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Biosorption of cadmium by various types of dried sludge: An equilibrium study and investigation of mechanisms

Sun Beom Choi, Yeoung-Sang Yun *

Division of Environmental and Chemical Engineering, Research Institute of Industrial Technology,
Chonbuk National University, Chonbuk 561-756, Republic of Korea

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Abstract

Batch equilibrium sorption experiments were used for screening for cost-effective four types of sludge, which were DWS (drinking water treatment plant sludge), LLS (landfill leachate sludge), ADSS (anaerobically digested sewage sludge), and SS (sewage sludge). SS removed cadmium most efficiently from aqueous solution (0.38 mmol/g), and showed the highest desorption efficiency (26.3%). Only the SS can be fitted by Langmuir isotherm model ($r^2 = 0.996$). The FT-IR spectra of SS and cadmium loaded SS indicated that carboxyl groups were major binding sites of cadmium binding sites. In kinetic experiment, it was found that the uptake of the metal by the SS was accompanied with proton release, indicating that the metal binding occurs via an ion exchange as well as by electrostatic interaction between carboxylate groups and cadmium ions. This sorbent may have a potential for use as high-value biosorbent of heavy metals and it deserves further investigations into the details of practical application, for example on the development of desorption methods and on sorption process optimization.

Keywords: Biosorption; Sludge; Cadmium; Binding site; Binding mechanism

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1. Introduction

Alternative methods of metal removal and recovery based on biological materials have been considered. Certain types of microbial biomass can retain relatively high quantities of metals by means of a passive process known as biosorption, which is dependent on the affinity between the metallic species or its ionic forms and the binding sites on the molecular structure of the cellular wall [1]. Binding sites are present in cell wall, composed of lipopolysaccharide, peptidoglycan, and phospholipids, and also present in EPS (exopolymeric substances) composed of the neutral sugar compounds galactose and glucose, with minor amounts of mannose, xylose, arabinose, rhamnose, fucose, and two *O*-methyl sugar [2]. In contrast to mineral surfaces, the surfaces of microorganisms contain multiple reactive layers, each with a distinct structure and chemical composition.

The sorption of heavy metals on to these biomaterials is attributed to their constituents which are mainly proteins, carbohydrates and phenolic compounds which contain functional groups such as carboxyl, hydroxyl and amine that are responsible for the binding of metal ions [3,4]. Therefore, identification of functional groups, responsible for the metal binding, is important. Spectroscopic examination of the dried microorganism suggests the presence of reactive functional groups.

Large numbers of microorganisms have been used as sorbents for heavy metals [5,6]. Some of the these alternative adsorbent materials are algae, almond husk, clays, yeast biomass, perlite, maple sawdust, seaweeds, pine bark, fly ash, etc. for the removal of heavy metal from wastewater [7]. Activated sludge is one of the most abundant source of microbial biomass. Although this microbial biomass is potentially recyclable until now most has been dumped at sea and/or buried in landfill at least in Korea. Therefore, the feasibility for reusing it as a value-added biosorbent deserves to be assessed.

The purpose of this study was testing capacities of metal loading of various types of sludge, and selecting the most effective biosorbent. In this study, sewage sludge, anaerobically digested sludge, drinking water treatment plant sludge, and leachate sludge were tested. Cadmium was chosen for the sorbate material because of its simple water chemistry.

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* Corresponding author. Tel.: +82 63 270 2308; fax: +82 63 270 2306.
E-mail address: ysyun@chonbuk.ac.kr (Y.-S. Yun).

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Table 1
Change of sewage sludge's metal contents by acid-treatment

	Before acid-treatment (mg/g sludge)	After acid-treatment (mg/g sludge)
Al	514.8	510.2
Ca	106.08	20.34
Cd	0.02	0.01
Cu	3.97	2.62
Zn	9.70	4.42
Ni	0.63	0.58
Pb	0.83	0.49

Determined by acid digestion under reflux and ICP-MS.

2. Materials and methods

2.1. Materials

The two types of sludge which were LLS (landfill leachate sludge) and SS (sewage sludge) were obtained from sewage treatment plant at Jinan in Korea. DWS (drinking water treatment plant sludge) was obtained from biological water treatment process of waterworks plant at Jinan in Korea and ADSS (anaerobically digested sewage sludge) was obtained from sewage treatment plant at Jeonju in Korea. Every type of material was treated with a 1 N HNO_3 solution for 24 h, replacing the natural mix of ionic species with protons. The effects of acid-washing are given in Table 1 in case of SS. All kinds of metal ions were decreased after acid-treatment. The acid-treated sludges were washed with deionized distilled water several times and thereafter dried at 60 °C in an oven for about 24 h. The resulting dried sludges were used as a biosorbent in the experiments.

All chemicals employed in this research were analytical grade. The 1 M Cd stock solution (pH 4) was prepared using $Cd(NO_3)_2 \cdot 4H_2O$. To adjust the pH, concentrated NaOH solutions were used. For all batch isotherm experiments, 100 ml plastic bottles were used. Bottles and all glassware were washed in 1 N HNO_3 for 24 h before use and rinsed with deionized water.

2.2. Batch adsorption experiments

Cd(II) concentrations ranging from 0 to 5×10^{-3} M were mixed with dried sludge at 5 g/l. Suspensions were agitated at room temperature (20 ± 2 °C) and the pH was controlled using 1 M NaOH. Samples were taken periodically to analyze the cadmium concentration. Detailed standard procedure for determination of the sorption isotherm has been reported elsewhere [5,6].

2.3. Sorption dynamics experiments

To determine the contact time required for the sorption equilibrium experiments, dried sewage sludge (5 g/l) was mixed with synthetic wastewater (500 ml containing 3 mM Cd^{2+}). Samples were intermittently removed from the vessels to analyze the cadmium concentration. The total volume of withdrawn samples did not exceed 1% of the working volume. During the contact time, pH adjustment was not conducted to monitor the pH change.

2.4. Measurements of cadmium uptake

Before analysis of cadmium concentration, all samples were filtered through 0.45 μm pore size hydrophilic membranes (HVLP01300, Millipore, USA). The dissolved cadmium concentration of samples was analyzed using an Anodic Stripping Voltammetry (TEA3000V, MTI Instruments, Australia). In order for the change of working volume (up to 5%) by added Cd^{2+} stock and NaOH solutions, the metal uptake (q) was calculated from the mass balance as follows:

$$q = \frac{V_0 C_0 - V_f C_f}{M}, \tag{1}$$

where V_0 and V_f are the initial and final (initial plus added base solution) volumes, respectively. M stands for the weight of dried sludge used.

2.5. Desorption experiments

To evaluate the desorption efficiency the Cd^{2+}-loaded sludge was dried at 60 °C for 24 h after equilibrium sorption experiments at pH 5. The dried sludge was contacted with 1 M HNO_3 for 24 h to allow cadmium to be released from the sludge. Thereafter, the desorbed cadmium was analyzed and the desorption efficiency was calculated as follows:

$$\text{desorption efficiency (\%)} = \frac{\text{released cadmium (mmol)}}{\text{initially sorbed cadmium (mmol)}} \times 100 \tag{2}$$

2.6. FT-IR analysis

Infrared spectra of the protonated sewage sludge was obtained using a Fourier transform infrared spectrometer (FT/IR-300E, Jasco) in order to investigate the functional groups present in the SS. Infrared spectra for cadmium loaded SS was also carried out to investigate the possible cadmium binding sites.

3. Results and discussion

3.1. Selection of sorbent for the cadmium removal

Fig. 1 shows the sorption isotherms of the cadmium biosorption using four types of dried sludges. The isotherms were drawn based on equilibrium cadmium concentration. All experiments were carried out initial cadmium concentration ranging 0–5 mM and the equilibrium pH was 5.

SS was the most effective waste product biosorbent for removal of heavy metal ions from aqueous solution. The amount of cadmium adsorbed to SS was the highest for the four types of sludge examined with an uptake of 0.38 mmol/g at an equilibrium concentration of 3.29 mM. The cadmium adsorption capacities of DWS, LLS, and ADSS were

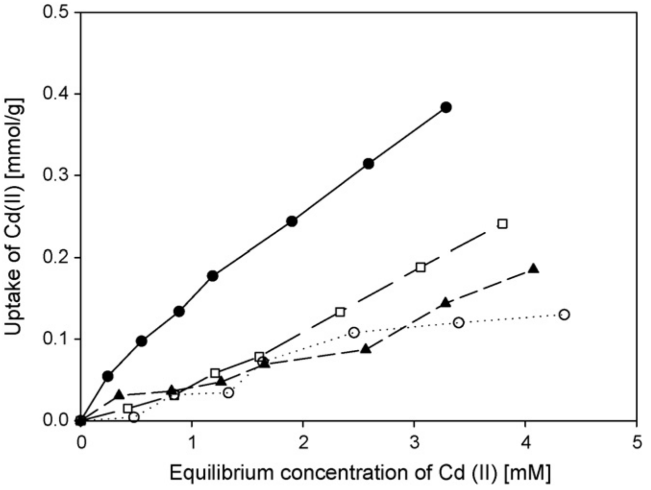

Fig. 1. The comparison of cadmium sorption isotherms at pH 5; sewage sludge (●), landfill leachate sludge (□), anaerobically digested sewage sludge (▲) and drinking water treatment plant sludge (○). Sludge concentration was 5 g/l.

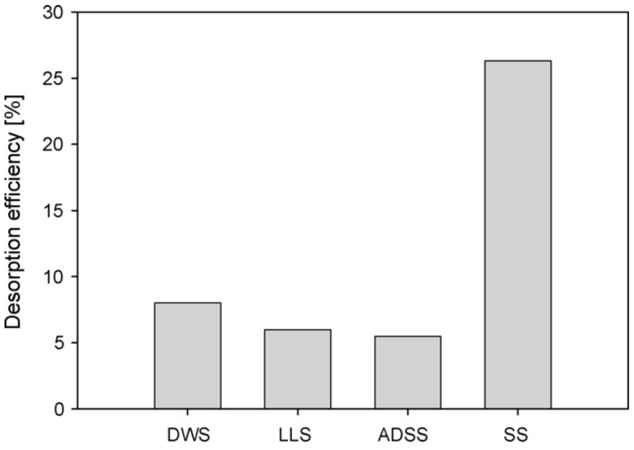

Fig. 2. The comparison of desorption efficiency: DWS (drinking water treatment plant sludge), LLS (landfill leachate sludge), ADSS (anaerobically digested sewage sludge) and SS (sewage sludge).

determined to be 0.13, 0.24, and 0.18 mmol/g, respectively (Table 2).

The Langmuir adsorption model did not fit the data obtained for DWS, LLS, and ADSS, but well represented that obtained for SS (correlation coefficient, $r^2 = 0.996$). The estimated maximum capacity, $q_{\max}$ was 1.08 mmol/g, and affinity coefficient, b was 0.16 l/mmol. Although there is a large difference between predicted (1.08 mmol/g) and experimental (0.38 mmol/g) maximum capacities, further experiments was not conducted because the purpose of this experiments was to select one sorbent which show the best performance.

Cadmium adsorption on DWS, LLS, and ADSS do not indicate any maximum value, and cannot be fitted by Langmuir or Freundlich isotherm model because of S-shaped isotherm curve and linear-shaped isotherm curve. It can be concluded that metal ions do not occupy specific ion-exchange sites. Therefore, further mechanistic studies were conducted only on biosorption of SS.

Fig. 2 displays desorption efficiencies of cadmium. In application to real wastewater, the desorption of heavy metal ions in the biosorbent is important process. SS was the most effective waste biosorbent in desorption efficiency (26.3%) as well as uptake capacity. The desorption efficiencies of DWS, LLS, and ADSS were determined to be 8.0, 6.0, and 5.5%. Although desorption efficiency of SS shows the highest value, the absolute quantity is relatively low. However, as the initial concentration of cadmium in the sorption experiment was decreased, the desorption efficiency increased (Fig. 3). Similar results were reported for lead biosorption using waste biomass of *Corynebacterium glutamicum* [8] although lead was used as metal species instead of cadmium. Therefore, further studies to choose the proper eluents, other than nitric acid, and to optimize the desorption conditions are needed for the repeated reuse of the biomass.

In this study, SS showed the highest uptake capacity and desorption efficiency which means the most suitable sorbent for the removal of heavy metal ions.

Table 2
Comparison of the equilibrium uptakes of cadmium

Sorbent	pH	$q_{\max}$ (mmol/g)	Remarks	Reference
Padina sp.	5.5	0.75	Saturated	[16]
Sargassum sp.	5.5	0.76	Saturated	[16]
Ulva sp.	5.5	0.58	Unsaturated	[16]
Pseudomonas aeruginosa PU21 (Rip64)	6.0	0.51	Saturated	[17]
Sewage sludge	5	0.38[a]	Unsaturated	This study
Gracillaria sp.	5.5	0.3	Saturated	[16]
Landfill leachate sludge	5	0.24[a]	Unsaturated	This study
Anaerobically digested sewage sludge	5	0.18[a]	Unsaturated	This study
Sewage sludge	5.8	0.15	Unsaturated	[18]
Seafood processing waste sludge	5	0.14	Saturated	[19]
Drinking water treatment plant sludge	5	0.13[a]	Saturated	This study
Paper mill sludge	4	0.11	Saturated	[20]
Paper mill sludge–soil mixture	6.7	0.09	Saturated	[21]

[a] The value was the observed maximum capacity at the experimental range, not Langmuir parameters. Therefore, the comparison with other sorbents is not fair.

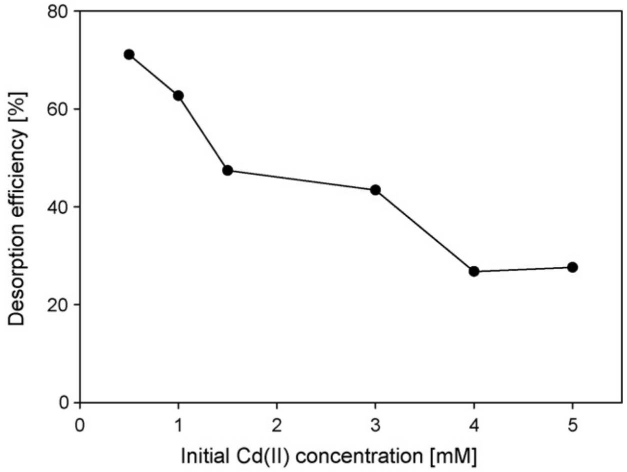

Fig. 3. Desorption efficiency of cadmium from SS when different concentrations of cadmium are present in synthetic wastewater to be treated by biosorption.

3.2. Biosorption dynamics using sewage sludge

Just after the dried sludge was contacted with the cadmium-bearing solution, the cadmium uptake increased over the initial 30 min. Thereafter, the biosorption decreased to a very slow rate until approximately 200 min. This tendency typically occurs in biosorption with various types of biomass [5,6,9] As shown in Fig. 4, a contact time of 4 h was sufficient to achieve equilibrium.

During the contact between SS and the cadmium-containing aqueous solution, the concentrations of cadmium ions and pH were measured without pH control. As shown in Fig. 4, the solution pH was decreased as the cadmium ions were bound to the biomass. This indicates that the protons attached to the sewage sludge were being exchanged for cadmium. However, since a constant ratio of cadmium–proton exchange was not found, other mechanisms must have been coupled with ion exchange, e.g. complexation [9].

3.3. Binding sites and mechanisms

In order to investigate the functional groups of sewage sludge and possible cadmium binding sites, a FT-IR study was carried out. As shown in Fig. 5, the FT-IR spectrum displays a number of absorption peaks, indicating the complex nature of the sludge examined. In the literature dealing with FT-IR spectroscopy of cell samples, measured FT-IR spectra of SS was very similar to bacterial cells.

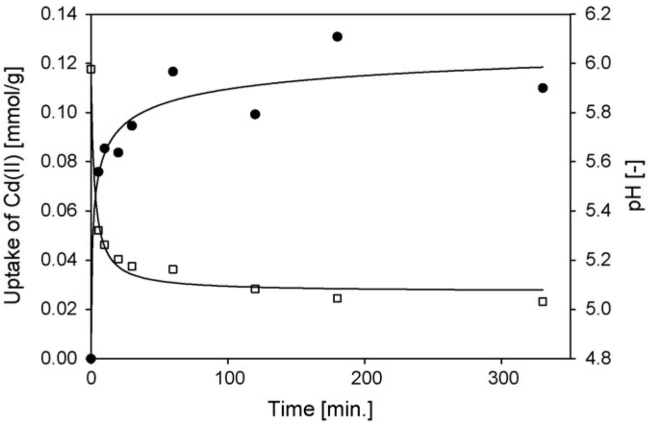

Fig. 4. Time course of cadmium uptake and pH; cadmium uptake (●) and pH (☐). Initial concentration of cadmium was 3 mM. Sludge concentration was 5 g/l.

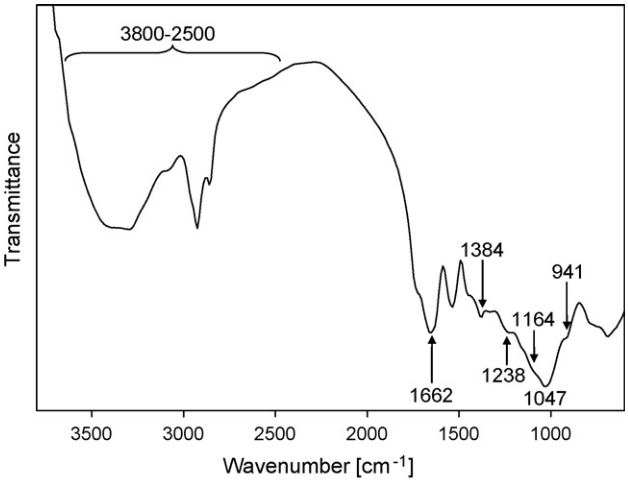

Fig. 5. Fourier transform infrared absorption spectra of the protonated sewage sludge. The absorption peaks around 1662 and 1238 cm^{-1} are indicative of the existence of amine groups. The absorption peaks at 3800–2500 and 1384 cm^{-1} correspond to carboxyl groups. The absorption peaks around 1164, 1047 and 941 cm^{-1} indicate the phosphonate groups.

The FT-IR spectroscopic analysis showed strong bands at 3800–2500 cm^{-1}, which is indicative of –OH in the carboxyl group [10,11,12] A medium strength absorption peak at 1384 cm^{-1} can be assigned to the symmetrical stretching of the carboxylate anion [12]. Like many types of bacteria [13], the SS did not show a band at 1730–1745 cm^{-1} featuring the C=O vibrations of carbonyl in carboxylic groups. Some absorption bands (P=O stretching at 1164 cm^{-1}; P–OH stretching at 941 cm^{-1}; P–O–C stretching at 1047 cm^{-1}) were considered to be indicative of phosphonate group [14]. The FT-IR spectra of the SS showed some characteristic absorption bands of amine group [15]: N–H bending band at 1662 cm^{-1}; N–H out of plane bending band near 700 cm^{-1}; and C–N stretching band at 1238 cm^{-1}. An N–H stretching band in the range of 3500–3300 cm^{-1} was not visible possibly because it was occupied by a strong and large band of carboxyl group in the range of 3800–2500 cm^{-1}.

Results of cadmium binding studies for native and cadmium loaded SS are shown in Fig. 6. After the cadmium sorption experiment using SS, cadmium loaded SS was dried in an oven at 60 °C for removal of water. The only observable change in the spectrum of the cadmium exposed SS was in the symmetrical stretch of the carboxyl group, which showed higher intensity. Similar change which shifted from 1405 to 1375 cm^{-1} was observed earlier by Ashkenazy et al. [12] when acetone washed yeast biomass sorbed lead ions. This shift can be attributed to a change in the counter ion associated with the carboxylate anion. This suggests that acidic groups, especially carboxylate, contribute to the metallic ion uptake.

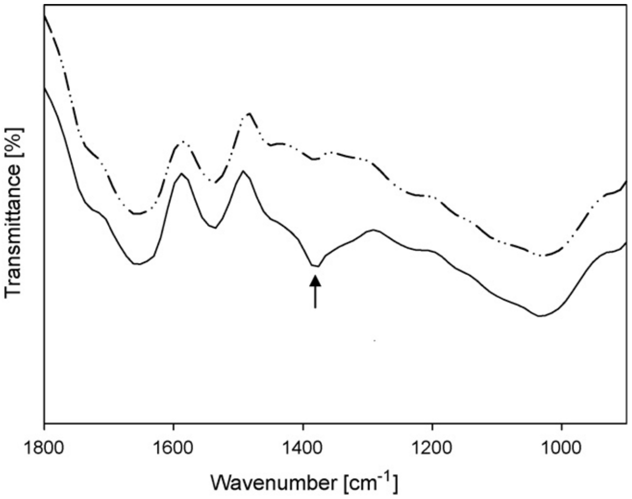

Fig. 6. Fourier transform infrared absorption spectra of the protonated sewage sludge (dotted line) and cadmium loaded sewage sludge (solid line).

From the experimental and analytical results, it can be noted that the underlying mechanisms can be both ion exchange and electrostatic interaction depending on the solution pH. At $\text{pH} < \text{p}K_a$ of carboxylic sites, the removal is obviously an ion exchange process, because the binding sites are mainly occupied by protons. However, at $\text{pH} > \text{p}K_a$, the carboxyl groups are negatively charged, the metal ions may bind to the binding sites by electrostatic attraction.

4. Conclusions

Dried sewage sludge and three other types of dried sludges have been examined for potential utilization as low-cost materials for the uptake of heavy metals from wastewaters. Different metal removal capacities and desorption efficiencies were observed when different sorbent were applied. While DWS, LLS, and ADSS resulted in similar biosorption behavior, and low uptake capacities, SS showed relatively high uptake capacity and different biosorption behavior. Because cadmium adsorption on DWS, LLS, and ADSS do not indicate any maximum value, and cannot be fitted by Langmuir or Freundlich isotherm model (S-shaped isotherm curve, linear-shaped isotherm curve), it can be concluded that metal ions do not occupy specific ion-exchange sites. Although SS also does not show maximum value, the isotherm was well represented by Langmuir isotherm model ($r^2 = 0.996$).

In kinetic experiment, solution pH was decreased according to increasing of cadmium uptake. The mechanism that governs cadmium removal by SS was an ion exchange. FT-IR showed the presence of carboxylate groups on the surface of the biosorbent. Because marked change observed at carboxyl group peak ($1384\,\text{cm}^{-1}$) in cadmium loaded SS, carboxyl groups were the dominant species in the cadmium biosorption mechanism by SS.

Conventional technologies to clean up heavy metal ions from contaminated waters have been utilized, but they remain cost-ineffective. Sewage treatment plants generate a huge amount of sludge, which is biological solid waste. Although this sludge is potentially recyclable, until now most has been dumped at sea and/or buried at landfill. Therefore, the use of sludge for the removal of heavy metals from contaminated waters may be a novel and cost-effective alternative.

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