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Biosorption of mercury(II) ions from aqueous solution by garlic (*Allium sativum* L.) powder

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Abstract−A biosorbent was prepared by drying garlic (*Allium sativum* L.) under vacuum and tested in its powder form for its mercury adsorption capability in aqueous solution. Results show that garlic powder has a good adsorption capacity for mercury and that the mercury concentration of the solution has a significant impact on the adsorption capacity of the biosorbent. The Langmuir and Freundlich adsorption isotherms were also constructed. The adsorption capacity, q_{max}, adsorption efficiency, b, and correclation confficient, r^2 for the Langmuir model were 0.6497, 0.4903, and 0.9980, respectively. For the Freundlich model, the model parameters, K_F, 1/n, and r^2 for mercury were 4.1879, 0.3467, and 0.9518, respectively. Langmuir adsorption isotherm was better suited for the adsorption of mercury onto garlic powder, and that the maximum amount of mercury adsorbed (q_{max}) was 0.6497 mg/g.

Key words: Biosorption, Mercury, Garlic (*Allium sativum* L.), Adsorption Isotherm

INTRODUCTION

Industrial development and urbanization have led to a continuous increase in the production of toxic substances. These toxic agents are discharged into the environment, putting living organisms at risk and potentially constituting serious hazards to public health [1,2]. Among heavy metals, mercury (Hg) is the most widespread concern to human health. Recently, the use of microbial biosorbent has become an alternative to traditional methods of industrial wastewater treatment, such as ion-exchange, reverse osmosis, filtration, precipitation, adsorption and coagulation. Biosorption is a low-cost and non-hazardous option for removing hazardous substances from contaminated wastewater, and it also may permit the recovery of the heavy metals from the adsorbing biosorbent [3-7]. Previous studies have found that biosorption is a metabolism-independent process that takes place in the cell wall [8], and the mechanisms responsible for the pollutant uptake may differ according to the biosorbent type [9]. Garlic was used in this study because the organosulfur compounds present in garlic have been shown to have significant antioxidant effects, and garlic is known for its capacity to take up and accumulate cadmium ions. In addition, metallothioneins found in garlic are thought to sequester excess amounts of certain metal ions and reduce the toxic effects of cadmium on plants [10,11]. It was found that at high concentrations, cadmium inhibits root growth and cell division in plants such as onions [12,13]. Furthermore, despite the fact that most of the Hg in soil is firmly bound to organic matter or sulfides, many studies suggest that garlic vine (*Pseudocallyma alliacium*), garden pea (*Pisum sativum* L.), spring wheat (*Triticum aestivum* L.), sugar beet (*Beta vulgaris* L.), oil-seed rape (*Brassica napus* L.), and rice seedlings (*Oryza sativa* L.) could restore mercury-contaminated soil by taking up Hg, translocating it to the leaves, and eventually releasing it into the environment [14-18]. Previous studies also suggest that garlic (*Allium sativum* L.) is a feasible, affordable, easily accessible, and environmentally friendly mercury biosorbent and that mercury accumulation is directly related to the weight of the garlic root [19]. In addition, garlic has a high potential for heavy metal sorption because it grows in water. In this study, the structure and characteristics of garlic powder and raw garlic are compared, and the mercury biosorption capacity of garlic powder is investigated using Freundlich and Langmuir adsorption isotherms.

EXPERIMENTAL

All chemicals used in this study were of analytical reagent grade. A commercially available standardized solution of Hg (product code 1641d) by the National Institute of Standards and Technology (NIST, USA) and de-ionized (DI) water were used throughout this study.

1. Preparation of the Biosorbent

Fresh garlic bulbs were obtained from a local market (Seoul, Korea) and stored in a refrigerator at 4 °C. Medium-sized cloves were selected and sliced into pieces of approximately 2 cm wide and of different thicknesses. Garlic cloves were also granulated in order to determine the effect of preparation method on Hg adsorption capacity. The initial moisture content of wet samples ranged from 69.2 to 76.8%. Garlic slices and granulated pieces were dried in a vacuum oven at 65 mm Hg pressure and at 40 °C for 3 days. The color of the garlic pieces changed to a darker yellow after drying. The pieces were also air-dried in order to compare the BET surface area of vacuum and air-dried samples. The dried material was pulverized in a mill to a powder with a thickness of 0.02 mm. The BET surface area of prepared garlic powder was determined by an ASAP 2020 sorptometer.

2. Adsorption Experiments

Adsorption of mercury by the dried garlic powder (DGP) was

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investigated by batch adsorption-equilibrium experiments. Experiments were conducted in a 50-mL glass vial at room temperature. A range of mercury ion concentrations was prepared using a NIST standard solution of the mercuric nitrate salt in DI water. The amount of DGP biosorbent added to the solution was maintained at 12.5 g/L. After adsorption, the adsorbents were separated by filtration using a glass microfiber (Grande GF/C, Whatman, USA) at predetermined time intervals. The mercury content of the biosorbent was analyzed using US EPA method 7471B. In this method, Hg in the biosorbent sample is dissolved in strong acids at high temperature and high pressure. Once Hg is reduced to its elemental form, it is vaporized and Hg concentration is analyzed by a cold vapor atomic absorption (CVAA) Hg analyzer (RA-915$^+$, Lumex Ltd., Russia). The detection limit of the Hg analyzer used for this study is 0.5 ng/L. The principle of operation of a CVAA Hg analyzer is based on the mercury vapor's absorption of radiation at a 253.7 nm wavelength. The characteristics of the biosorbent were determined by a scanning electron microscope (SEM; JSM6500 F, JEOL, Japan) and Fourier transform infrared spectrometer (FT-IR; FTS 3000MX, Digilab, USA).

The duration of the adsorption experiments was one hour. To determine the equilibration time for the mercury adsorption, standard solutions with various concentrations from 0.01-5.0 mg/L were prepared.

RESULTS AND DISCUSSION

1. Stabilization of Hg(II) in Blank Solution

Prior to the experimental adsorption of the biosorbent, a stabilization test of Hg(II) in blank solution was conducted. Three different samples of Hg solution (200 μg/L) were prepared with 5% HCl, HCl : HNO_3=3 : 1, and without acid. Hg concentrations of each solution were monitored and the results are shown in Fig. 1. In the absence of acid, Hg is volatile in a solution and its concentration decreases with time. However, we observed significant stabilization of Hg in the two samples containing added acid, consistent with the property of Hg to form very strong complexes with chloride ions. As a result, an Hg solution with 5% HCl was used for the remainder of this study.

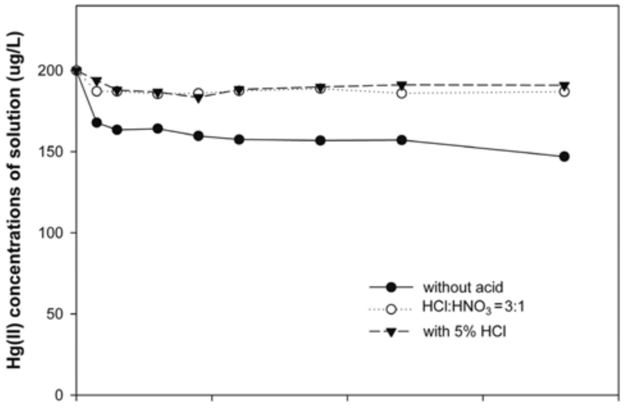

Fig. 1. Stabilization of Hg(II) in blank solution.

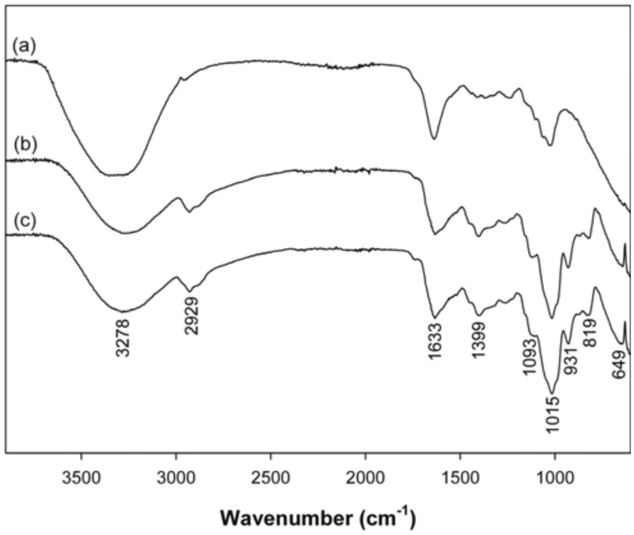

Fig. 2. FT-IR spectra of (a) raw garlic, (b) dried sliced garlic powder, (c) dried granulated garlic powder.

2. Surface Properties of DGP Biosorbent

Changes in functional groups and surface properties of garlic powder were examined by comparing FT-IR spectra before and after drying. Fig. 2 shows IR spectra of (a) garlic before drying, (b) sliced and (c) granulated garlic powder after drying. The broad -OH absorption between 3,600-3,000 cm^{-1} was decreased and the signals from the C-S(O)S-C absorption between 1,093-959 cm^{-1} and CH_3 absorption between 2,993 and 2,843 cm^{-1} were greatly increased once the garlic pieces were dried. On the other hand, spectra of the dried garlic showed S-S absorption between 783-634 cm^{-1} and S-C absorption between 853-789 cm^{-1}. These results indicate that the S-S, S-C and C-S(O)S-C bonds in the garlic compounds were increased due to broken S=S bonds, and alliin in the garlic compounds was converted to allicin. IR spectra of sliced and granulated garlic powder are almost identical, except for the absorption at 1,093 cm^{-1}. As mentioned above, this peak corresponds to C-S(O)S-C absorption. The BET surface area of vacuum-dried garlic powder (0.1259 m^2/g) was significantly higher than that of air-dried garlic powder (0.0086 m^2/g). Since many studies suggest that surface area is proportional to the adsorption capacity, vacuum-dried garlic powder was used for the remainder of this study.

3. Adsorption Rate

The adsorption rate of Hg(II) on the DGP biosorbent was determined by analyzing Hg concentrations of the solution over time and comparing them to the initial Hg concentration of the solution. First, the adsorption capacity of dried garlic powder (granulated and sliced) was tested. Fig. 3 clearly shows that the sliced garlic powder has a higher adsorption capacity. For the remainder of this study, only sliced garlic powder was used. The Hg adsorption rate was high at the beginning of adsorption, and the saturation level was reached at about 60 min. After this saturation period, the amount of adsorbed Hg(II) on the DGP biosorbent did not change significantly with time. This result indicates that the binding of Hg(II) and the biosorbent occurs through interactions with functional groups located on the surface of the biosorbent.

A few researchers have reported that there are other parameters

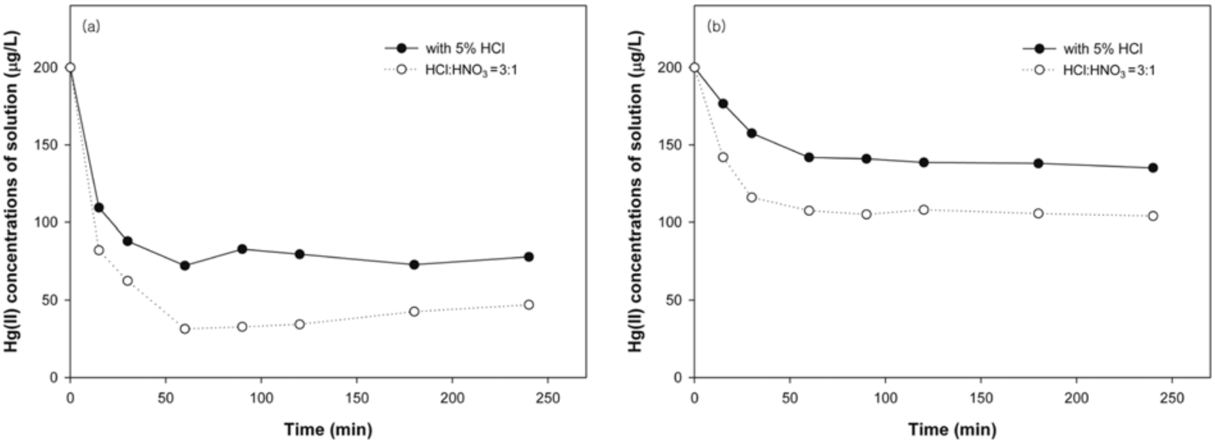

Fig. 3. Hg(II) adsorption capacities of (a) sliced and (b) granulated DGP.

that affect the adsorption rate, such as the temperature, stirring rate of the aqueous phase, and the structural properties of the adsorbent [20-23]. For example, Bel'chinskaya and Tkacheva [24] reported that the adsorption capacity increased with increasing rotational speed of the stirring rod up to a certain level. In this study, these parameters that might have effect on the adsorption rate were maintained constant in order to minimize their influences.

4. Adsorption Capacity

The Hg biosorption isotherm of the DGP biosorbent is shown in Fig. 4. It also shows the Langmuir and Freundlich models for the DGP biosorbent. Typical L-shaped sorption isotherms were observed for both models. The linearized Langmuir and Freundlich adsorption isotherms for mercury ions on the DGP biosorbent are shown in Fig. 5. The biosorption capacity of the biomass increased with increasing initial concentration of Hg(II) and reached a saturated value. The experimental data were analyzed via a pseudo-second order kinetic adsorption model. Adsorption isotherm data was analyzed using the Langmuir (1) and Freundlich (2) models, which are represented by the following equations:

$$q_e=\frac{q_{max}bC_e}{1+bC_e} \tag{1}$$

$$q_e=K_F C_e^{1/n} \tag{2}$$

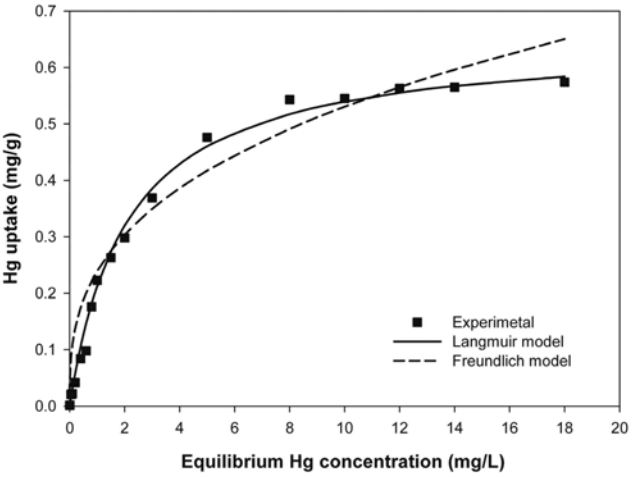

Fig. 4. Adsorption isotherms for Hg(II) ions on the DGP biosorbent.

where q_e is the amount of adsorbed metal (mg/g), q_{max} is the maximum monolayer sorption capacity (mg/g), b is the Langmuir equilibrium constant (L/mg), C_e is the equilibrium concentration of the metal in solution (mg/L), and K_F (L/g) and n are the Freundlich con-

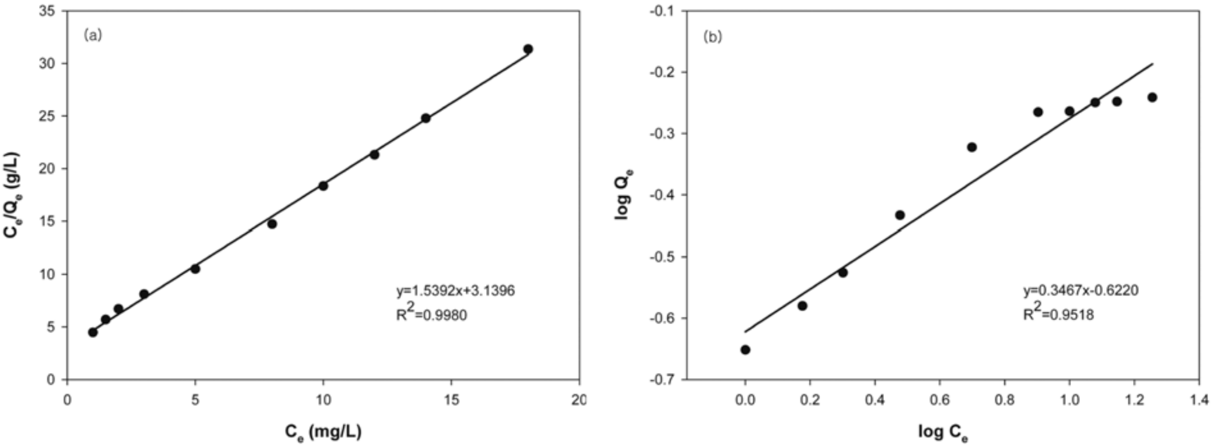

Fig. 5. Linearized (a) Langmuir and (b) Freundlich isotherms for Hg(II) adsorption by DGP.

stants. The Langmuir equation can be rearranged into linear form for the convenience of plotting and determining the Langmuir constant as shown below (3):

$$\frac{C_e}{q_e}=\frac{1}{bq_{max}}+\frac{C_e}{q_{max}} \tag{3}$$

The Freundlich equation can also be linearized in logarithmic form (4):

$$\ln q_e=\frac{\ln C_e}{n}+\ln K_F \tag{4}$$

Figs. 4 and 5 show that the Langmuir equation is a better fit for the adsorption isotherm for mercury ions on the DGP biosorbent, indicating that the mercury adsorption on DGP obeys a pseudo-second order rate expression.

The model parameters, q_{max}, b, and r^2 for the Langmuir isotherm were 0.6497, 0.4903, and 0.9980, respectively. For the Freundlich isotherm, the model parameters, K_F, 1/n, and r^2 were calculated to be 4.1879, 0.3467, and 0.9518, respectively. The specific uptake of Hg(II) found in this study was comparable with previous values reported in the literature. The biosorption capacity of Hg(II) was found to be 3.23 mg/g for coal fly ash [18], 93.8 mg/g for extracellular biopolymer [23], 3.23 mg/g and 18.9 mg/g for rice husk ash [14,21], and 336.3 mg/g for Lentinus edodes [25].

Fig. 6 compares the FT-IR spectra of used DGP biosorbents in a blank and an Hg solution. The test conditions were identical, except for the Hg concentration of the solution. Similar peaks were observed for both spectra, but the intensities were smaller for the DGP biosorbent tested in Hg solution. This result indicates that the functional groups of the DGP biosorbent are involved in the biosorption process of Hg. FT-IR spectra of used DGP biosorbent in blank solution can be also compared with unused DGP biosorbent (Fig. 2). Peaks of both spectra were different because only water-insoluble compounds in the biomass are analyzed in Fig. 6. This was verified by the weight decrease of the biosorbent after the adsorption experiment. Leftover DGP powder was dried and weighted, demonstrating that approximately 10% of the biosorbent was water insoluble.

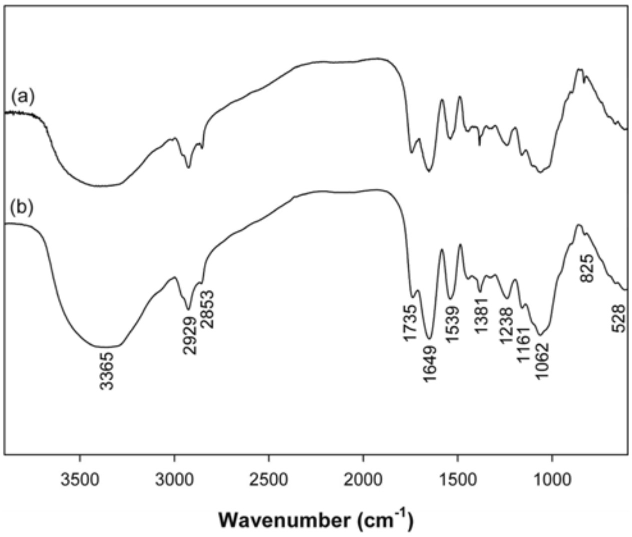

Fig. 6. FT-IR spectra of used DGP biosorbent; in blank and in Hg solution, 1-h contact time.

CONCLUSION

DGP biosorbent has been successfully used as a biosorption agent for the removal of mercury from aqueous solution. Experimental results indicated that the DGP biosorbent yielded a high biosorption capacity for Hg(II). Furthermore, the mechanism and kinetics of mercury ion adsorption on the surface of the DGP biosorbent depended significantly on the Hg concentration of the solution. The equilibrium was well described by a Langmuir adsorption isotherm. Together with the knowledge that DGP biosorbent is cheap, easily accessible, and non-hazardous, the results of this study provide a rationale for further research into the use of DGP biosorbent for heavy metal removal.

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