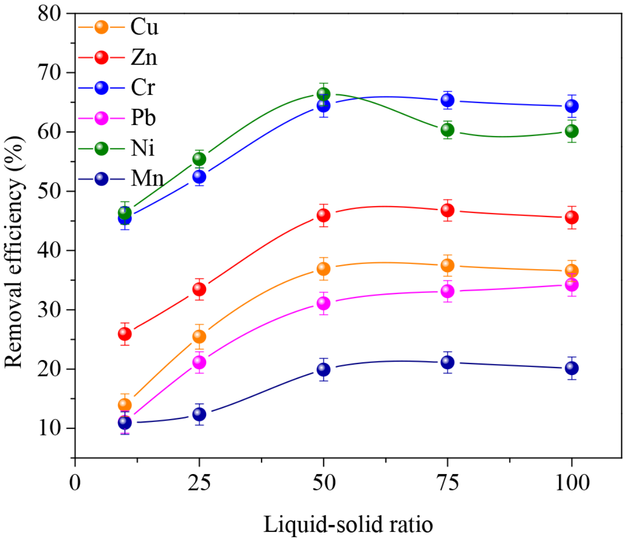

Fig. 5. Effect of liquid to solid ratio on heavy metals extraction efficiencies (without pH adjustment, temperature = 25°C, sophorolipid solution = 2.0 g/L, contact time = 24 h).

has great impact on liquid transferred into the sludge interspace and dissolved heavy metals ions. Therefore, the most optimal liquid to solid ratio has a good extraction efficiency. However, heavy metals extraction efficiencies increased slowly or decreased predominantly with the increasing liquid to solid ratio from 50 to 100. At this stage, oxidizable and residual fractions were difficult to extract. Also, the higher liquid to solid ratio led to heavy metal content was diluted, heavy metals transferred into the solution and reached equilibrium immediately. Meanwhile, the sludge particles could adsorb heavy metals ion from solution, a larger amount of inorganic and organic matter could be transferred from sludge particles into the solution [29]. In addition, Ni and Cr have higher removal efficiencies than other heavy metals, due to higher affinity toward functional groups, such as carboxyl and hydroxyl present in sophorolipid [19], which may enhance extraction of heavy metals from sludge. However, Mn and Pb obtained the lower extraction efficiencies than other heavy metals, due to Mn and Pb mainly existed oxidizable and residual fractions in the sludge. These fractions were difficult to remove from the sludge using the sophorolipid. Consider the heavy metal removal efficiency and the process cost. Therefore, the optimal liquid to solid ratio is 50.

3.6. Heavy metal fractions distribution before and after the extraction

The factors which affected the heavy metal extraction efficiency from the sludge included not only the sophorolipid concentrations and pH, but also the heavy metals fractions distribution and the total content in the sludge. The heavy metals fractions distribution in the sample sludge before and after extraction with sophorolipid was shown in Fig. 6. The test was performed at sophorolipid solution = 2.0 g/L and without pH adjustment. As can be observed in Fig. 6, Cu mainly existed oxidizable and residual fractions in the sludge before treatment. The percentage of oxidizable

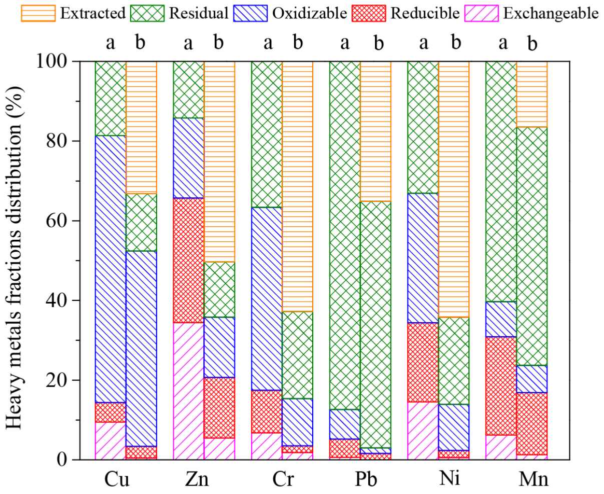

Fig. 6. Distribution of heavy metals fractions in the sludge before (a) and after (b) extraction with sophorolipid (without pH adjustment, temperature = 25°C, sophorolipid solution = 2.0 g/L, contact time = 24 h, liquid to solid ratio = 50).

and the residual fractions were 67.02% ± 3.89% and 19.41% ± 1.49%, respectively. Zn mainly existed exchangeable and reducible fractions, which percentages were 34.46% ± 1.82% and 31.25% ± 2.43%, respectively. Cr and Ni mainly existed oxidizable and residual fractions, which percentages were 45.88% ± 2.32%, 36.85% ± 2.23%, 32.54% ± 1.45% and 34.92% ± 3.21%. Pb mainly existed residual fraction, which percentage was 88.89% ± 5.43%. Mn predominately existed reducible and residual fractions, which percentages were 24.64% ± 3.89% and 60.90% ± 3.23%, respectively. Heavy metals exchangeable and reducible fractions could be easily released under the acidic condition. Also, heavy metals exchangeable and reducible fractions were sensitive to the environmental conditions, it can be easily extracted under the ordinary conditions. On the contrary, the oxidizable fraction could be partly extracted, the residual fraction is steady which is difficult to extract.

After treating the sludge, the heavy metals were predominantly existed residual fractions in the sludge, while the heavy metal exchangeable and reducible fractions decreased significantly. The results demonstrated that the sophorolipid mainly extracted exchangeable and reducible fractions from the sludge. After the extraction, the Cu, Zn, Cr, Pb, Ni and Mn exchangeable fractions removal efficiencies were 9.00% ± 1.21%, 29.00% ± 1.45%, 5.00% ± 1.23%, 0.59% ± 0.12%, 14.00% ± 1.32% and 5.00% ± 1.56%, respectively, reducible fractions removal efficiencies were 2.00% ± 0.89%, 16.00% ± 2.34%, 9.00% ± 1.34%, 3.00% ± 1.21%, 18.01% ± 1.12% and 9.00% ± 1.21%, respectively, oxidizable fractions removal efficiencies were 18.00% ± 1.45%, 5.00% ± 1.21%, 34.00% ± 2.21%, 6.00% ± 2.34%, 21.00% ± 2.11% and 2.00% ± 1.21%, respectively, residual fractions removal efficiencies were 7.00% ± 1.11%, 0.00% ± 0.23%, 4.00% ± 0.89%, 17.00% ± 1.34%, 10.00% ± 1.23% and 5.00% ± 1.11%, respectively. Meanwhile, the total removal efficiencies of Cu, Zn, Cr, Pb, Ni and Mn were 5.00% ± 1.21%, 2.00% ± 1.34%, 15.00% ± 1.34%, 27.00% ± 2.13%, 13.00% ± 1.32% and 1.00% ± 0.34%, respectively. Exchangeable and oxidizable fractions of Cu were extracted from the sludge, however, exchangeable and reducible fractions of Zn were extracted, oxidizable and residual fractions of Cr and Ni were removed, exchangeable and reducible fractions of Pb and Mn were extracted. The results demonstrated that prominent correlation between the heavy metal extraction efficiency and the fractions distribution before and after treatment. Additionally, according to Fig. 3, the heavy metals exchangeable and reducible fractions extraction efficiencies would be less effective with the pH increasing in the system. Therefore, without adjustment the pH in the system, which would be beneficial to the heavy metals extraction from the sludge. Also, it avoids adjusting the pH after treated sludge for compost.

Previous studies elucidated that the sophorolipid could effectively reduce the surface tension between soil surface and heavy metals. Therefore, increasing the heavy metals mobility from the soil which may lead to the desorption of inferior chemical bond heavy metals from the soil surface. The exchangeable and reducible fractions mainly extracted from the soil with the sophorolipid due to these fractions easily exchanged and chelated with the sophorolipid anion groups [18–20,24,25,30–32]. The sophorolipid can remove heavy metals or organic contaminants from the soils and sediments. Metal ions such as zinc, copper, lead, chrome, cadmium, nickel, manganese and mercury due to their complexation ability and anionic characteristic. Individual heavy metal could complex with monomers or micelles of sophorolipid, which substitute for other fractions except the exchangeable of heavy metals [18,31,32]. Fig. 6 demonstrates that the sophorolipid could enhance the insoluble into soluble fractions. Heavy metals might be combined with the monomers or micelles through ion-exchangeable reaction or through the metal-bridging mechanism which enhance heavy metals extraction from the sludge. Furthermore, the sophorolipid might ameliorate the humidity of the sludge in the process and particles of the sludge became more penetrable for the sophorolipid solution washing. Anion exchange between heavy metals and sophorolipid which was possible mechanism for elucidating heavy metals mobilization by sophorolipid. The sophorolipid adsorbed on the surface of mine tailings could augment the negative zeta potential of the mine tailings. Therefore, extraction of heavy metals through electrostatic repulsive interactions [17,33].

These results demonstrated that sophorolipid has a great potential for heavy metals removal and risk reduction from the sludge. The biodegradable biosurfactant sophorolipid was applied to enhance extraction of heavy metals from sediments, sludges, soils, either ex situ or in situ which could consider as promising method to improve the conventional extraction of heavy metals from the contaminant. Meanwhile, it may use as pretreatment approaches for sequential treatment approaches such as bioremediation, stabilization and reinforcement in electrokinetic removal contaminants from soil and sediment. The sophorolipid solution should be consider cyclic utilization, which led to the cost reduction.

3.7. Fertilizing characteristics preservation in sludge before and after treatment

The effects of extraction with the sophorolipid on the fertilizing properties of the sludge are shown in Table 2. Organic carbon in the sludge decreased from 289.45 ± 5.12 to 254.12 ± 4.23 g/kg after extraction, because some dissolved organic carbon being transferred into the solution. While, the total N (TN), total P (TP) and total K (TK) contents in the sludge were not obviously affected as a result of treatment with the sophorolipid. In China, the average contents in soil were 10.00–40.00 g/kg for organic matter, 0.44–0.85 g/kg for TP, 1.00–2.00 g/kg for TN and about 16.00 g/kg for TK [3]. In comparison with these values, the content of organic carbon, TN and TP in the after treatment sludge were higher. While the TK content in the before and after treatment sludge was lower than the average TK content in soil. Overall, these results indicated that the treated dewatered sludge can be used for agricultural land to improve fertilizer efficiency.

4. Conclusions

The biodegradable biosurfactant sophorolipid was employed to extract heavy metals from dewatered sludge. The extraction performances were studied by the extraction of Cu, Zn, Cr, Pb, Ni and Mn from the sludge, where the effects of sophorolipid concentration, pH value, contact time and liquid to solid ratio on the extraction efficiencies were evaluated. The sophorolipid property was related not only to the heavy metals extraction efficiencies, but also to the heavy metals fractions distribution, contact time of reaction, pH conditions, as well as the concentrations of sophorolipid. The results indicated that heavy metals removal efficiencies increased with the increased of sophorolipid concentration, contact time and liquid to solid ratio, and with the decreased of the original pH value of sophorolipid extraction solution. The optimal sophorolipid concentration was 2.0 g/L, extraction efficiencies of Cu, Zn, Cr, Pb, Ni and Mn were 35.90% ± 2.45%, 48.90% ± 3.14%, 65.42% ± 4.12%, 32.07% ± 2.15%, 65.34% ± 5.30% and 17.89% ±2.14%, respectively. The extracted Zn, Ni and Cr mainly came from exchangeable, reducible and oxidizable fractions, and Cu, Pb and Mn mainly came from exchangeable and oxidizable fractions, oxidizable and residual fractions, and exchangeable and residual fractions. This research indicated that the biodegradable biosurfactant sophorolipid, as potential substitute of the conventionally chelating agent (EDTA), supply particular insights in the effective extraction of heavy metals from dewatered sludge.

Table 2
Physicochemical properties of dewatered sludge before and after treatment with sophorolipid

Before or after extraction	Organic carbon (g/kg)	TN (g/kg)	TP (g/kg)	TK (g/kg)
Before extraction	289.45 ± 5.12	14.40 ± 1.21	22.59 ± 1.54	5.92 ± 3.21
After extraction	254.12 ± 4.23	12.54 ± 1.43	19.45 ± 1.11	4.56 ± 1.13

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