

# A comparative study for the sorption of Cd(II) by K-feldspar and sepiolite as soil components, and the recovery of Cd(II) using rhamnolipid biosurfactant

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## Abstract

This study investigated the sorption characteristics and recovery of selected heavy metal Cd(II) from K-feldspar and sepiolite, representative soil components, using rhamnolipid biosurfactant. Although the proposed technique was classified as a soil bioremediation process, it can also be applied to treatment of waste waters containing Cd(II) ions with minor modifications. The effect of initial Cd(II) concentration on sorption capacity was characterized by determining the sorption isotherms. Of the four models examined, the Freundlich model showed the best fit for the sorption of Cd(II) on K-feldspar, whereas the Langmuir-model was used successfully to characterize the sorption of Cd(II) on sepiolite. Although a high Cd(II) uptake of 7.49 mmol/kg by K-feldspar was obtained, sepiolite was a superior Cd(II) accumulator, with a maximum Cd(II) uptake of 24.66 mmol Cd(II)/kg. The presence of Cd(II) in the sepiolite or K-feldspar prior to addition of the rhamnolipid generally resulted in less rhamnolipid sorption to sepiolite or K-feldspar. The maximum Cd(II) desorption efficiency by rhamnolipid from K-feldspar was substantially higher than that of sepiolite and determined to be 96% of the sorbed Cd(II), whereas only 10.1% of the sorbed Cd(II) from sepiolite was recovered by rhamnolipid solution.

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## 1. Introduction

Due to its acute toxicity, cadmium together with lead and mercury forms the “big three” of heavy metals with the greatest potential hazard to humans and the environment. The industrial uses of cadmium are increasing in electroplating, paint pigments, plastics, silver–cadmium and nickel–cadmium battery industry and smelter operations, often affecting the environment at distances of a 100 km order of magnitude (Volesky, 1990; Farquhar et al., 1997). Anthropogenic activities such as industrial waste disposals and sewage sludge disposals on land have led to accumulation of Cd in soil (Vig et al., 2003). In addition,

intensive agriculture in developed countries has shown up the use of important quantities of intrans, i.e. fertilisers and amendments like activated sludges or manure (Lebeau et al., 2002). The relevant EU Directive, as well as the US EPA, and the FAO/WHO have set the maximum contaminant level Cd(II) cations in domestic water and in soil to be  $5 \mu\text{g l}^{-1}$  and  $70 \mu\text{g day}^{-1}$ , respectively (Vig et al., 2003; Zouboulis et al., 2004).

Remediation of soil contaminated with toxic metal cations has conventionally involved the excavation and disposal in landfills or capping of the contaminated site. However, these traditional technologies do not actually remediate the soils, and very expensive (Mulligan et al., 2001a). The search for novel technologies has recently been directed to the application of bioremediation. Technologies using microorganisms and biosorbents to remove heavy

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metals from wastewaters have been extensively studied (Bruins et al., 2000; Sağ et al., 2003a, b). Biosorption involves a combination of active and passive transport mechanisms, starting with the diffusion of metal ions to the surface of microbial biomass. Metal ion uptake by passive transport mechanisms may involve the contribution of adsorption, chelation, complexation, coordination or micro-precipitation mechanisms (Yılmaz, 2003; Lin and Lin, 2005). Sorption by any of these mechanisms effectively limits the availability of metals for removal by flushing. Soil pores vary greatly in size ranging from less than 2 µm, whereas the size of a bacterial cell is as large as 0.2 mm in diameter. The smallest pores can act as a filter for metal-binding microorganisms and transport of the metal through the soil is prevented (Miller, 1995). As an alternative technology, biosurfactants produced by bacteria and yeasts could be used for the environmental remediation of heavy metals from soils, surface and subsurface waters (Christofi and Ivshina, 2002). With respect to size, biosurfactants have a distinct advantage over wholecells and exopolymers. In the pH range of 6.0–7.0, rhamnolipid structures are predominantly small vesicles, <50 nm in diameter, and micelles, approximately 5 nm in diameter (Tan et al., 1994; Herman et al., 1995). Surfactants have both hydrophilic (polar), usually referred to as the head, and hydrophobic/lipophilic (nonpolar), known as the tail, portions in the molecule (Zhang and Miller, 1992; Christofi and Ivshina, 2002; Zouboulis et al., 2003). The heads of the surfactant molecules point toward the surrounding aqueous solution while the tails face inward toward the hydrophobic center of the structure. The anionic biosurfactant carries a negative charge, so when the molecule encounters a cationic metal, an ionic bond is formed (Frazer, 2000; Kim et al., 2000). If this bond is stronger than the metal's bond with the soil, it will be enough to pump water through the soil to remove the contaminant. The biosurfactant used in this study, a rhamnolipid, was from the glycolipid group and was produced by *Pseudomonas aeruginosa*, a common soil microorganism (Sandrin et al., 2000; Mulligan and Wang, 2006).

Addition to type of biosurfactant, type of soil, pH of soil, cation exchange capacity, particle size, permeabilities and contaminants all affect metal removal efficiencies (Frazer, 2000; Alumaa et al., 2001; Mulligan et al., 2001b; Markiewicz-Patkowska et al., 2005; Shawabkeh, 2005; Pu and Cutright, 2006). 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. 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. Feldspars are the name of an important group of rock-forming minerals which make up perhaps as much as 60% of the Earth's crust,

commonly found in rocks, sediments, and soils. K-feldspar (KAlSi<sub>3</sub>O<sub>8</sub>; microcline or orthoclase) and Na-feldspar (albite; NaAlSi<sub>3</sub>O<sub>8</sub>) in a significant proportion of feldspar ores exist in the same matrix usually in quantities of about 3–5% Na<sub>2</sub>O and K<sub>2</sub>O (Farquhar et al., 1997; Demir et al., 2003). On the other hand, sepiolite [Mg<sub>4</sub>Si<sub>6</sub>O<sub>15</sub>(OH)·6H<sub>2</sub>O], a zeolite like clay mineral, is a hydrous magnesium silicate characterized by its fibrous morphology and intracrystalline channels. Sepiolite contains a continuous two-dimensional tetrahedral sheet of T<sub>2</sub>O<sub>5</sub> (T = Si, Al, Be,...) but has no continuous octahedral sheets. Sepiolite has molecular sized channels (3.6 × 10<sup>6</sup> Å) and large specific surface area with more than 200 m<sup>2</sup> g<sup>-1</sup> (Garcia-Sanchez et al., 1999; Sabah et al., 2002; Vico, 2003; Kocaoba and Akyuz, 2005). Because of this excellent fibrous structure, organic and inorganic ions can penetrate into the structure of sepiolite, and this makes it an important industrial raw material in sorptive, rheological and catalytic applications. Most of the world's sepiolite reserves are found in Turkey.

The objective of this study was to determine the sorption of Cd(II) ions onto K-feldspar and sepiolite as well as to research rhamnolipid-mediated desorption of Cd(II) ions from K-feldspar and sepiolite. There is little literature published about the sorption/desorption of heavy metal ions onto soil components such as K-feldspar, sepiolite, kaolin (Aşçı et al., 2007). This technique with small changes can also be applied to the removal and recovery of heavy metal ions from wastewaters using K-feldspar and sepiolite as sorbent and rhamnolipid as complexation or chelating agent. In addition, the sorption of rhamnolipid to K-feldspar and sepiolite was investigated. Little is currently known about the sorption of biosurfactant monomers or aggregate structures by soil components.

## 2. Materials and methods

### 2.1. Biosurfactant

The rhamnolipid used (JBR 425) was obtained from Jeneil Biosurfactant Co., Llc, Saukville, WI. The rhamnolipid used is a mixture of two major rhamnolipids, monorhamnolipid, α-L-rhamnopyranosyl-β-hydroxydecanoate (R1: C<sub>26</sub>H<sub>48</sub>O<sub>9</sub>) and dirhamnolipid, 2-O-α-L-rhamnopyranosyl-α-L-rhamnopyranosyl-β-hydroxydecanoate (R2: C<sub>32</sub>H<sub>58</sub>O<sub>13</sub>). Molecular weights of R1 and R2 are 504 and 650, respectively. 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 unstable at extreme pH due to hydrolysis of the glycosidic linkage between sugar and lipid. The biosurfactant is stable to 121 °C for at least 1 h and at room temperature. The rhamnolipid used has a critical micelle concentration (CMC) of 50 mg/L (≈0.1 mM) and a surface tension of 29 mN/m (Jeneil Biosurfactant Co., LLC, 2001).

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