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Biosorption of heavy metals and uranium by starfish and *Pseudomonas putida*

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ABSTRACT

Biosorption of heavy metals and uranium from contaminated wastewaters may represent an innovative purification process. This study investigates the removal ability of unit mass of *Pseudomonas putida* and starfish for lead, cadmium, and uranium by quantifying the adsorption capacity. The adsorption of heavy metals and uranium by the samples was influenced by pH, and increased with increasing Pb, Cd, and U concentrations. Dead cells adsorbed the largest quantity of all heavy metals than live cells and starfish. The adsorption capacity followed the order: U(VI) > Pb > Cd. The results also suggest that bacterial membrane cells can be used successfully in the treatment of high strength metal-contaminated wastewaters.

1. Introduction

Contamination of soils and groundwater with mixed wastes, which are a mixture of radionuclides and heavy metals, is of great concern for government, industry and communities [1]. These metals and radionuclides have been introduced into the environment from the industrial activities and the processing of ore mining [2].

Biosorption of metals is one of the possible innovative technologies involved in the removal of toxic metals from industrial wastes and subsurface environment [3]. Biosorption involves the accumulation of metals by biological material either by metabolically mediated methods or by purely physio-chemical means. Unlike physical and chemical treatments, biosorption can reduce the operational costs and many potential sources of biological material are cheaply and readily available [3]. Several recent studies sought to quantify the adsorption of heavy metals onto microorganisms [4,5]. The starfish have been tested as a biosorbent to remove the toxic metals since it is inexpensive, abundant, and contain calcium oxide compounds that are capable of precipitating and sorbing significant quantities of metals. The toxicity and mobility of heavy metals and radionuclides between biosorbent and adsorptive depends on the pH, the chemical nature of the metal species, the stability of metal complexes, the binding power of the functional groups, and the ionic strength [6].

More research is needed, however, to better understand the interactions of these contaminants with biosorbent in the contaminated soil and water. The present understanding in the ability of bacteria to remove various these metals related to microorganisms is incomplete, and it is still not known which microorganisms or other biosorbents, like starfish, are the most effective to remove these metals in the subsurface environment.

The objectives of the experiments were to determine the ability of *Pseudomonas putida* and starfish to uptake heavy metals and uranium. Results from this study should be useful in understanding bioavailability and further in the remediation of subsurface media polluted with mixed wastes.

2. Materials and methods

2.1. Bacteria and starfish

P. putida was obtained as single specie from American Type Culture Collection (ATCC 17484) and used as a bacterial strain. The bacterium was grown until the stationary phase for 24 h at 30 °C on the rotary shaker (150 rpm) in 50 mL of nutrients broth (Difco 0001, Difco Laboratory, Detroit, MI). One milliliter of the culture was used as an inoculum for 1 L of the medium. The cells were collected by centrifugation at 4 °C (15 min at 7000 rpm) and washed twice with distilled water. We determined the dry weight of *P. putida* suspension by drying them for 24 h at 60 °C. Dead cells were obtained by treatments suggested by Kurek et al. [7]. The dead cells were also washed with distilled water. The bacterial cells were suspended at 0.02 mg (dry weight) mL^{-1}. Cell suspensions without heavy metals and uranium were prepared as a control.

Starfish collected from a local beach area of East Sea in Korea was air dried and ground in a crushing mill to a particle size <1 mm.

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Table 1
The composition of starfish analyzed by X-ray fluorescence spectrometer (mass%)

Na_2O	0.61
MgO	2.97
Al_2O_3	0.48
SiO_2	1.02
P_2O_5	1.25
SO_3	2.51
K_2O	0.28
CaO	45.29
TiO_2	0.08
MnO	0.11
Fe_2O_3	0.00
Others	0.48
LOI[a]	44.56

[a] Loss on ignation.

After washing with ultra-pure water at three times, the ground starfish was air dried again. The composition of starfish is analyzed by X-ray Fluorescence Spectrometer (Rigaku, ZSX100E) and given in Table 1.

2.2. Batch experiments

MINTEQA2 [8] was used to determine the upper concentration limit to avoid the supersaturation of the metals in this study. Since the chemical speciation of these metals and uranium have a different selective affinity to biosorbent and toxicity to microorganisms [9], all experiments were conducted at pH 6.0 on the basis of the result from modeling.

All adsorption experiments were conducted at room temperature. Adsorption isotherms were constructed for starfish and bacteria (live and dead cells) by equilibrating them with increasing Pb, Cd, and U concentrations. The range of contaminant concentrations [as $PbNO_3$, $CdNO_3$, and $(UO_2(NO_3)_2{\cdot}6H_2O)$] and the solid to solution ratio, were set up based on the result of preliminary adsorption tests [10], to get measurable and statistically significant measurements. The solutions contained Pb, Cd, and U were placed in 50 mL tubes and 25 mL of $NaNO_3$ (0.05 M) was used as a background solution. Initial pH of the solution was adjusted to 6 by adding small amounts of 1 M HNO_3 or 1 M NaOH. They were shaken for 48 h at 200 rpm (orbital shaker) and then centrifuged at 10,000 rpm for 20 min. Supernatants were analyzed for Pb and Cd using Atomic Absorption Spectrophotometer (AAS, Varian 240 FS), and for U with a kinetic phosphorescence analyzer (CHEMCHECK Inst. Inc., Model KPA-11). All experiments were conducted in triplicate.

The pH edge studies of adsorption were carried out by mixing each 1.0 mg L^{-1} $PbNO_3$, $CdNO_3$, and $UO_2(NO_3)_2{\cdot}6H_2O$ with 0.1 g *P. putida* or 0.1 g starfish to 30 mL of 0.05 M $NaNO_3$ solution, and pH values were adjusted from 2 to 12 by adding small amounts of 1 M HNO_3 or 1 M NaOH. The samples were equilibrated for 24 h at 200 rpm (orbital shaker) and then centrifuged at 12,000 rpm for 20 min. The final pH of the supernatant was measured using a pH meter (Fisher, Model Accumet 25).

Adsorption kinetic experiments were carried out with the same mass used on adsorption experiment: total concentration of 1 mg L^{-1}, final pH of 6.0, and ionic strength of 0.05 M $NaNO_3$. The samples were placed on a reciprocating shaker table and agitated for designated time periods. After the desired time, the samples were centrifuged and filtered to remove particle larger than 0.2 μm.

The uptake percentages were calculated from the difference between the initial and final concentrations after equilibrating for 5 days. Blank samples without the metals were prepared to verify no contribution from the original material.

Table 2
Parameters of pseudo-second order adsorption kinetics

Sorbent	Chemicals	q_e (mg g^{-1})	k (g mg^{-1} min^{-1})	r^2
Starfish	Pb	0.1495 ± 0.0053	0.2203 ± 0.0047	0.9688
Live cell	Pb	0.1315 ± 0.0047	0.3379 ± 0.0053	0.9650
Dead cell	Pb	0.2383 ± 0.0013	0.3620 ± 0.0011	0.9980
Starfish	Cd	0.1197 ± 0.0055	0.3162 ± 0.0039	0.9459
Live cell	Cd	0.1010 ± 0.0047	0.6703 ± 0.0036	0.9345
Dead cell	Cd	0.2020 ± 0.0036	0.4525 ± 0.0032	0.9893
Starfish	U	0.1745 ± 0.0053	0.3124 ± 0.0051	0.9730
Live cell	U	0.1529 ± 0.0043	0.2653 ± 0.0031	0.9789
Dead cell	U	0.2599 ± 0.0024	0.3629 ± 0.0010	0.9971

2.3. Pseudo-second order kinetic model

In order to examine the controlling mechanism of the biosorption process, kinetic models are used to test the experimental data. The pseudo-second order kinetic equation is widely used by many researchers to express the kinetic of metal ion biosorption on biological materials because it always provided a more appropriate description than the first order equation [11,12]. It can be expressed in a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (1)$$

where q_t is the amount of sorbate on sorbent at time t (mg g^{-1}), k is the equilibrium rate constant of pseudo-second order sorption kinetics (g mg^{-1} min^{-1}), and q_e is the equilibrium uptake (mg g^{-1}).

Equation (1) can be rearranged to obtain a hyperbolic equation [12]:

$$q_t = \frac{q_e t}{(1/kq_e) + t} \quad (2)$$

The parameters q_e and k were estimated by applying a nonlinear regression by least squares method performed with SigmaPlot software (see Table 2). The pseudo-second order kinetic equation shows how the adsorption capacity of adsorbate depends on time. If the equilibrium adsorption capacity of adsorbate and the rate constant k are known, then the adsorption capacity of adsorbate at any time can be calculated.

3. Results and discussion

The chemical speciation of metals may controls their mobility and adsorption [4,9]. The calculated speciation of chemicals changes with pH in the experimental system. Fig. 1 shows the speciation for heavy metals from pH 2 to 13, and clearly illustrates that below pH 6.0, both Pb and Cd do not complex with anions such as hydroxide ion in system. The speciation profile predicted that most of heavy metals are present as electrically positive and no precipitation with anions at pH 6.0. As pH increases in an open system, the concentration of hydroxide ions increases and heavy metals (Pb and Cd) may precipitate. Because the precipitation occurred in the solution at pH value above 7.0, we conducted all experiments at pH 6.0.

Uranium(VI) exists as UO_2^{2+} in acid environment. As pH increases in an open system, composite hydrolyzed ionic species predominate, the concentration of dissolved carbonate increases, and the degree of U(VI) complexation with carbonate increases as well. Mononuclear and multinuclear ions appear as hydrolysis products. It appears that loss of H^+ from coordinated H_2O is followed by polymerization involving –OH-bridges and yielding species such as UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$. Carbonate complexes, UO_2CO_3 (aq) and $UO_2(CO_3)_2^{2-}$, are to predominate in the pH range 7–9. Additionally, competition between