

A comparative study for the sorption of Cd(II) by soils with different clay contents and mineralogy and the recovery of Cd(II) using rhamnolipid biosurfactant

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Abstract

Recent research has demonstrated that biosurfactants, especially rhamnolipids, can enhance recovery of soil-bound metals. To propose the success of remediation process of soils by rhamnolipids, both sorption and desorption characteristics of soils having different clay mineralogy should be known exactly. To assess sorption of Cd(II), batch equilibrium experiments were performed using three soils characterized with different proportions of clay minerals from Eskişehir region of Turkey. Soil pH, initial metal concentration and clay mineralogy affected the sorption process. For comparisons between soils, the sorption process was characterized using the Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan sorption models. The Freundlich model showed the best fit for the Cd(II) sorption data by the soils, while the Langmuir-type models generally failed to describe the sorption data. Soils with higher clay content characterized by having smectite as a dominant component had the greatest sorption capacity and intensity estimated by the K_F and n parameters of the Freundlich model. The soil C has the highest sorption efficiency of 83.9%, followed by soils B and A with sorption efficiencies of 76.7% and 57.9%, respectively. After the soils were loaded by different doses of Cd(II), batch washing experiments were used to evaluate the feasibility of using rhamnolipid biosurfactant for the recovery of Cd(II) from the soils. The Cd(II) recovery of the soils were investigated as a function of pH, amount of Cd(II) loaded to the soils, and rhamnolipid concentration. Cd(II) recovery efficiencies from the soils using rhamnolipid biosurfactant decreased in the order of soil A > soil B > soil C. This order was the reverse of the Cd(II) sorption efficiency order on the soils. When 80 mM rhamnolipid was used, the recovery efficiencies of Cd(II) from the soils A, B, and C was found to be 52.9%, 47.7%, 45.5% of the sorbed Cd(II), respectively. Rhamnolipid sorption capacity of the soils in the presence of Cd(II) ions decreased in the order of soil A > soil B > soil C.

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1. Introduction

Metals are found in soils as natural ingredients. However, in the last quarter of a century, considerable changes in the worldwide resources of heavy metals at the earth's surface have occurred. Anthropogenic activities such as industrial waste disposals, fertiliser application and sewage sludge disposals on land can result in significant input of heavy metals [1,2]. The presence of even low concentrations of heavy metals in the soils are known to have potential impact on environmental quality

and human health via ground water, surface water, plants and agricultural products. The case of cadmium is of great interest because of its high toxicity and mobility in soil. In some cases it would be necessary to reduce the amount of cadmium in the soils [3,4]. Nevertheless, for economic and also technical reasons, the cleaning-up of metal-polluted soils cannot be realised by conventional treatments used in the industry.

As metals in the contaminated sites are not degraded, they must be either immobilized or removed. Metal immobilization, removal and recovery are complex processes that require an understanding of the behavior of metals in the environment. The complexity arises because metal behavior is dependent on a variety of factors including metal speciation, complexation, precipitation, and sorption–desorption reactions. These reactions

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are defined by mineral composition and soil chemical properties, as well as variable environmental conditions such as pH, salinity, and redox [5–8].

The use of surfactants to enhance the removal of soil contaminants has received increasing attentions in recent years. Surfactants promote the wetting, solubilization, and emulsification of various types of organic and inorganic contaminants. They are amphiphilic molecules with both hydrophilic and hydrophobic portions. They act as a bridge between the air and liquid interface, and reduce the surface tension of water to approximately 25 ± 5 mN/m [9,10]. Biosurfactants can be biologically produced by yeasts or bacteria from substrates such as sugars, oils, alkanes and wastes. 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 of approximately 10^6 and have minimal surface activity. Biosurfactants have low molecular masses ranging from 500 to 1500 Da [11–13]. Other distinct advantages of biosurfactants over synthetic surfactants include higher selectivity for metals and organic compounds [5], lower toxicity, higher biodegradability, higher foaming [9], better environmental compability, less expensive, more tolerant to pH, salt, and temperature variation [11], the ability to be synthesized from renewable feedstocks, and the possibility to be produced them in situ at contaminated sites [12,13]. Solubility and surface-active properties of biosurfactants are also dependent on orientation of residues. Biosurfactants can be classified into several groups: glycolipids, lipopeptides, lipopolysaccharides, phospholipids, and fatty acids/neutral lipids. The largest and best-known group is the glycolipid group, which includes a form called as rhamnolipids. *Pseudomonas* sp. produce rhamnolipids either as the monorhamnolipid (R1) form, or more frequently, as a mixture of the mono- and dirhamnolipid (R2) forms [14,15].

The amount of surfactant needed to obtain the lowest possible surface tension is defined as the critical micelle concentration (CMC). Biosurfactants have low critical micelle concentrations (CMCs) ranging from 1 to 200 mg/L [10]. Rhamnolipid has a very low CMC indicating the strong surface activity shown at low concentrations (50 mg/L or ≈ 0.1 mM). In aqueous solutions, rhamnolipid is characterized by low surface tension (29 mN/m) for water and electrolyte solutions with very low interfacial tensions for water/hydrocarbon systems. Rhamnolipid is an excellent emulsifier and co-emulsifier for a wide range of organic solvents. Rhamnolipid can also produce stable close-celled foams in aqueous solutions and acts as a foam stabilizer for other surfactants [16,17]. Because of the reasons mentioned above, rhamnolipid is used in a wide range of application areas in environmental remediation as soil washing to remove hydrocarbons and heavy metals, wastewater treatment to remove hydrocarbons and heavy metals, and chelating agent [11].

After CMC is reached, surface tension remains constant, and surfactants begin to form 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 [18]. The possible mechanisms for the extraction of heavy metals by biosurfactants are ion exchange, precipitation–dissolution, and counterion binding. 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 [9,19]. Metal ions are bound to oppositely charged ions or replace the same charged ions (electrostatic interactions or ion exchange) or complex with agents forming chelates on the micelle surface. The polar head groups of micelles can bind metals. This makes the metals more soluble in water. Surfactant monomers likely acted to solubilize adsorbed Cd through formation of dissolved complexes. In addition, some binding of Cd(II) may occur to the anionic exterior of rhamnolipid micelles. Surface tension will predominately influence sorption that occurs through hydrophobic interactions such as partitioning of non-ionic organic compounds rather than metals. However, it is also postulated that the metals are removed by forming complexes with the biosurfactants on the soil surface, being detached into the soil solution due to the lowering of the interfacial tension, and hence associating with surfactant micelles [20–24].

Soil composition, clay mineralogy, permeability, pH, cation exchange capacity, particle size and other factors such as the presence of competing ligands, the ionic strength of the soil and the simultaneous presence of competing metals and contaminants significantly affect sorption–desorption processes and leaching potential through a soil profile [25,26]. Soil washing by biosurfactants and remediation 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 [22].

In the first part of the studies, we have undertaken batch equilibrium experiments to generate Cd(II) sorption isotherms using three soils characterized with different proportions of clay minerals. Results were characterized and compared for different soils using the sorption models, the total Cd(II) retained in the soils, soils characteristics (clay mineralogy). In the second part of the studies, we have evaluated the feasibility of using the rhamnolipid biosurfactant, to enhance the recovery of Cd(II) from the different soils by washing. The effects of pH, amount of Cd(II) loaded to soils, rhamnolipid concentration on the recovery of Cd(II) from the soils by rhamnolipid have been investigated. Sorption of rhamnolipid by the soil matrix components is a serious limitation to successful treatment applications. The objective of this study is also to determine the sorption of rhamnolipid on the soils characterized with different clay mineralogy.

2. Materials and methods

2.1. Biosurfactant

The rhamnolipid used (JBR 425) was obtained from Jeneil Biosurfactant Co., Llc, Saukville, WI. JBR 425 is an aqueous solution of rhamnolipids at 25% concen-

tration. It is produced from sterilized and centrifuged fermentation broth which has had all protein removed. The rhamnolipid used is a mixture of two major rhamnolipids, monorhamnolipid, α -L-rhamnopyranosyl- β -hydroxydecanoate (R1: C₂₆H₄₈O₉) of molecular mass 504 Da and dirhamnolipid, 2-O- α -L-rhamnopyranosyl- α -L-rhamnopyranosyl- β -hydroxydecanoate (R2: C₃₂H₅₈O₁₃) of molecular mass 650 Da. The rhamnolipid aggregate morphology undergoes significant changes in the pH region of 6.5–7.5. At pH 5.0, rhamnolipid begins to visibly precipitate out of solution. The rhamnolipid is not volatile, unstable at extreme pH due to hydrolysis of the glycosidic linkage between sugar and lipid, and readily biodegradable. The biosurfactant is stable to 121 °C for at least 1 h and at room temperature. The rhamnolipid used has a critical micelle concentration of 50 mg/L (\approx 0.1 mM) and a surface tension of 29 mN/m [17]. Therefore, a concentration above the CMC for all experiments was used to ensure the formation of micelles.

2.2. Soils

Soil A was brought from Eskişehir Esentepe region, the other two types of soils B and C was obtained from Eskişehir Anadolu University, Agriculture Faculty. The soils were ground and sieved to 0.140–0.425 mm size. The chemical compositions of the soil samples was first identified by X-ray diffraction (XRD). Qualitative X-ray diffraction analysis was performed on the soils using a Rigaku Rint 2200 model powder diffractometer with the K α radiation of Cu. Scans were conducted at a rate of 2° θ min⁻¹. Chemical analysis of the soil samples were performed using X-ray fluorescence spectroscopy technique (XRF, Rigaku ZSX Primus model). The chemical compositions and analysis of soils A, B, and C are shown in Tables 1 and 2, respectively. The soils were ground and then sieved to a particle size less than 65 μ m for XRD and XRF measurements. For XRF measurements, the soils were prepared by fluxing of powder samples with Li₂B₄O₇.

The analysis of the soil A revealed that it contains mainly SiO₂, Al₂O₃, Fe₂O₃ and CaO which they account for 87.2% of the total weight. Soils B and C contained mainly SiO₂, Al₂O₃ and Fe₂O₃ which they constitute 82.2 and 82.8% of the total weight, respectively.

Table 1
Chemical compositions of the soils identified by XRD

Component	Soil A	Soil B	Soil C
Smectite	Moderate	Dominant	Moderate–dominant
Serpentine	Moderate	Little–trace	Trace
Amphibole	Moderate	Trace	Little
Quartz	Little	Trace	Little
Feldspar	Moderate	Moderate	Moderate
Calsite	Trace	Little–trace	–
Dolomitic	Trace	–	–
Illite	Little	–	Moderate
Talc	–	Trace	–
Clay (%)	30	30	70

Table 2
Chemical analysis of the soils performed using XRF

Soil A		Soil B		Soil C	
Composition	Content (wt. %)	Composition	Content (wt. %)	Composition	Content (wt. %)
SiO ₂	47.7	SiO ₂	52.9	SiO ₂	58.1
Al ₂ O ₃	14.8	Al ₂ O ₃	16.4	Al ₂ O ₃	14.6
Fe ₂ O ₃	12.8	Fe ₂ O ₃	12.9	Fe ₂ O ₃	10.1
CaO	11.9	CaO	6.4	CaO	5.8
MgO	6.7	MgO	5.9	MgO	5.7
K ₂ O	0.7	K ₂ O	0.7	K ₂ O	1.3
Na ₂ O	2.0	Na ₂ O	3.4	Na ₂ O	3.4
TiO ₂	3.2	TiO ₂	1.3	TiO ₂	0.9
MnO	0.2	MnO	0.2	MnO	0.2

2.3. Cd(II) sorption by the soils

To investigate Cd(II) desorption by rhamnolipid from the soils, Cd(II) was firstly sorbed to the soils. A Cd(II) stock solution of 8.9 mM was obtained by dissolving CdN₂O₆·4H₂O in distilled water. The Cd(II) solutions in the concentrations varying from 0.20 to 6.68 mM were prepared by diluting stock solution of Cd(II). A 1.5 g of the soils placed into 50-mL centrifuge tubes was treated in 10 mL of metal ion solutions. Effect of pH on the sorption of Cd(II) by the soils A, B, C was studied in the pH range 6.0–7.4. Control experiments were performed with the same metal ion solutions without added the soils at each pH value. The centrifuge tubes were agitated on a shaker at 25 °C, at 150 rpm for 72 h until after reaching ultimate equilibrium, then the tubes were centrifuged at 19,000 \times g for 20 min and the supernatant was acidified to pH 2.0 with 1% HNO₃ for atomic absorption analysis (ATI-UNICAM 929 atomic absorption spectrophotometer, England). Sorbed Cd(II) concentration by the soils was calculated from the difference between initial Cd(II) concentration in solution and Cd(II) concentration remained in the supernatant after sorption. Cd(II) sorption to tube surfaces was not determined.

The sorption characteristics of the rhamnolipid onto the soils were also studied in the absence of Cd(II) ions and in the presence of 1 mM Cd(II) ions. The concentrations of rhamnolipid solutions were increased from 0 to 100 mM. The same sorption experimental procedure was performed. Biosurfactant loss due to sorption to tube walls was not observed. The rhamnolipid concentration in the supernatant was estimated by surface tension measurement using a surface tensiometer (KRÜSS Digital Tensiometer K9, KRÜSS GMBH, Wissenschaftliche Laborgerate, Borsteler Chaussee 85–99 a, D-22453 Hamburg), which employs the Du Nouy ring method. Rhamnolipid concentration was determined using a calibration curve relating surface tension (mN/m) to rhamnolipid concentration (mM). Surface tension decreased rapidly from 72 to 30 mN/m with small increases in the rhamnolipid concentration up to 0.1 mM. Further increases in the rhamnolipid concentration only slowly reduced the surface tension from 30 to 29 mN/m. Once the surface tension reached 29 mN/m, the further addition of rhamnolipid had no effect. For that reason, the calibration curve was constructed in the ranges which a linear relation between the surface tension and rham-

nolipid concentration was observed. Samples taken from the supernatant liquid were diluted in this linear function range.

2.4. Cd(II) desorption by rhamnolipid biosurfactant from the soils

The centrifuge tubes containing Cd(II)-sorbed soils mixed with 10 mL of increasing concentrations of rhamnolipid solutions in the range 0–100 mM were placed on a shaker at 25 °C and 150 rpm for 72 h and then centrifuged at $19,000 \times g$ for 20 min. The control solution was used to determine whether distilled water alone desorbed soil-bound Cd(II) or not. The supernatant was analyzed for Cd(II) concentration by atomic absorption analysis and for rhamnolipid concentration by surface tension measurement. The pH of supernatant samples was then adjusted with concentrated HNO₃ to <2 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. Cd(II) did not desorb by distilled water spontaneously. To ensure that all the Cd(II) was desorbed from the rhamnolipid pellet, the pellet was washed a second time with 1% HNO₃ and the supernatant was analyzed by atomic absorption for Cd(II).

3. Results and discussion

3.1. Sorption of Cd(II) by the soils

3.1.1. Effect of pH

Effect of pH on the sorption of Cd(II) by the soils A, B, C was studied in the pH range 6.0–7.4 with optimized 1.5 g soil dose and at temperature 25 °C. This pH range generally good represents the pH values of both the natural and metal-contaminated soils, and also was determined as optimum pH range for the sorption of Cd(II) ions by various sorbents [27]. The sorption efficiency of Cd(II) onto the soils appears to be independent of pH with in studied pH range and initial Cd(II) concentration. When the soils A, B, C was treated with 1.0 mM Cd(II) solution, the sorption efficiency for all the soils was determined as 100% (6.81 mmol Cd(II) sorbed/kg soil) at all pH values tested. In fact, the charges on the inner and outer surfaces of the swellable three-layer minerals such as smectites and illites are caused by the amphoteric properties of some functional groups like the hydroxyl groups on the sides and edges of the clay minerals [28,29]. These groups can be charged positively or negatively according to the pH of the surrounding solution. Hydroxyl groups tend to dissolve protons at higher pH, while they absorb protons in acidic pH. Therefore, such surfaces usually bear positive charges at low pH and negative values at higher pH.

3.1.2. Effect of initial Cd(II) concentration

Initial concentrations of Cd(II) were varied over the 0.20–6.68 mM ranges for the soils, while the soil weight in each sample was constant at 1.5 g. The sorption experiments were performed at pH 6.8. The sorption capacity of the soils for Cd(II) decreases in the order of soil C > soil B > soil A (Fig. 1). The

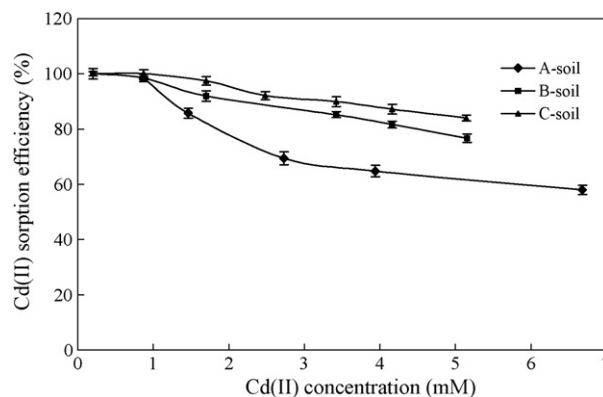


Fig. 1. Effect of initial Cd(II) concentration on Cd(II) sorption efficiencies by soils (pH, 6.8; temperature, 25 °C; amount of soil, 1.5 g; stirring rate, 150 rpm).

sorption efficiencies of Cd(II) for all the soils decreased with increasing initial Cd(II) concentration whereas the sorbed Cd(II) quantity per unit weight of the soils increased. As expected, the relative number of binding sites available to the metal ion would reduce while the concentration of the metal ion was increased. The soils became nearly saturated at high initial Cd(II) concentrations. The soil C has the highest saturation capacity with a sorption efficiency of 83.9%, followed by soils B and A with sorption efficiencies of 76.7% and 57.9%, respectively.

3.1.3. Application of sorption isotherms

The sorption equilibrium of Cd(II) onto the soils was described by four models, three of which originate from saturation type-sorption isotherm, and one of which uses heterogeneous energetic distribution of active sites on the surface of sorbent and is established empirically.

The Langmuir model has a theoretical basis, which relies on a postulated chemical or physical interaction (or both) between solute and vacant sites on the sorbent surface, and the heat (ΔH) of sorption is independent of the fraction of surface covered by the sorbed solute ($\theta = q_{eq}/Q^0$) [30]. The Langmuir isotherm model has the form:

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

where C_{eq} is the metal concentration in solution, the Langmuir constant, Q^0 , is the amount of sorbate per unit weight of sorbent to form a complete monolayer on the surface, K is a constant related to the energy of sorption. The Langmuir equation obeys Henry's Law at low concentrations.

The Freundlich model can be derived by assuming a logarithmic decrease in the heat of sorption with the fraction of surface covered by the sorbed solute [31].

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

In this expression, K_F (sorption capacity) and $1/n$ (sorption intensity) are Freundlich constants. Magnitude of K_F and n shows easy separation of metal ions from wastewater and favorable sorption. If sorption is favorable, then $1/n < 1$ or $n > 1$. n is a constant representing the mutual interaction of sorbed species. Experimental values of n are usually greater than unity and

this means that the forces between the sorbed molecules are repulsive. In addition, the closer the n value of the Freundlich sorption equation is the zero, the more heterogeneous is the system.

Another isotherm equation such as a three-parameter isotherm proposed by Redlich–Peterson seems to more adequately fit the broad range of equilibrium data [32]:

$$q_{\text{eq}} = \frac{K_{\text{R}}C_{\text{eq}}}{1 + a_{\text{R}}C_{\text{eq}}^{\beta}} \quad (3)$$

where the exponent β , lies between 0 and 1. If β is equal to 1, then Eq. (3) becomes the Langmuir equation. If $a_{\text{R}}C_{\text{eq}}^{\beta}$ is much greater than 1, then it becomes the Freundlich equation. If $a_{\text{R}}C_{\text{eq}}^{\beta}$ is much less than 1, which occurs at low concentrations, then it becomes a linear isotherm equation.

Another three-parameter Langmuir–Freundlich type empirical model proposed to improve the fit for a wide range of initial sorbate concentration is called as Koble–Corrigan model and is given by [33]:

$$q_{\text{eq}} = \frac{AC_{\text{eq}}^b}{1 + BC_{\text{eq}}^b} \quad (4)$$

when $b = 1$, the Koble–Corrigan equation reduces to the Langmuir equation. If BC_{eq}^b is much less than 1, sorption is relatively low, then it becomes the Freundlich equation. If BC_{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:

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

A DataFit (trial version) computer program was used to estimate the sorption model constants from the sorption data of Cd(II) ions on soils A, B, and C. The Langmuir, Freundlich, Redlich–Peterson and Koble–Corrigan constants and the 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 3.

The sorption data of Cd(II) by soil A were well characterized by using the empirical Freundlich and Koble–Corrigan models (Fig. 2). In the figures where metal uptake equilibrium data are shown, the model profiles are presented as dashed lines while the symbols denote experimentally obtained values (Figs. 2 and 3). In the Koble–Corrigan model, as BC_{eq}^b was much less than 1, then it became the Freundlich equation. The similar sorption equilibrium data were obtained for the Cd(II) sorption by soils B and C. For the sorption of Cd(II) by soils B and C, as the Redlich–Peterson exponent, β , is equal to 1, the Redlich–Peterson equation reduced to the Langmuir equation. The Freundlich and Koble–Corrigan models provided the best fit with experimental and predicted values for the Cd(II) sorption by soils B and C. However, as BC_{eq}^b was much less than 1, the Koble–Corrigan model was also converted to the Freundlich model. The Freundlich model showed the best fit for the Cd(II)

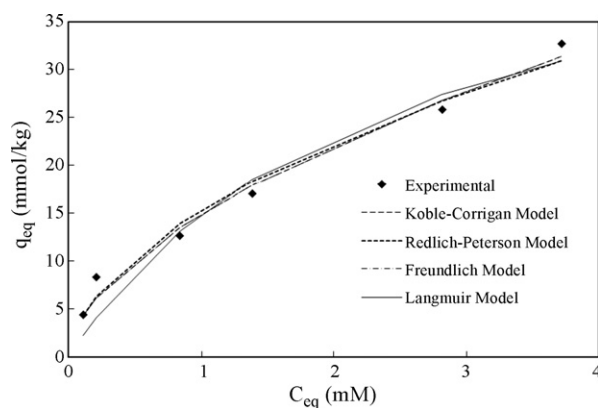


Fig. 2. Comparison of the Langmuir, Freundlich, Redlich–Peterson, and Koble–Corrigan sorption isotherms for Cd(II) sorption onto soil A (pH, 6.8; temperature, 25 °C; amount of soil A, 1.5 g; stirring rate, 150 rpm).

sorption data by the soils, while the Langmuir-type models generally failed to describe the sorption data (Fig. 3). The Freundlich isotherm is an empirical model assuming a logarithmic decrease in the heat of sorption with the fraction of surface covered by the sorbed solute. Surfaces of soil components are expected to have heterogeneous energies for sorbing metals, and therefore a good fit was expected. The magnitude of the Freundlich constant, K_{F} , an indication of the sorption capacity of the sorbent, followed a trend of soil C > soil B > soil A. The same order of selectivity was obtained in terms of the n , in agreement with the Cd(II) sorption efficiencies. As the values of sorption capacity, K_{F} , and intensity, $1/n$, for soils C and B are found to be very close to each other, these values also indicate a decidedly better soil C and B affinity for, and higher sorption of Cd(II) ions versus soil A.

The three soils tested differed in the clay fraction and mineralogical composition of the clay. Soil C with a higher clay content (70%) had the greatest sorption efficiency and sorption capacity as estimated by the maximum sorption capacity (K_{F}) and intensity (n) of the Freundlich equation. The clay fraction of soil C was dominated by well crystallized smectite and a sizable proportion of feldspar and illite that provide the soil with permanent surface charge. The presence of smectite as the dominant clay ensures high metal sorption capacity as it

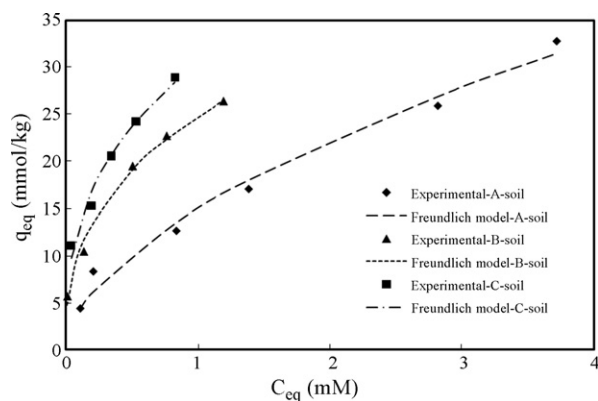


Fig. 3. Freundlich sorption isotherm for Cd(II) sorption onto soils A, B and C (pH, 6.8; temperature, 25 °C; amount of soil, 1.5 g; stirring rate, 150 rpm).

Table 3
Comparison of the sorption isotherm coefficients and R^2 and R_a^2 values between experimental and predicted values using by Langmuir, Freundlich, Redlich–Peterson and Koble–Corrigan models

Langmuir model														
Soil A				Soil B				Soil C						
Q^0 (mmol kg ⁻¹)	K (L mmol ⁻¹)	R^2	R_a^2	Q^0 (mmol kg ⁻¹)	K (L mmol ⁻¹)	R^2	R_a^2	Q^0 (mmol kg ⁻¹)	K (L mmol ⁻¹)	R^2	R_a^2			
51.03	0.411	0.9454	0.9318	30.73	3.839	0.9329	0.9105	31.79	6.401	0.8546	0.8061			
Freundlich model														
Soil A				Soil B				Soil C						
K_F (mmol ⁿ kg ⁻¹ L ⁿ)	n	R^2	R_a^2	K_F (mmol ⁿ kg ⁻¹ L ⁿ)	n	R^2	R_a^2	K_F (mmol ⁿ kg ⁻¹ L ⁿ)	n	R^2	R_a^2			
14.90	1.786	0.9843	0.9804	24.72	2.625	0.9915	0.9887	30.36	2.740	0.9782	0.9710			
Redlich–Peterson model														
Soil A					Soil B					Soil C				
K_R (L kg ⁻¹)	a_R (L ^β mmol ^{-β})	$β$	R^2	R_a^2	K_R (L kg ⁻¹)	a_R (L ^β mmol ^{-β})	$β$	R^2	R_a^2	K_R (L kg ⁻¹)	a_R (L ^β mmol ^{-β})	$β$	R^2	R_a^2
164.97	9.757	0.50	0.9828	0.9786	118.52	3.839	1	0.9329	0.9105	203.48	6.401	1	0.8546	0.8061
Koble–Corrigan model														
Soil A					Soil B					Soil C				
A (mmol ^{1-b} kg ⁻¹ L ^b)	B (L ^b mmol ^{-b})	b	R^2	R_a^2	A (mmol ^{1-b} kg ⁻¹ L ^b)	B (L ^b mmol ^{-b})	b	R^2	R_a^2	A (mmol ^{1-b} kg ⁻¹ L ^b)	B (L ^b mmol ^b)	b	R^2	R_a^2
14.90	0.0001	0.56	0.9843	0.9804	24.96	0.01	0.383	0.9914	0.9886	30.65	0.010	0.367	0.9780	0.9707

provides the soil with high cation exchange capacity, an established factor regulating the sorption of heavy metals by soils. The structure and chemical composition, exchangeable ion type and small crystal size of smectite are responsible for several properties, including a large chemically active surface area, a high cation exchange capacity and inter-lamellar surface having unusual hydration characteristics [28,34]. Both soils B and C had similar proportions of smectite and feldspar in the clay fraction so had similar sorption properties. On the other hand, soil A contained less smectite and illite, and had the lower clay content than soil C. As a result, it had the lowest sorption and ion-exchange capacity.

The most important clay mineral groups which are used for environmental purposes are kaolins, smectites, illites and chlorites. The sorption capacities of clay minerals are reported to decrease in the order of smectites > chlorites > illites > kaolins. The kaolin minerals belong to the two-layer minerals. The most common kaolin mineral is kaolinite which consists of a single-silica tetrahedral sheet and a single-alumina octahedral sheet which form the kaolin unit layer [35]. Smectite is a member of the three-layer minerals and is composed of units consisting of two silica tetrahedral sheets with a central alumina octahedral sheet. As the lattice has an unbalanced charge due to isomorphic substitution of alumina for silica in the tetrahedral sheet and of iron and magnesium for alumina in the octahedral sheet, the attractive force between the unit layers in the stacks is weak. The cations and polar molecules are able to enter between the layers and cause the layers to expand [36]. Illite is a more general term used for a mica-like clay whose basic structural unit is similar to that of montmorillonite, a widely used smectite. As there is a large replacement of silica for alumina in the tetrahedral sheet, illites are typically characterized by a charge deficiency which is balanced by potassium ions that bridge the unit layers. As a result, illites are nonexpandable clay minerals [29].

Other clay mineral groups like chlorites and the mixed-layer clays consist of mixtures of the unit layers on a layer-by-layer basis, e.g., illite–smectite, smectite–chlorite, illite–chlorite, etc. Two-layer minerals like kaolins have no additional ions between their silicate layers. On the contrary kaolins, the silicate layers of three-layer minerals bear an electric charge due to isomorphic substitution [37]. As the charge of the surrounding structure of oxygen and hydroxyl ions remains unchanged, there is a permanent negative-charge excess of the silicate ions. Al(III) instead of Si(IV) is often included into the tetraheders and Fe(II)/Zn(II) is incorporated into the octaheders. In addition, K(I), Na(I), Ca(II), Mg(II) are intercalated between the silicate layers to compensate this negative-layer charge. These cations are called interlayer cations [38]. The charge on the inner surfaces of the swellable three-layer minerals is always negative and is caused by the replacement of Al ions in the tetraheder layers. It is completely compensated by the exchangeable interlayer cations. Internal surfaces of smectites can reach as high as 97% of the total area. The aluminosilicate layers cause also negative charges on the outer surface. The negative charges generated by substitution are independent from the surrounding location and are permanent charges [39,40].

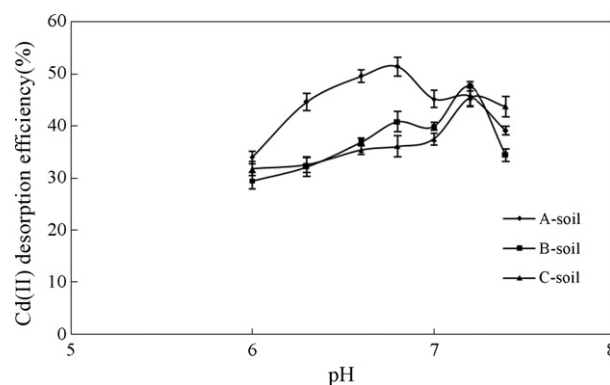


Fig. 4. Effect of pH on Cd(II) desorption efficiencies from soils A, B and C using rhamnolipid biosurfactant ($C_{\text{Rhamnolipid conc.}}$, 80 mM; $q_{\text{Soil A}}$, 7.71 mmol kg⁻¹; $q_{\text{Soil B}}$, 6.81 mmol kg⁻¹; $q_{\text{Soil C}}$, 6.81 mmol kg⁻¹; temperature, 25 °C; amount of sorbent, 1.5 g; stirring rate, 150 rpm).

3.2. Recovery of Cd(II) from soils using rhamnolipid biosurfactant

3.2.1. Effect of pH

Effect of pH on the recovery of Cd(II) from the soils was investigated in the pH range of 6.0–7.4. The maximum recovery efficiency of Cd(II) from the soil A at 1.15 mM initial Cd(II) concentration (7.71 mmol Cd(II)/kg soil A) and at 80 mM rhamnolipid concentration was obtained at pH 6.8, and determined as 51.5% of the sorbed Cd(II). On the other hand, the best recovery efficiencies, 47.7% and 45.5% of the sorbed Cd(II) from the soil B and soil C, respectively, were achieved by adjusting the initial pH value to 7.2 at 1.0 mM initial Cd(II) ion concentration in solution (6.81 mmol Cd(II)/kg soil) and at 80 mM rhamnolipid concentration (Fig. 4). At equilibrium, a majority of metals found in soil are bound or precipitated on the soil surfaces. Surfactants are amphoteric molecules consisting of a nonpolar/hydrophobic tail and a polar/ionic/hydrophilic head. The polar head groups of micelles can bind metals. This makes the metals more soluble in water. At low concentrations, biosurfactants are present as single molecules (monomers). At higher concentrations, these monomers spontaneously aggregate into complex structures such as bilayers, vesicles or micelles. As the concentration of the surfactant is increased, a concentration is reached where no further change in interfacial properties takes place. The amount of surfactant needed to reach this concentration is called the CMC. Effective use of biosurfactants in soil systems to enhance recovery of metals will depend on the size of the complex formed and whether the complex is sorbed or trapped by the soil. The type and size of aggregate formed depends on the solution pH and the surfactant structure. At a low pH (4.3 < pH < 5.8), rhamnolipids form liposome-like vesicles. Between pH 6.0 and 6.6, rhamnolipids form either lamella-like structures (6.0 < pH < 6.5) or lipid aggregates (6.2 < pH < 6.6). When the rhamnosyl moiety is negatively charged above pH 6.8, micelles form, the most effective structure for metal immobilization [10]. As the cationic metals have an affinity for the negatively charged surfactants, the anionic surfactants like rhamnolipids give higher recovery efficiencies. Soil pores vary greatly in size, however, they are generally less than 2 μm in

diameter [13]. The smallest pores can act as a filter for metal-binding microorganisms or exo-polysaccharides and transport of the metal through the soil is prevented. With respect to size, biosurfactants have a distinct advantage over whole cells and exopolymers, which have molecular weights of approximately 10^6 . The average molecular weight of the rhamnolipid used in this study is 573 g [17]. On the other hand, micelles are the smallest basic structure formed, generally less than 5 nm in diameter, and the main effective structure for the metal recovery. Vesicles are second in size and range from 10 nm to more than 500 nm in diameter. Vesicles are composed of surfactant bilayers, which are similar in structure to biological membranes. The addition of Cd(II) to rhamnolipid solutions at pH 6.8 was also shown to stabilize the formation of small vesicles in the 20–30 nm size range [20]. Filtration has little effect on movement of particles of less than 50 nm in diameter through soil. Rhamnolipid surfactant works better in the pH range of 6.5–7.5, in accordance with the optimum pH range found in this study. The surface tension of rhamnolipid solutions is also quite sensitive to pH. The biosurfactant could enable more metal removal due to the more effective interfacial surface tension lowering. The surface activity of the rhamnolipid is highest between pH 7.0 and 7.5. As the pH is increased above 7.5, there is a slight decrease in surface activity that results in an increase in surface tension from 30 to 32 mN/m. After increasing to 32 mN/m at pH 8.0, the surface tension of rhamnolipid solutions remains comparatively stable, even at pH 11. As the pH is decreased from 7.0 to 5.0, surface activity decreases significantly, resulting in a considerable increase in surface tension from 30 to >40 mN/m [10]. Precipitation of rhamnolipid was not obvious until the pH was decreased below 5.0.

3.2.2. Effect of rhamnolipid concentration

When the initial Cd(II) ion concentration in solution was held constant as 0.91–0.98 mM, the rhamnolipid concentration was varied from 0 to 100 mM at pH 6.8 and it was seen that this affected the amount of metal recovered from the soils. In the case of desorption from soil A and soil B, the Cd(II) complexation efficiency increased with increasing rhamnolipid concentration up to 80–100 mM, and the recovery efficiency was approximately 42.6 and 44.8% of the sorbed Cd(II) ($5.78 \text{ mmol (kg soil A)}^{-1}$ and $6.37 \text{ mmol (kg soil B)}^{-1}$), respectively for the 80 mM rhamnolipid concentration. In the case of the soil C, the Cd(II) recovery efficiency also increased with increasing rhamnolipid concentration up to 25–80 mM, and Cd(II) recovery efficiency reached a plateau value of 30.2–32.1% of the sorbed Cd(II) ($6.46 \text{ mmol (kg soil C)}^{-1}$) (Fig. 5). This was an expected order. Because the sorption of Cd(II) by the soil A is weak, the desorption of Cd(II) from the soil A by rhamnolipid biosurfactant is relatively high. On the other hand, Cd(II) ions are sorbed strongly by the soil C, the release of Cd(II) ions from the soil C is weak.

Biosurfactants used for soil treatment are required to have minimal sorptive interactions applied to the soil system, in other words, most of the biosurfactant should remain in the aqueous phase. Biosurfactant sorption in general is likely the reason that

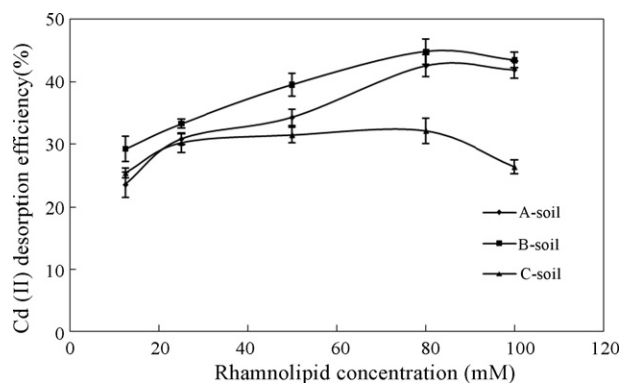


Fig. 5. Effect of rhamnolipid concentration on Cd(II) desorption efficiencies from soils A, B and C (pH, 6.8; $q_{\text{Soil A}}$, $5.78 \text{ mmol kg}^{-1}$; $q_{\text{Soil B}}$, $6.37 \text{ mmol kg}^{-1}$; $q_{\text{Soil C}}$, $6.46 \text{ mmol kg}^{-1}$; temperature, 25 °C; amount of sorbent, 1.5 g; stirring rate, 150 rpm).

high rhamnolipid concentrations are required for effective metal removal. Due to the strong sorption of rhamnolipid by soil A, high levels of rhamnolipid treatment were required in order to successfully mobilize soil A-bound metals. In the absence of Cd(II) ions, rhamnolipid sorption to soil A was 100% sorbed at lower rhamnolipid concentrations tested (12.5–50 mM). Rhamnolipid sorption capacity of the soils decreased in the order of soil A > soil C > soil B. In case of soil C, liquid phase rhamnolipid concentration increased from 25.2 to 66.8% as the amount of rhamnolipid added was increased between 0 and 100 mM. Although the general change of rhamnolipid sorption onto soil B with increasing rhamnolipid concentration was the same with soil C, liquid phase rhamnolipid concentration varied between 0 and 76.8% as the amount of rhamnolipid added was increased. Soil B adsorbed effectively rhamnolipid at lower rhamnolipid concentrations.

In the presence of 1 mM Cd(II), rhamnolipid sorption capacity of the soils was of the order soil A > soil B > soil C. Due to the strong sorption of rhamnolipid by soil A, the presence of soil A-bound Cd(II) affected less rhamnolipid sorption to soil A. Liquid phase rhamnolipid concentrations increased only from 25 to 65% as the amount of rhamnolipid added was increased. When soil B was used as sorbent, supernatant rhamnolipid concentration increased from 56.8 to 100% as the amount of rhamnolipid was increased. On the other hand, when 1 mM Cd(II) was present, sorption of rhamnolipid by soil C inhibited substantially, resulting in higher aqueous phase concentrations of rhamnolipid. The presence of soil C-bound Cd(II) resulted in less rhamnolipid sorption to soil C than was evident in the absence of Cd(II), liquid phase rhamnolipid concentrations varied between 68.5 and 100%. The major factors influencing the movement of particles of less than 50 nm in diameter through soil are advection, dispersion and adsorption by soil surfaces. Little is presently known about the sorption of microbial surfactant monomers such as rhamnolipids or aggregate structures by soil or soil constituents. However, analogous to bacteriophage, viral particles or microspheres behavior, sorption of rhamnolipid can be expected to depend on its molecular characteristics, e.g., charge and hydrophobicity, as well as on soil characteristics.

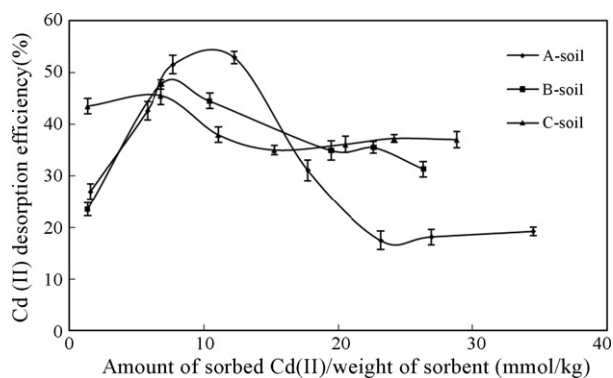


Fig. 6. Effect of amount of Cd(II) loaded to soils A, B and C on Cd(II) desorption efficiencies (pH, 6.8 for soil A; pH, 7.2 for soils B and C; $C_{\text{rhamnolipid conc.}}$, 80 mM; temperature, 25 °C; amount of sorbent, 1.5 g; stirring rate, 150 rpm).

3.2.3. Effect of amount of Cd(II) loaded on to the soils

After contact of the soil A to Cd(II) solutions in the range of concentrations varying from 0.20 to 6.68 mM at pH 6.8, the amounts of desorbed Cd(II) by the rhamnolipid biosurfactant were determined. Desorption of Cd(II) was found to be dependent on the initial Cd(II) ion concentration in solution or the amount of Cd(II) loaded to the soil A. The metal-ion loading to the soil A was increased from 1.57 to 12.27 mmol (kg soil A)⁻¹, the Cd(II) recovery efficiency increased, then it began to decrease. At this metal loading and at 80 mM rhamnolipid concentration, 52.9% of the sorbed Cd(II) was recovered from the soil A (Fig. 6).

After treatment of the soils B and C to Cd(II) solutions in the range of concentrations varying from 0.20 to 6.68 mM, the amounts of desorbed Cd(II) by 80 mM rhamnolipid solution were determined at pH 7.2. When the metal-ion loading to the soil B was increased from 1.36 to 26.32 mmol (kg soil B)⁻¹, the highest Cd(II) recovery efficiency was obtained as 47.7% of the sorbed Cd(II) at the metal-ion loading of 6.81 mmol (kg soil B)⁻¹, then the Cd(II) recovery efficiency decreased with increasing amount of Cd(II) loaded to the soil B. When the metal-ion loading to the soil C was increased from 1.36 to 28.81 mmol (kg soil C)⁻¹, a slight increase in the Cd(II) desorption efficiency was observed with increasing amount of Cd(II) loaded to the soil C up to 6.81 mmol kg⁻¹, and 45.5% of loaded Cd(II) was recovered, then a similar decrease trend in desorption efficiency was observed.

Cd(II) recovery efficiencies from the soils using rhamnolipid biosurfactant decreased in the order of soil A > soil B > soil C. This order was the reverse of the Cd(II) sorption efficiency order on the soils. As Cd(II) was strongly adsorbed by the soil C, the lowest desorption efficiencies were obtained in case of the soil C. However, the metal-ion loading to the soils was further increased, it was seen that this desorption order changed as soil C > soil B > soil A. When the amount of metal-ion loaded to the soil A was increased from 12.27 mmol (kg soil A)⁻¹ to 26.94 mmol (kg soil A)⁻¹, the desorption efficiency decreased strongly, and was 18.1% of the sorbed Cd(II). When the amounts of metal-ion loaded to the soils B and C was increased from 6.81 mmol (kg soil B)⁻¹ to 26.32 mmol (kg soil B)⁻¹ and from 6.81 mmol (kg soil C)⁻¹ to 28.81 mmol (kg soil C)⁻¹, the des-

orption efficiencies remained approximately constant, and were found to be very close to each other as 31.3%, 37.0% of the sorbed Cd(II), respectively. This was also an expected result. The lower liquid phase rhamnolipid concentrations because of the strong sorption of rhamnolipid by soil A decreased the desorption efficiency of Cd(II) from the soil A at higher metal ion loadings to the soil A.

There are limited in number studies published in the literature concerning the use of biosurfactants to recover metals. Recovery of Cd(II) from liquid media [20] and Cd(II), Pb(II), and Zn(II) from a Hayhook sandy loam soil [21] 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 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 [21]. In our previous study, the urban soil which has a high clay content dominated feldspar, kaolin, mica and quartz, was used. After 0.96 mM Cd(II) solution was loaded to the urban soil, which has a high clay content, 92.6% of the Cd(II) (2.98 mmol kg⁻¹) was sorbed, and 54.3% of the sorbed Cd(II) was recovered by a 70 mM rhamnolipid solution (unpublished data). Utilization of saponin, a plant-derived biosurfactant, was shown to be effective for recovery of heavy metals from soils, attaining 90–100% of Cd extractions [41]. Addition to type of biosurfactant, type of soil, pH of soil, cation exchange capacity, particle size, permeabilities and contaminants all affect metal removal efficiencies. When the type of soil changes, the efficiency of metal removal process from soil using biosurfactant will also be change. For that reason the metal desorption efficiency using rhamnolipid biosurfactant must be searched in various components of soil rather than in various soils. A highest Cd(II) desorption efficiency by rhamnolipid biosurfactant from kaolin was obtained 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) [23]. A best recovery efficiency from K-feldspar, approximately 96% of the sorbed Cd(II) (1.87 mmol kg⁻¹) was achieved by using the rhamnolipid concentrations in the range 50–80 mM [24]. On the other hand, in case of sepiolite, the Cd(II) recovery efficiency remained 10.12% of the sorbed Cd(II) (7.71 mmol kg⁻¹) by the 50 mM rhamnolipid solution [24]. In this study, a maximum recovery efficiency of 52.9% of the sorbed Cd(II) using soil A was obtained at a high attainable metal-ion loading of 12.27 mmol (kg soil A)⁻¹ and at the rhamnolipid concentration of 80 mM. This recovery efficiency seems to be satisfactory in comparison with recovery efficiencies of similar systems in the literature.

4. Conclusions

The efficiency and success of biosurfactants in facilitating removal of heavy metal contaminants from soil systems will depend largely on the soil texture, structure, clay content, predominant clay type, cation exchange capacity, permeability, ionic strength, etc. For this purpose, this study investigated the sorption characteristics and release of Cd(II) from typical urban soil materials from Eskişehir Esentepe region and Eskişehir

Anadolu University, Agriculture Faculty. Cd(II) sorption by the soils followed the order: soil C > soil B > soil A. It was concluded that smectite, feldspar and illite are the most important soil constituents exerting the greatest effect on Cd(II) sorption. Sorption of Cd(II) to the soils was nonlinear, and the soil-Cd(II) isotherms fitted well the Freundlich model, and have similar shapes (n -values > 1, showing favorable sorption). The highest Cd(II) sorption capacity, K_F ($30.36 \text{ mmol}^n \text{ kg}^{-1} \text{ L}^n$), and intensity, n (2.740), was obtained for the soil C. At low Cd(II) loadings to the soils, the Cd(II) recovery efficiency by rhamnolipid biosurfactant was the reverse of the Cd(II) sorption efficiency order on the soils. The relative order of Cd(II) release from the soils was soil A > soil B > soil C. However, at Cd(II) loadings to the soils greater than $17.0 \text{ mmol kg soil}^{-1}$, the order changed to soil C > soil B > soil A. The success of rhamnolipids in increasing recovery of heavy metal contaminants from soils will also depend on the amount of rhamnolipid present in the aqueous phase. Because of the strong sorption of rhamnolipid by the soil A, the lower liquid phase rhamnolipid concentrations resulted in the lower desorption efficiencies observed at higher metal ion loadings to the soil A. High concentrations of rhamnolipids (80–100 mM) were required for effective Cd(II) recovery from the soil A where as 25–80 mM rhamnolipid concentrations were enough to efficiently Cd(II) desorption from the soil C.

In conclusion, the biosurfactant-washing technology provides a better candidate for the remediation of heavy metal polluted soils. This technology can be applied to recovery various soil contaminants, e.g., petroleum hydrocarbons together with heavy metals. It has perfect compatibility with the existing remediation technologies such as soil excavation and transport of contaminated soil to hazardous waste sites for landfilling, thermal extraction for volatile metals and electrokinetics. Conventional treatment technologies are becoming less popular due to the process economics. However, for future development there are many factors to be researched thoroughly. Soil composition and components, clay mineralogy, organic matter content, metal speciation, presence of competing metals or other contaminants in soil, selection of surfactant and concentration, effectiveness of batch and continuous operations must be deeply investigated.

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