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Studies on biosorption equilibrium and kinetics of Cd^{2+} by *Streptomyces* sp. K33 and HL-12

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ABSTRACT

The sorption of Cd^{2+} by *Streptomyces* sp. K33 and HL-12 was investigated. The removal efficiency increased with pH, but no obvious differences with different temperatures. Fourier transform infrared (FT-IR) was used to characterize the interaction between Cd^{2+} and K33 and HL-12. Results revealed that the presence of amino, carboxyl, hydroxyl and carbonyl groups were responsible for the biosorption of Cd^{2+}. Strain HL-12 had more changes in the functional groups than K33. Biosorption equilibrium was established earlier by strain K33 than that by HL-12, and K33 had higher adsorption ratio. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms were used to describe the adsorption experiment, Langmuir model fitted the experiment data best. Strain K33 showed greater sorption capacities with 38.49 mg Cd^{2+}/g dry cells. Pseudo-first-order and second-order kinetic models were used to describe the kinetic data, and second-order kinetic model fitted better. About 70% recovery of Cd^{2+} could be obtained at pH $\leq$ 3 from metal-loaded biomass of strains HL-12 and K33.

1. Introduction

Biosorption is an innovative technology that employs inactive and dead biomass for the recovery of heavy metals from aqueous solutions. As an alternative to traditional methods, its promising results are now being considered for application by the scientific community. So, alternative methods of metal removal and recovery based on biological materials have been considered increasingly day by day. 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, such as galactose and glucose, with minor amounts of mannose, xylose, arabinose, rhamnose, fucose and two *O*-methyl sugars [2]. In contrast to mineral surfaces, the microbial surface contains multiple reactive layers, each with a distinct structure and chemical composition. The use of biological materials, including living and non-living microorganisms, to remove and possibly recover toxic or precious metals from industrial wastewaters, has gained important credibility during recent years, because of the perfect performance and lower cost of these sorbent materials. The sorption of heavy metals on to these biomaterials is attributed to their constituents which are mainly proteins, carbohydrates and phenolic compounds containing 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 binding the metals, is important. Spectroscopic examination of the dried microbial cells has suggested the presence of reactive functional groups.

Large numbers of microorganisms have been used as sorbents for heavy metals [5,6]. Some of 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]. Although a lot of studies using different types of biomass have proved that biosorption is a more effective method for heavy-metal removal than the conventional ones, further investigation is still needed to optimize the maximum efficiency of heavy-metal removal, which is expected to lead to its large-scale exploitation [8]. Studies are indispensable on the testing capacities of metal loading of various types of streptomycetes, and identifying functional groups responsible for the metal binding as the information on biosorption of heavy metal by streptomycetes is still little until now and streptomycetes have abounding biomass

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and rapid growth capability. The cell wall of streptomycetes generally contains three components: peptidoglycan, teichoic acid and surface protein. These compounds may contain several functional groups (amino, carboxyl, sulphate, hydroxyl, etc.) which could play an important role in the biosorption process.

In this study, *Streptomyces* sp. K33, isolated from industrial metal mine and exhibited high resistance to a variety of heavy metals, and *Streptomyces* sp. HL-12 sensitive to heavy metals, isolated from a farmland uncontaminated by heavy metal on Huajiachi campus of Zhejiang University were tested for their biosorption. Cadmium (Cd) was used as the target metal pollutant in this work, which is frequently found in the industrial effluents and wastes in China.

Fourier transform infrared (FT-IR) analysis, equilibrium of biosorption, kinetics and desorption efficiency of Cd^{2+} from loaded biosorbents were used to further evaluate the feasibility of applying the two strains in practical heavy-metal removal processes. These results would contribute to a better understanding of biosorption phenomena and be beneficial in the development of potential biosorbents that possess high capacities for heavy-metal uptake from aqueous environments.

2. Materials and methods

2.1. Culture conditions of Streptomyces strains tested and preparation of biosorbents

Strain K33 and HL-12 were used in this study, which were isolated from industrial metal mine and a farmland uncontaminated by heavy metals, respectively. Strain K33 showed much higher metal resistance than another isolate HL-12. The bacterial cultures were typically incubated in LB broth at 28 °C. 150 rpm agitation was employed for the shake-flask culturing. Then the cells were harvested by centrifugation (10,000 × *g*, 8 min) from early stationary cultures with a cell density of approximately 2.0–2.5 g l^{-1}, and resuspended in Cd^{2+} solution for the biosorption experiments after twice rinsed with deionized water.

2.2. Measurements of cadmium uptake

The heavy-metal adsorbate used in this study was Cd ($CdCl_2{\cdot}2.5H_2O$). Heavy metal in solutions was measured with Polarized Zeeman Atomic Absorption Spectrometer (AAS, Shimadzu Model-AAA-6650, Japan). Before measured by AAS, the heavy-metal solutions were appropriately diluted with deionized water to ensure that the heavy-metal concentration in the sample was linearly dependent on the absorbance detected.

2.3. Effects of pH and temperature on biosorption

Effects of pH and temperature on biosorption were studied at pH values of 3–7 and temperatures of 20 to 40 ± 1.5 °C at 50 mg l^{-1} initial metal concentration and 24 h of incubation.

2.4. Batch adsorption experiments

The biomass was suspended in solutions containing Cd^{2+} concentrations of 0.5–100 mg l^{-1}. The cell concentration in the solutions was ranged from 1.5 to 2.5 g l^{-1}. The cell/metal suspension was gently agitated (125 rpm) at 28 °C. The pH of the solution was initially adjusted to 6.0 for Cd^{2+}, for avoiding precipitation of it in the form of metal hydroxides. Samples were taken from the solutions after 24 h of incubation (28 °C, 125 rpm) and the metal concentration in the supernatants was measured with AAS.

2.5. Sorption dynamics experiments

To determine the contact time required for the sorption equilibrium, the biosorbents were suspended in 100 ml of heavy-metal solutions (1.0, 10.0 and 50.0 mg l^{-1}) in a glass container, making a cell concentration of 1.5–2.5 g l^{-1}. The adsorption conditions (temperature, pH and agitation rate) were the same as those used in batch adsorption experiments. Samples were intermittently taken from the vessels for analyzing the Cd^{2+} concentration.

2.6. Desorption experiments

Cd-loaded biosorbents were harvested from the cell/metal solutions with the Cd^{2+} concentration of 50.0 mg l^{-1} after biosorption experiments and then rinsed and resuspended with metal-free deionized water. Proper amounts of 0.1 mol l^{-1} HCl [9,10] were added into solutions containing metal-loaded biomass to adjust the pH value to 1, 2, 3, 4, 5, 6 and 7. Samples were taken from the suspensions after 24 h gentle agitation and centrifuged immediately and the metal concentration in the supernatant was detected. Thereafter, the desorbed cadmium was analyzed and the desorption efficiency was calculated as follows:

$$\text{The desorption efficiency}\,(\%) = \frac{\text{released Cd (mg)}}{\text{initially sorbed Cd(mg)}} \times 100 \quad (1)$$

2.7. FT-IR analysis

Infrared spectra of the Cd-loaded and Cd-non-loaded strains were obtained using a Fourier transform infrared spectrometer (FT/IR-300E, Jasco, Japan) in order to investigate the functional groups and the possible cadmium binding sites present in the strains.

3. Results and discussion

3.1. Effect of pH and temperature on the biosorption capacity

Experiment concerning the effect of pH on the sorption was carried out with the range of pH that was not influenced by the metal precipitation (as metal hydroxide). The calculation from the solubility product equilibrium constant (K_{sp}) demonstrated that the suitable pH range for Cd^{2+} is 1–8 [11]. Fig. 1 illustrated that in most cases, the removal efficiency increased steadily with pH. The sorption at the low pH range usually took place with low removal efficiency. This occurred because there was a high concentration of proton in the solution and this proton competed with metal ions in forming a bond with the active sites (the functional groups) on the surface of the strains. These bonded active sites

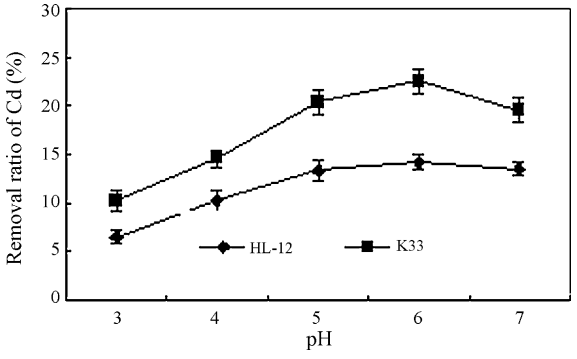

Fig. 1. Effect of pH on removal efficiency by *Streptomyces* sp. HL-12 and K33.