

Sorption of Cd(II) onto kaolin as a soil component and desorption of Cd(II) from kaolin using rhamnolipid biosurfactant

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Abstract

In this study, a microbial surfactant, rhamnolipid, was investigated for its potential to enhance recovery of Cd(II) from kaolin, a representative soil component. The study was divided into two parts. In the first part, the sorption of Cd(II) ions to kaolin was investigated as a function of pH and initial Cd(II) ion concentration. Kaolin was also shown to be a good sorbent for treatment of Cd(II) ions from waste waters. The equilibrium sorption capacity for Cd(II) ions was measured and extrapolated using the Langmuir, Freundlich, Redlich–Peterson, and Koble–Corrigan sorption models. The best correlation between experimental and model predicted equilibrium uptake was obtained using the Koble–Corrigan sorption model. The values of parameters of the Koble–Corrigan model were determined as $A = 11.13$ ($\text{mmol}^{1-b} \text{kg}^{-1} \text{L}^b$); $B = 0.39$ ($\text{L}^b \text{mmol}^{-b}$); $b = 0.48$. In the second part, the desorption of Cd(II) from kaolin was investigated as a function of pH, rhamnolipid concentration, and the amount of sorbed Cd(II) by kaolin. The highest Cd(II) desorption efficiency by rhamnolipid biosurfactant from kaolin was obtained at pH 6.8, at an initial Cd(II) ion concentration of 0.87 mM (4.42 mmol Cd(II)/kg kaolin) and at a rhamnolipid concentration of 80 mM and found to be 71.9% of the sorbed Cd(II). © 2006 Elsevier B.V. All rights reserved.

Keywords: Sorption; Desorption; Cadmium; Kaolin; Rhamnolipid

1. Introduction

Heavy metal contamination in soils and freshwater environments is one of the world's major environmental problems, posing significant risks to human health as well as to ecosystems. Growing attention is being given to the treatment of metal-contaminated soils, surface and subsurface water bodies. Because of its high toxicity and mobility in soil, the case of cadmium is of great interest. Cadmium is accumulated in roots, stems and leaves and in the edible parts of crops in the soil–plant system [1]. Cadmium has no known biological function, occurs with an average content of 0.2 mg kg^{-1} in the geosphere. The concentration of Cd in rocks range from 0.1 to 11 mg kg^{-1} . In soils with no anthropogenic inputs of Cd, soil solution concentrations could range from 0.3 to $22.5 \mu\text{g l}^{-1}$. Cd concentrations seldom exceed $10 \mu\text{g l}^{-1}$ in solutions of agricultural soils. Anthropogenic activities such as industrial waste

disposals, fertiliser application and sewage sludge disposals on land have also led to accumulation of Cd in soil [2]. The waste waters of nickel-cadmium batteries, pigments, stabilizers, coatings, alloys and specific compounds for electronics may contain undesirable amounts of Cd(II) ions. Non-ferrous metals (zinc, lead and copper), iron and steel, fossil fuels (coal, oil, gas, peat or wood), cement, and phosphate fertilizers may also contain Cd(II) as an impurity [3]. The recommended maximum tolerable intake of Cd by FAO/WHO is $70 \mu\text{g day}^{-1}$.

A number of remediation technologies have been applied for heavy metal contaminated soils such as soil excavation and transport of contaminated soil to hazardous waste sites for land-filling, thermal extraction for volatile metals (e.g. evaporation of mercury, arsenic and cadmium is required high temperatures such as 800°C), electrokinetics, solidification/stabilization, vitrification, chemical oxidation, soil flushing, and bioremediation [4–6]. Due to the great expense and time of traditional remediation, alternate cost-effective remedial techniques are needed.

Novel biochemistries using microorganisms and microbial products to remove heavy metals have been successfully applied

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to wastestreams such as sewage sludge, industrial effluents, and mine water [7–9]. Biosorption of metal-contaminated soils presents a more complex separation problem [10,11]. The mineral, organic matter composition and surface area of the soil will determine the amount of metal sorbed. Movement of metals in soils is also limited by soil texture, structure, and organic matter content. The size of a bacterial cell is approximately as large as 0.2 mm in diameter, whereas soil pores vary greatly in size ranging from less than 2 μm . Metal–cell complexes would be filtered out by the smallest pores and prevented transport through the soil. Other microbial products such as bacterial and algal exopolysaccharides also bind a variety of metals. Although exopolysaccharides exhibit strong affinities for oil–water interfaces, they differ from biosurfactants in that they are large, have molecular weight approximately 10^6 and have minimal surface activity. Biosurfactants may present a distinct advantage over exopolysaccharides in the remediation of soils because of their relatively small size (generally molecular weight <1500) [12–14].

Surfactants can be synthetic but are also naturally produced by plants, animals, and many different microorganisms. These molecules reduce surface and interfacial tensions in both aqueous solutions and hydrocarbon mixtures. Biosurfactants have the following advantages compared with synthetic surfactants: lower toxicity, higher biodegradability, better environmental compatibility, higher foaming, higher selectivity for metal ions and organic compounds, more tolerant to pH, salt and temperature variation, the ability to be synthesized from renewable sources, and in some cases less expensive. Biosurfactants can be classified as glycolipids, lipopeptides, phospholipids, fatty acids and neutral lipids. The largest and best-known group is the glycolipid group, which includes a form known as rhamnolipids [15–17].

Surface active materials adsorbed on interface reduce surface tension to a certain value. The amount of surfactant needed to obtain the lowest possible surface tension is defined as the critical micelle concentration (CMC). After CMC is reached, surface tension remains constant, and surfactants begin to form micelles [18]. At concentrations above the CMC, the rhamnolipid forms a variety of micellar, ≈ 5 nm in diameter, and vesicular structures, <50 nm in diameter, which depend on solution pH [14]. The surfactant molecules themselves spontaneously aggregate into complex structures such as micelles. A micelle is composed of a monolayer of surfactant molecules where the polar heads are oriented toward the surrounding aqueous solution and the nonpolar tails are oriented toward the hydrophobic center of the micelle. The anionic biosurfactant such as rhamnolipid carries a negative charge, so when the molecule encounters a cationic metal such as Cd(II) that carries a positive charge, an ionic bond is formed. This bond is stronger than the metal's bond with the soil. The polar head groups of micelles can bind metals. This makes the metals more soluble in water. Metal ions are bound to opposite charged ions or replace with same charged ions or complex with agents forming chelates on micelle surface. The micelles help recover the metals from the soil surfaces and move them into solution, making them easier to recover by flushing [13,19].

There are limited number studies published in the literature concerning the use of biosurfactants to recover metals [15]. Complexation of Cd(II), Pb(II), and Zn(II) from a Hayhook sandy loam soil [14], and Cd(II) from liquid media [12] by a monorhamnolipid biosurfactant was investigated. After exposure of the soil to a 1 mM concentration of Cd(II) ions, 73% of Cd(II) ($1.46 \text{ mmol kg}^{-1}$) was reported to sorb by the soil and 55.9% of the Cd(II) was showed to desorb by a 80 mM rhamnolipid solution [14]. Surfactin from *Bacillus subtilis*, rhamnolipid from *Pseudomonas aeruginosa* and sophorolipid from the yeast *Torulopsis bombicola* were used to remove Cu(II) and Zn(II) ions from a metal-contaminated sediment (110 mg/kg Cu(II) and 3300 mg/kg Zn (II)) [20]. A single washing with rhamnolipid was reported to remove 65% of the Cu(II) and 18% of the Zn(II), whereas sophorolipid removed 25% of the Cu(II) and 60% of the Zn (II). Surfactin was less effective, removing 15% of the copper and 6% of the zinc. Utilization of saponin, a plant-derived biosurfactant, was shown to be effective for recovery of heavy metals from soils, attaining 90–100% of Cd and 85–98% of Zn extractions [15].

The existence of toxic heavy metals at many of the contaminated sites all over the worldwide poses a severe threat to the environment. Very few technologies, such as soil washing and bioremediation, are available to treat these metal-contaminated wastes. However, these technologies may be ineffective due to several reasons such as inability to treat contaminants in low permeability soils or in soils containing high clay or iron oxide [19]. In the present study, the feasibility of using rhamnolipid biosurfactant for the recovery of Cd(II) from kaolin, low permeability soil, is investigated. Laboratory bench-scale bioremediation experiments were conducted in two stages using kaolin as a model low permeability clayey soil. In the first stage of experiments the sorption of Cd(II) ions by kaolin was investigated as a function of pH and initial Cd(II) ion concentration in solution. The Cd(II) sorption equilibrium on kaolin was characterized with sorption models such as Langmuir, Freundlich, Redlich–Peterson and Koble–Corrigan. In the second stage, the recovery or desorption of Cd(II) from kaolin using rhamnolipid biosurfactant was investigated as a function of pH, rhamnolipid concentration, loaded Cd(II) quantity per unit weight of kaolin (mmol Cd(II)/kg kaolin). As kaolin is thought as a low-cost natural sorbent, the results of the first and second stages can also be applied to the removal and recovery of Cd(II) ions from waste waters. Besides, the sorption of rhamnolipid by kaolin was investigated.

2. Materials and methods

2.1. Biosurfactant

The rhamnolipid biosurfactant (JBR 425) was supplied by Jeneil Biosurfactant Co. (Saukville, WI) as an aqueous solution of rhamnolipids at 25% concentration. It is produced from sterilized and centrifuged fermentation broth which has had all protein removed. Two major types of rhamnolipids, RLL (R1) and RLL (R2) are present in the solution. R1 ($\text{C}_{26}\text{H}_{48}\text{O}_9$) is L-rhamnosyl- β -hydroxydecanoyl- β -

Table 1
Chemical analysis of kaolin used in this study

Composition	Content (wt.%)
SiO ₂	48.04
Al ₂ O ₃	39.18
Fe ₂ O ₃	0.8
CaO	0.22
MgO	0.53
P ₂ O ₅	0.12
K ₂ O	2.78
Na ₂ O	0.17
LOI	8.16

hydroxydecanoate. R2 (C₃₂H₅₈O₁₃) is L-rhamnosyl-β-L-rhamnosyl-β-hydroxydecanoyl-β-hydroxydecanoate. The rhamnolipid used has a critical micelle concentration of 50 mg/L (≈0.1 mM) and a surface tension of 29 mN/m.

2.2. Kaolin

The component of soil, kaolin, was supplied from Söğüt Ceramic Factory, Bilecik, Turkey. It was ground and sieved to 0.140–0.425 mm size. Typical chemical properties of the kaolin used for sorption/desorption experiments are presented in Table 1. The analysis to this material revealed that it contain mainly silica and alumina, which they account for 87.22% of the total weight.

2.3. Rhamnolipid sorption by kaolin

The kaolin were autoclaved to inhibit biodegradation of rhamnolipid. To measure rhamnolipid sorption, 1.5 g of kaolin was placed into 40-mL centrifuge tubes, and then kaolin were suspended in 5 mL of varying concentrations of rhamnolipid (0–100 mM). Blind solutions contained the rhamnolipid solutions at the same concentration without added kaolin. The tubes were incubated for 48 h on a shaker at 150 rpm and at 25 °C, and then centrifuged. Rhamnolipid concentration in the supernatant was determined using surface tension analysis. Surface tension was measured using a surface tensiometer (KRÜSS) which employs the Du Nouy ring method of quantifying surface tension. To measure unadsorbed concentration of rhamnolipids, a calibration curve relating surface tension (mN/m) to rhamnolipid concentration (mM) was used.

2.4. Cd(II) sorption by kaolin

To investigate Cd(II) recovery by rhamnolipids from the kaolin, firstly the kaolin sorbed Cd(II). A 1.5 g of kaolin was placed into 40-mL centrifuge tubes and treated in 5 mL of metal ion solutions. Cd(II) solutions were prepared by diluting 8.9 mM stock solution of Cd(II), obtained by dissolving CdN₂O₆·4H₂O in distilled water. The range of concentrations of prepared Cd(II) ion solutions varied from 0.25 to 5.29 mM. Blind experiments were performed with the same metal ion solutions without added kaolin. The tubes containing Cd(II) ions and kaolin as a sorbent or the corresponding blind solution were incubated for 48 h on

a shaker at 150 rpm and at 25 °C. After reaching ultimate equilibrium, the tubes were centrifuged at 19,000 × g for 20 min and the supernatant was acidified to pH 2.0 with 1% HNO₃ for atomic absorption analysis. A calibration curve for Cd(II) was constructed using atomic absorption standard solutions that were diluted into 1% HNO₃. Sorbed Cd(II) concentration by kaolin was calculated from the difference between initial Cd(II) ion concentration in solution and Cd(II) ion concentration remained in the supernatant after sorption.

2.5. Recovery of Cd(II) by rhamnolipid biosurfactant from kaolin

The Cd(II)-loaded kaolin was suspended in 5 mL of varying concentrations of rhamnolipid (0–100 mM). The blind solution was used to determine whether distilled water alone recovered soil-bound Cd(II) or not. The centrifuge tubes containing kaolin mixed with rhamnolipid solution or the corresponding blind solution without added rhamnolipid were agitated on a shaker at 25 °C and 150 rpm for 72 h and then centrifuged at 19,000 × g for 20 min. The supernatant was analyzed for Cd(II) concentration by atomic absorption analysis. Rhamnolipid has a pK of 5.6 [21] and thus precipitates on acidification. The supernatant samples used for atomic absorption analysis were acidified to a pH < 2 using 0.1 mL of concentrated HNO₃ to precipitate the rhamnolipid. To recover the rhamnolipid pellets, each sample was centrifuged and then the supernatant was diluted in 1% HNO₃ for atomic absorption analysis.

3. Results and discussion

3.1. Sorption of rhamnolipid by Kaolin

Surfactants can be sorbed onto clay fractions, reducing their availability. Low sorption of surfactant to soil is a desirable surfactant characteristic. To determine the rhamnolipid availability for metal complexation, the sorption of rhamnolipid to kaolin was determined over a rhamnolipid concentration range of 12.5–100 mM. Rhamnolipid concentrations in aqueous phase were determined by surface tension analysis. At the lower rhamnolipid concentrations examined (12.5 and 25 mM), rhamnolipid sorption to kaolin was found to change between 23.2 and 33.2%. Liquid phase rhamnolipid concentration increased as the amount of rhamnolipid added was increased from 25 to 100 mM. At higher rhamnolipid concentrations (50 and 100 mM), rhamnolipid sorption was reduced to between 24.9 and 13.2%. Rhamnolipid sorption to kaolin was strongly affected by the presence of Cd(II) in kaolin. When 1 mM Cd(II) (4.8 mmol Cd(II)/kg kaolin) and 2.67 mM Cd(II) (8.92 mmol/kg) were added to kaolin, no rhamnolipid sorption was observed at all tested rhamnolipid concentrations.

3.2. Sorption of Cd(II) ions by kaolin

3.2.1. Effect of pH

The pH of the Cd(II) solutions was varied over the pH range of 6.0–7.4 to determine whether there was an effect of pH on

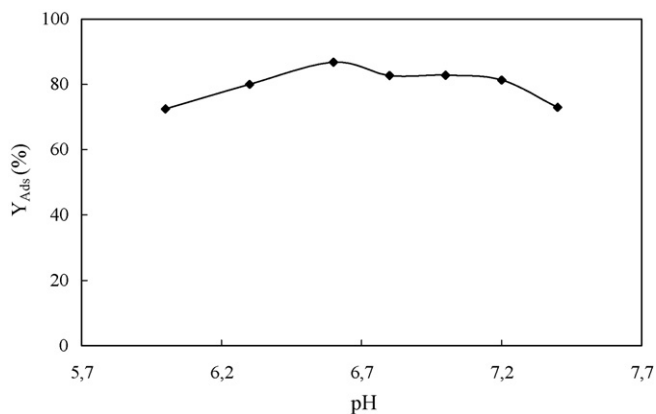


Fig. 1. Effect of pH on Cd(II) sorption efficiencies by kaolin ($C_{Cd,i}$, 0.94 mM; temperature, 25 °C; amount of kaolin, 1.5 g; stirring rate, 150 rpm).

sorption. There were several reasons for the chosen pH range. Because of aggregate morphology, the rhamnolipid biosurfactant is effective in this pH range. The pH range of 6.0–7.4 represents the natural pH value of low permeability clayey soil. Above pH 7.5, Cd(II) ions begin to precipitate in solution depending on solubility equilibrium. The sorption efficiency of Cd(II) ions by kaolin increased with increasing pH up to 6.6 at a constant initial Cd(II) ion concentration of 0.94 mM in solution, and determined as 86.8% (Fig. 1).

3.2.2. Sorption equilibrium of Cd(II) ions on kaolin

To determine the sorption isotherms, initial Cd(II) ion concentrations were varied between 0.25 and 5.29 mmol L⁻¹ while the kaolin weight in each sample was constant at 1.5 g. At an initial Cd(II) ion concentration of 0.25 mmol L⁻¹, 92.9% of the Cd(II) was bound to the kaolin. The Cd(II) sorption efficiencies of the kaolin decreased with increasing initial metal ion concentration (Fig. 2). This trend seems reasonable since the relative number of binding sites available to the metal ion would reduce as the concentration of the metal ion was increased, especially when the kaolin was nearly saturated at high initial concentrations. To quantify the agreement between the sorption models and experimental observations for the behaviour of

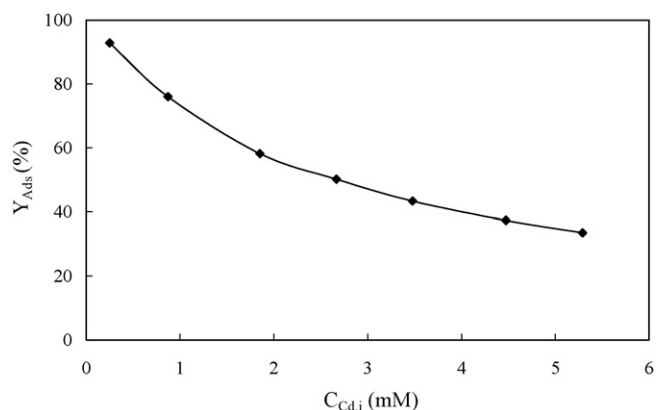


Fig. 2. Effect of initial Cd(II) concentration on Cd(II) sorption efficiencies by kaolin (pH, 6.8; temperature, 25 °C; amount of kaolin, 1.5 g; stirring rate, 150 rpm).

the Cd(II)–kaolin system, four different sorption models, Langmuir, Freundlich, Redlich–Peterson, and Koble–Corrigan were used.

The most widely used isotherm equation for modeling of the sorption equilibrium data is the Langmuir equation [22]:

$$q_{eq} = \frac{Q^0 K C_{eq}}{1 + K C_{eq}} \quad (1)$$

q_{eq} is the amount of solutes sorbed per unit weight of sorbent at equilibrium concentration, C_{eq} . Q^0 is the maximum amount of sorbed material required to give a complete monolayer on the surface, K is a measurement of relative sorption affinity and is a constant related to the energy of sorption. A large value of Langmuir constant, K , implies strong bonding.

The Freundlich expression is an empirical equation based on sorption onto a heterogeneous surface [23]:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

In this expression K_F and $1/n$ are characteristic constants relating to temperature, pH, sorbate and sorbent. K_F is an indication of the sorption capacity of the sorbent; $1/n$ indicates the effect of concentration on the sorption capacity and represents the sorption intensity. If sorption is favourable, then $n > 1$.

A further empirical isotherm has been developed by Redlich and Peterson, incorporating three parameters [24]:

$$q_{eq} = \frac{K_R C_{eq}}{1 + a_R C_{eq}^\beta} \quad (3)$$

where the exponent β , lies between 0 and 1. When $\beta = 1$, the Redlich–Peterson equation reduces to the Langmuir equation. If $a_R C_{eq}^\beta$ is much greater than 1, then it becomes the Freundlich equation. If $a_R C_{eq}^\beta$ is much less than 1, which occurs at low concentrations, then it becomes a linear isotherm equation.

Another Langmuir–Freundlich type isotherm equation is called as Koble–Corrigan sorption model and incorporates three parameters [25]:

$$q_{eq} = \frac{A C_{eq}^b}{1 + B C_{eq}^b} \quad (4)$$

When $b = 1$, the Koble–Corrigan equation reduces to the Langmuir equation. If $B C_{eq}^b$ is much less than 1, sorption is very low, then it becomes the Freundlich equation. If $B C_{eq}^b$ is much greater than 1, sorption is very high, the sorbed sorbate quantity per unit weight of sorbent at equilibrium remains constant and is defined by the following equation:

$$q_{eq} = \frac{A}{B} \quad (5)$$

Although the Langmuir and Freundlich models have been widely used to define equilibrium parameters of sorption, the application of the Redlich–Peterson and Koble–Corrigan equations to sorption is scarce in the literature.

The sorption model constants were estimated from the sorption data of Cd(II) ions on kaolin by using a DataFit

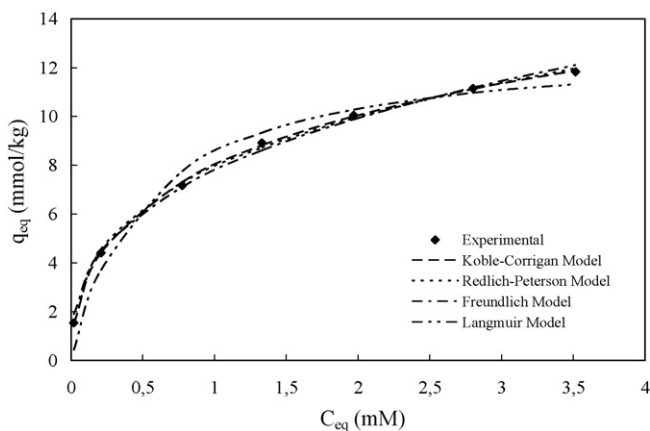


Fig. 3. Comparison of the Langmuir, Freundlich, Redlich–Peterson, and Koble–Corrigan sorption isotherms for Cd(II) sorption onto kaolin (pH, 6.8; temperature, 25 °C; amount of kaolin, 1.5 g; stirring rate, 150 rpm).

(trial version) computer program. The Langmuir, Freundlich, Redlich–Peterson and Koble–Corrigan sorption isotherms obtained at pH 6.8 for Cd(II) ions are shown in Fig. 3. In all the figures where metal uptake equilibrium data are shown, the model profiles are presented as dashed lines and the experimentally obtained values are given by symbol. The Langmuir, Freundlich, Redlich–Peterson and Koble–Corrigan constants and the residual sum of squares (SSE), standard error of the estimate (σ), coefficient of multiple determination (R^2) and adjusted coefficient of multiple determination (R_a^2) between the experimental values and the predicted values using the models are given in Table 2. Comparing the values of SSE, σ , R^2 and R_a^2 obtained from the sorption models shows that the fit between the experimental values and the predicted values using the models were generally very good for the various models except for the Langmuir model. However, the Koble–Corrigan model provided the best correlation for the sorption of Cd(II) ions by the kaolin.

Table 2
Comparison of the sorption isotherm coefficients and SSE, σ , R^2 and R_a^2 values between experimental and predicted values using by Langmuir, Freundlich, Redlich–Peterson and Koble–Corrigan models

Q^0 (mmol kg ⁻¹)	K (L mmol ⁻¹)	SSE	σ	R^2	R_a^2	
Langmuir model						
13.03	1.90	2.5949	0.7204	0.9694	0.9632	
K_F (mmol ⁿ kg ⁻¹ L ⁿ)	n	SSE	σ	R^2	R_a^2	
Freundlich model						
7.78	2.84	0.3396	0.2606	0.9960	0.9952	
K_R (L kg ⁻¹)	a_R (L ^{β} mmol ^{-β})	β	SSE	σ	R^2	R_a^2
Redlich–Peterson model						
220.16	26.75	0.69	0.1130	0.1681	0.9987	0.9980
A (mmol ^{1-b} kg ⁻¹ L ^{b})	B (L ^{b} mmol ^{-b})	b	SSE	σ	R^2	R_a^2
Koble–Corrigan model						
11.13	0.39	0.48	3.68×10^{-2}	9.59×10^{-2}	0.9996	0.9993

3.3. Desorption of Cd(II) from contaminated kaolin using rhamnolipid biosurfactant

3.3.1. Effect of pH

The medium pH must be optimized to minimize the size of the metal–ligand complex, thus preventing filtration by small kaolin pores. At concentrations above the critical micelle concentration, the rhamnolipid forms a variety of micellar and vesicular structures which depend on solution pH. At pH 5.0, rhamnolipid begins to visibly precipitate out of solution. The structures are predominantly small vesicles and micelles at pH > 6.0 [14]. For that reason, the pH of the medium was varied over the pH range of 6.0–7.4 to determine whether there was an effect of pH on complexation. The best recovery efficiency, 70.6–70.2% of the sorbed Cd(II), was achieved by adjusting the initial pH value to 6.8–7.0 at 1.15 mM initial Cd(II) ion concentration in solution (6.3 mmol Cd(II)/kg kaolin) and at 80 mM rhamnolipid concentration. Recovery efficiencies of Cd(II) showed more intense increase with increasing pH in the range 6.0–6.8, compared to the decrease in the pH region between 7.0 and 7.4 (Fig. 4). The possible mechanisms for the recovery of heavy metals by surfactants were reported to include ion exchange, precipitation-dissolution and counterion association [26]. The metals are removed by forming complexes with the surfactants on the soil/soil-component surface. The detachment of metal ions from the soil/soil component into the soil solution occurs due to the lowering of the interfacial tension, and therefore association with surfactant micelles [6]. Different rhamnolipid structures that are strictly dependent on pH can form. At a low pH ($4.3 < \text{pH} < 5.8$), the rhamnosyl moiety is at least 50% unchanged and rhamnolipids form liposome-like vesicles. Between pH 6.0 and 6.6, rhamnolipids form either lamella-like structures ($6.0 < \text{pH} < 6.5$) or lipid aggregates ($6.2 < \text{pH} < 6.6$). When the rhamnosyl moiety is negatively charged above pH 6.8, micelles form [18,19]. As expected, the anionic surfactants like rhamnolipids give better results because the cationic metals have an affinity for the negatively charged surfactants. The biosurfactant used in this study could also allow more metal recovery due to the more

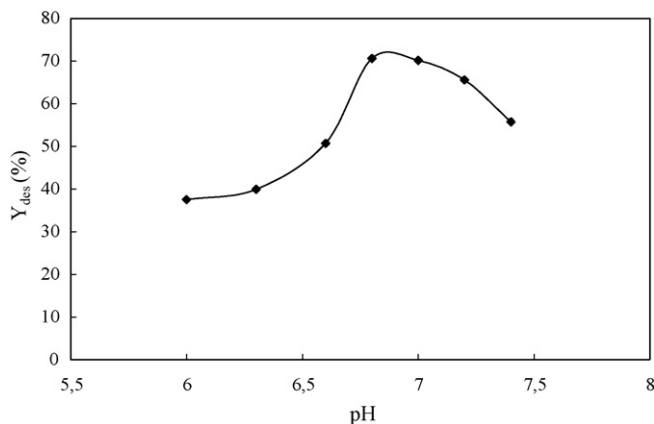


Fig. 4. Effect of pH on Cd(II) desorption efficiencies from kaolin using rhamnolipid biosurfactant ($C_{\text{rhamnolipid conc.}}$, 80 mM; temperature, 25 °C; amount of kaolin, 1.5 g; stirring rate, 150 rpm).

effective interfacial surface tension lowering. The surface tension of rhamnolipid solutions is also quite sensitive to pH. The surface activity of the rhamnolipid was reported to be highest between pH 7.0 and 7.5. As the pH was increased above 7.5, a slight decrease in surface activity was observed that resulted in a small increase in surface tension. As the pH was decreased from 7.0 to 5.0, surface activity decreased significantly, resulting in a considerable increase in surface tension [18].

3.3.2. Effect of amount of Cd(II) loaded to kaolin

After contact of the kaolin to Cd(II) solutions in the range of concentrations varying from 0.25 to 5.29 mM, the amounts of desorbed Cd(II) by the rhamnolipid biosurfactant were determined. Desorption of Cd(II) was found to be dependent on initial Cd(II) ion concentration in solution or the amount of Cd(II) loaded to the kaolin, and increased with increasing metal ion concentration in solution up to 0.87 mM or metal-ion loading to the kaolin up to 4.42 mmol kg⁻¹ (Fig. 5). At this metal loading and at 80 mM rhamnolipid concentration, 71.9% of the sorbed Cd(II) was recovered from the kaolin.

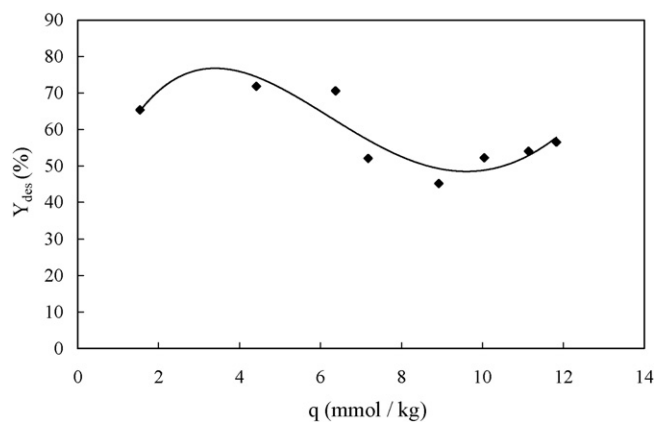


Fig. 5. Effect of amount of Cd(II) loaded to kaolin on Cd(II) desorption efficiencies (pH, 6.8; $C_{\text{rhamnolipid conc.}}$, 80 mM; temperature, 25 °C; amount of kaolin, 1.5 g; stirring rate, 150 rpm).

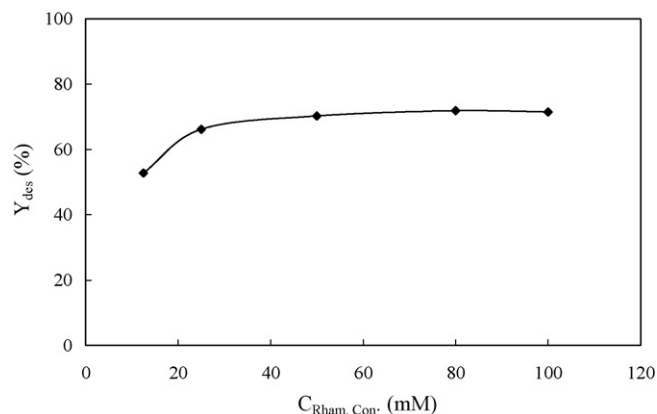


Fig. 6. Effect of rhamnolipid concentration on Cd(II) desorption efficiencies (pH, 6.8; temperature, 25 °C; amount of kaolin, 1.5 g; stirring rate, 150 rpm).

3.3.3. Effect of rhamnolipid concentration

When the initial Cd(II) ion concentration was held constant as 1.0 mM (4.8 mmol Cd(II)/kg kaolin), the rhamnolipid concentration was varied from 0 to 100 mM and it was seen that this affected the amount of metal removed from kaolin. The Cd(II) complexation efficiency increased with increasing rhamnolipid concentration up to 50–100 mM, and Cd(II) recovery efficiency reached a plateau value of 70.3–71.5% of the sorbed Cd(II) (Fig. 6). Therefore, the most convenient rhamnolipid concentration range seems to be approximately 50–100 mM for kaolin treatment to avoid introduction of excess rhamnolipids into soils containing kaolin as a dominant component. High concentrations of biosurfactant solutions are often required to overcome dilution and losses of the biosurfactant due to binding on the soil/soil component. However, there are many reasons to avoid injection of excess biosurfactant into soils. Firstly use of excess biosurfactant is not desired in point of process economy. Although the degree of biodegradability and toxicity of the rhamnolipid biosurfactant meet the EPA requirements, secondly use of excess biosurfactant may be lead to another environmental pollution. Higher concentrations of biosurfactants can also result in plugging in soil pores by the dispersion of fine materials, or by the formation of viscous emulsions [6].

4. Conclusions

In application of rhamnolipid as soil-washing agent to metal-contaminated soils, the efficiency of rhamnolipid treatment process must be improved. To do this, rhamnolipid sorption to soil must be minimized. High kaolin content of soil seems to provide a good advantage. Rhamnolipid biosurfactant was seen to be weakly sorbed to kaolin. At rhamnolipid concentrations higher than 80 mM, sorption to kaolin was lower than 17.7% of the rhamnolipid added. Moreover, the presence of Cd(II) ions in kaolin prior to addition of the rhamnolipid was found to prevent the sorption of rhamnolipid. A number of different rhamnolipid structures that are dependent on pH can form. The type of rhamnolipid structure formed is especially sensitive to pH in the range of 6.0 to 7.5. The best recovery efficiency was achieved by adjusting the initial pH value to 6.8–7.0. When the

kaolin was treated with 0.87 mM Cd(II) solution, 76.0% of the Cd(II) ($4.42 \text{ mmol kg}^{-1}$) was sorbed, and 71.9% of the sorbed Cd(II) was recovered by a 80 mM rhamnolipid solution. In our previous study, the urban soil which has a high clay content was used. After 0.96 mM Cd(II) solution was loaded to the urban soil, 92.6% of the Cd(II) ($2.98 \text{ mmol kg}^{-1}$) was sorbed, and 54.3% of the sorbed Cd(II) was recovered by a 70 mM rhamnolipid solution (unpublished data). Components of the urban soil other than clay may have been increased the removal of Cd(II) from liquid phase, and hindered the recovery of Cd(II) from the urban soil using rhamnolipid biosurfactant.

In summary, these results suggest that rhamnolipid technology as soil-washing process can be used successfully in the remediation of heavy metal contaminated kaolin, low permeability clayey soil. However, little is currently known about the desorption of heavy metal ions by biosurfactants from various clay minerals and other soil components. The heterogeneities that occur in soil composition, texture, structure, and organic matter content limit success of recovery process of heavy metal ions from soils using rhamnolipid biosurfactant. To propose success of the process on a certain type of soil, the heavy metal recovery capacity of rhamnolipid biosurfactant from components constituting that soil must be known exactly. Otherwise, increasing number of experiments performed on various types of soils will not enough to obtain expected results for simulation of real heavy metal-polluted environment.

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References

- [1] T. Lebeau, D. Bagot, K. Jézéquel, B. Fabre, Cadmium biosorption by free and immobilised microorganisms cultivated in a liquid soil extract medium: effects of Cd, pH and techniques of culture, *Sci. Total Environ.* 291 (2002) 73–83.
- [2] K. Vig, M. Megharaj, N. Sethunathan, R. Naidu, Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review, *Adv. Environ. Res.* 8 (2003) 121–135.
- [3] A.I. Zouboulis, M.X. Loukidou, K.A. Matis, Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils, *Process Biochem.* 39 (2004) 909–916.
- [4] K.R. Reddy, U.S. Parapudi, S.N. Devulapalli, C.Y. Xu, Effects of soil composition on the removal of chromium by electrokinetics, *J. Hazard. Mater.* 55 (1997) 135–158.
- [5] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Remediation technologies for metal-contaminated soils and groundwater: an evaluation, *Eng. Geol.* 60 (2001) 193–207.
- [6] S. Wang, C.N. Mulligan, Rhamnolipid foam enhanced remediation of cadmium and nickel contaminated soil, *Water Air Soil Pollut.* 157 (2004) 315–330.
- [7] Y. Sağ, Biosorption of heavy metals by fungal biomass and modeling of fungal biosorption: a review, *Sep. Purif. Meth.* 30 (2001) 1–48.
- [8] F. Veglio, A. Esposito, A.P. Reverberi, Standardisation of heavy metal biosorption tests: equilibrium and modelling study, *Process Biochem.* 38 (2003) 953–961.
- [9] K.A. Matis, A.I. Zouboulis, N.K. Lazaridis, I.C. Hancack, Sorptive flotation for metal ions recovery, *Int. J. Miner. Process.* 70 (2003) 99–108.
- [10] C.-C. Lin, H.-L. Lin, Remediation of soil-contaminated with the heavy metal, *J. Hazard. Mater.* A122 (2005) 7–15.
- [11] G.M. Gadd, Microbial influence on metal mobility and application for bioremediation, *Geoderma* 122 (2004) 109–119.
- [12] H. Tan, J.T. Champion, J.F. Artiola, M.L. Brusseau, R.M. Miller, Complexation of cadmium by a rhamnolipid biosurfactant, *Environ. Sci. Technol.* 28 (1994) 2402–2406.
- [13] R.M. Miller, Biosurfactant-facilitated remediation of metal-contaminated soils, *Environ. Health Perspect.* 103 (1995) 59–62.
- [14] D.C. Herman, J.F. Artiola, R.M. Miller, Removal of cadmium, lead, and zinc from soil by a rhamnolipid biosurfactant, *Environ. Sci. Technol.* 29 (1995) 2280–2285.
- [15] K.-J. Hong, S. Tokunaga, T. Kajuchi, Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils, *Chemosphere* 49 (2002) 379–387.
- [16] S.H. Kim, E.J. Lim, S.O. Lee, J.D. Lee, T.H. Lee, Purification and characterization of biosurfactants from *Nocardia* sp. L-417, *Biotechnol. Appl. Biochem.* 31 (2000) 249–253.
- [17] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Surfactant-enhanced remediation of contaminated soil: a review, *Eng. Geol.* 60 (2001) 371–380.
- [18] Y. Zhang, R.M. Miller, Enhanced octadecane dispersion and biodegradation by a *Pseudomonas* rhamnolipid surfactant (biosurfactant), *Appl. Environ. Microbiol.* 58 (1992) 3276–3282.
- [19] L. Frazer, Innovations, lipid lather removes metals, *Environ. Health Perspect.* 108 (2000) A320–A323.
- [20] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Heavy metal removal from sediments by biosurfactants, *J. Hazard. Mater.* 85 (2001) 111–125.
- [21] Y. Ishigami, Y. Bama, H. Nagahora, H. Yamaguchi, H. Nakahara, T. Kamata, The pH-sensitive conversion of molecular aggregates of rhamnolipid biosurfactants, *Chem. Lett.* 5 (1987) 763–766.
- [22] L. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [23] H. Freundlich, Ueber die adsorption in Loesungen, *Zeitschrift Physikalische Chemie* 57A (1907) 385–470.
- [24] O. Redlich, D.L. Peterson, A useful adsorption isotherm, *J. Phys. Chem.* 63 (1959) 1024–1029.
- [25] R.A. Koble, T.E. Corrigan, Adsorption isotherms for pure hydrocarbons, *Ind. Eng. Chem.* 44 (1952) 383–387.
- [26] R.A. Doong, Y.W. Wu, W.G. Lei, Surfactant enhanced remediation of cadmium contaminated soils, *Water Sci. Technol.* 37 (1998) 65–71.