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Binding sites and mechanisms of cadmium to the dried sewage sludge biomass

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HIGHLIGHTS

- The main functional groups of sewage sludge biomass were identified.
- Carboxyl and phosphonate groups played a role as binding sites for Cd.
- The binding mechanism was established to be complexation with binding groups.
- The contribution of functional groups on Cd binding was predicted and visualized.

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ABSTRACT

The Cd biosorption on the dried sewage sludge biomass were experimentally evaluated and mathematically modeled at different pH values. The potentiometric titration of the biomass was well fitted by the four-site model, which consists of three-negative and one-positive sites. The main functional groups were identified through the FTIR study. The pH edge study showed that both the carboxyl and phosphonate groups played an important role in the binding of Cd. From the dynamic biosorption experiments, the H^+/Cd^{2+} exchange ratios at pH 4, 5 and 6 were estimated; thereby the binding mechanisms were established to be complexation with carboxyl and phosphonate groups. Finally, biosorption model was developed based upon the binding mechanism, which was successfully applied for predicting the isotherms and pH edges. Using the developed model equation, the contribution of each functional group on Cd binding could be predicted and visualized.

1. Introduction

Biosorption has been considered as a promising technique for the treatment of heavy metals from metal-containing wastewaters (Davis et al., 2003). The main advantages of biosorption are cost-effectiveness, high efficiency and good biosorption performance. The use of microorganisms as biosorbents for heavy metals offers a potential alternative to the existing methods for the detoxification and recovery of these components from industrial wastewaters (Ahluwalia and Goyal, 2007; Vijayaraghavan and Yun, 2008). The biomass of sewage sludge is one of the most abundant microbial biomasses (Arican et al., 2002). Thus, these types of biomasses are easily available and very cheap compared to commercial sorbents such as activated carbons and ion exchange resins.

The biosorption of heavy metals by the biomasses has been attributed largely due to the cell wall, which consists of various functional groups like carboxyl, hydroxyl, amine and phosphate groups. In general, the biosorption mechanisms are based on the physicochemical interaction between the metal ions and the specific functional groups on the biomass via electrostatic interaction, ion exchange, chelation or complexation (Özer et al., 2004). Therefore, identification of functional groups on the biomass, in particular binding sites responsible for the metal binding, is useful to understand the biosorption mechanisms.

Biosorption modeling can be designed by two main different ways using empirical or mechanistic models. Conventional empirical models like Langmuir and Freundlich models have been frequently used to describe the biosorption equilibrium data. These empirical models provide information on metal uptakes at equilibrium and differences in metal uptake between various species (Kapoor and Viraraghavan, 1995). However, the empirical models cannot offer any mechanistic understanding of biosorption phenomena to predict systems operating under different conditions (Wang and Chen, 2006). On the contrary, the mechanistic models

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based on the mechanism of metal ion biosorption are an advanced approach for the description of biosorption behavior. They can be used as tools in understanding and screening of the physical and chemical mechanisms involved in metal biosorption (Pagnanelli et al., 2004). Moreover, the mechanistic modeling of biosorption processes is essential to the prediction, optimization and design for the biosorption performance. It is also required to make the use of biosorption and its potential more effective (Yun and Volesky, 2003).

In this work, the protonated biomass of sewage sludge was used as a biosorbent and cadmium was selected as a model heavy metal because of its high toxicity and simple water chemistry in aqueous solutions. The functional groups involved in Cd binding on the sewage sludge were examined through potentiometric titration, FTIR, and pH edge experiments. Dynamic biosorption and isotherm experiments were also conducted to evaluate the Cd binding mechanisms. Furthermore, Cd binding to each functional group was mathematically modeled and simulated by the modeling of Cd biosorption suggested in this study.

2. Materials and methods

2.1. Materials

The sewage sludge was obtained from a sewage treatment plant at Jinan, Korea. This plant treats domestic sewage through a conventional activated sludge process. The sewage sludge generated from primary and secondary sewage treatment processes was dewatered using a belt pressure filter following the addition of a polymer flocculent. It was sun-dried and then treated with 1.0 M HNO_3 for 24 h, which replaced the natural mix of ionic species with protons. The acid-treated sewage sludge biomass was washed with deionized distilled water several times and dried at 60 °C for 24 h in an oven. The resulted dried biomass was ground to fine powder of less than 0.25 mm particle size and used as a biosorbent in this work.

Analytical grade cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$) was purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan) and used as an adsorbate. Nitric acid (HNO_3, 60%) and sodium hydroxide (NaOH, >97%) were supplied by Showa Chemical Co., Ltd. (Tokyo, Japan) and Daejung Chemicals & Metals Co., Ltd. (Siheung, Korea), respectively.

2.2. Potentiometric titration

Potentiometric titration experiments were carried out using a similar method reported in literature (Won et al., 2005). Briefly, the biomass (40 g L^{-1}) and 20 mL of CO_2-free water were placed into each 50-mL polypropylene conical tube. Different volumes of 1.0 M NaOH were then added into the each tube. The tubes were stirred at 160 rpm and 25 °C for 24 h in a shaker. During the potentiometric titration experiments, the CO_2-free condition was maintained to avoid the influence of inorganic carbon on the solution pH.

2.3. FTIR analysis

Fourier transform infrared spectroscopy (FTIR) was used to identify the major functional groups on the biomass and to find the specific groups related to the Cd binding. The KBr pellets for FTIR analysis were prepared by applying pressure through hydraulic pressure pump on the finely ground biomass and KBr mixture. Infrared spectra of the sewage sludge biomass before and after Cd biosorption were recorded by a FTIR spectrometer (FT/IR-300E, Jasco, USA) within the range of 4000–400 cm^{-1}.

2.4. Dynamic biosorption experiments

For the dynamic biosorption experiments, the biomass (5 g L^{-1}) was suspended in 500 mL of CO_2-free deionized distilled water and the solution pH was adjusted to 4, 5 or 6 by the addition of 0.1 M NaOH. Then, 1.5 mL of the concentrated Cd solution was added into the biomass suspensions. The initial Cd concentration was 3 mmol L^{-1}. The mixture was agitated with 160 rpm at room temperature in nitrogen atmosphere to avoid the effect of atmospheric CO_2. During the experiments, the solution pH was maintained at the desired value (pH 4, 5 or 6) using 0.1 M NaOH. The samples were collected at predetermined time intervals. An additional amount of 0.1 M NaOH was monitored and calculated the amount of hydrogen ions (H^+) released.

2.5. pH edge experiments

An equilibrium relationship between the Cd uptake and the final pH is helpful to understand the pH dependence of biosorption. For this, the pH edge experiments were performed with 5 mmol L^{-1} of initial Cd concentration and 5 g L^{-1} of biomass. The pH of the suspension was initially adjusted and controlled using 0.5 M NaOH or 1.0 M HNO_3. The suspension was agitated with 160 rpm at 25 °C for 24 h in a shaker. After reaching equilibrium, the equilibrium solution pH was measured and the samples were centrifuged for liquid–solid separation. The supernatant portion was used to analyze the residual Cd concentration after appropriate dilution.

2.6. Isotherm experiments

The isotherm is a powerful tool to estimate the sorption capacity of a biosorbent. The isotherm experiments were conducted with 0.4 g biomass in 80 mL of the Cd solution. The initial Cd concentrations were varied from 0 to 5 mmol L^{-1}. The suspensions were stirred at 160 rpm and 25 °C. The solution pHs were controlled at the desired values using 0.1 M NaOH because the pH tended to decrease during the Cd biosorption. After the biosorption equilibrium was reached, the samples were taken from the bottles and properly diluted with deionized water for the analysis of the Cd concentration remained in the supernatant.

2.7. Measurement of Cd uptake

The dissolved Cd concentration of the samples was analyzed using an Anodic stripping voltammetry (TEA-3000 V, MTI Instruments, Perth, Australia). To adjust the change of the working volume (up to 5%) by the addition of NaOH or HNO_3 solution, the Cd uptake, q (mmol g^{-1}), was calculated using the following mass balance:

$$q = \frac{V_i C_i - V_f C_f}{M} \quad (1)$$

where C_i and C_f are the initial and final Cd concentrations (mmol L^{-1}), respectively. V_i and V_f are the initial and final (initial plus added acid or base solution) volumes (L), respectively. M represents the weight of biomass (g) used in the experiments.

3. Results and discussion

3.1. Characterization of functional groups on sewage sludge biomass

The functional groups on the biomass can be identified through the combined studies of potentiometric titrations of biomass suspensions and IR spectra of solid samples of biomass before and