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Short Communication

A new efficient forest biowaste as biosorbent for removal of cationic heavy metals

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HIGHLIGHTS

- Among various forest biowastes, chestnut bur was screened as efficient biosorbent.
- The biosorbent had 34.77 mg/g of Cd(II) uptake and 74.35 mg/g of Pb(II) uptake.
- Biosorption rate of Pb(II) was 3.12 times higher than that of Cd(II).
- This study is the first report showing the high potential of chestnut bur as biosorbent.

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ABSTRACT

Among various forest biowastes, chestnut bur had the highest uptake values of Cd(II) and Pb(II), and these values were higher than those of agricultural biowastes used as comparable biosorbents. This study is the first report showing the high potential of chestnut bur as biosorbent for the removal of cationic heavy metals. Pseudo-second-order equation satisfactorily described the biosorption behaviors of both metals. Biosorption rate of Pb(II) was 3.12 times higher than that of Cd(II). Langmuir model could fit the equilibrium isotherm data better than Freundlich model. The maximum uptake capacities of Cd(II) and Pb(II) were determined to be 34.77 mg/g and 74.35 mg/g, respectively. FTIR study showed that carboxyl group on the biosorbent was involved in biosorbing the cationic metals. In conclusion, abundant and cheap forest biowastes, especially chestnut bur, is a potent candidate for efficient biosorbent capable of removing toxic heavy metals from aqueous solutions.

1. Introduction

The use of biosorbents for removal of toxic heavy metals or for recovery of valuable metals from aqueous solutions is one of the most recent developments in environmental and bioresource technology (Park et al., 2010). The major advantages of this technology over conventional ones are its low cost, high efficiency, the minimization of chemical sludges, regeneration of biosorbent, and the possibility of metal recovery. The first challenge faced by biosorption researchers is to select the most promising types of biomass from extremely large pool of available and inexpensive biomass (Park et al., 2010). For this reason, many researchers have investigated the biosorptive capacities of various biomasses (Park et al., 2005; Salman et al., 2013; Seo et al., 2013).

Biosorbents primarily fail into the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes, natural residues, and other biomaterials (Park et al., 2010). There are many review papers that have quantitatively compared the hundreds of biosorbents reported thus far in the literature (Vijayaraghavan and Yun, 2008). According to the literature reviews, however, there are few studies on the use of forest biowastes as biosorbents (Arshad et al., 2008; Dundar et al., 2008). When choosing biomass, for large-scale industrial uses, the main factor to be taken into account is its availability and cheapness. Considering these factors, forest biowastes are potent candidates for biosorbent having low cost and high efficiency.

In this study, various forest biowastes, such as bark, chestnut bur, sawdust, pinecone, pine needle and pine-nut cone, were examined as biosorbents for the removal of cationic metals, *i.e.* Cd(II) and Pb(II). Kinetic and isotherm experiments were conducted to evaluate biosorptive rate and capacity of the biosorbent. To calculate the maximum uptake of each metal, Langmuir equation was used as isotherm model.

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2. Methods

2.1. Preparation of raw biomass

Forest biowastes used in this study were bark, chestnut bur, sawdust, pinecone, pine needle and pine-nut cone. As comparative materials, agricultural biowastes such as corncob, cornhusk, rice husk and rice straw were used. These materials were collected from mountain and farmland located in Wonju, Korea. Each biowaste was washed with deionized–distilled water several times and then dried in an oven at 100 °C for 24 h. The resulting dried biowastes were ground and sieved to a particle size of 500–1000 μm. To evaluate the biosorptive potential of the native biowastes, any pretreatment method was not used in this study. The sieved particles were then stored in a desiccator, until being used as biosorbent in subsequent batch experiments.

2.2. Batch experiments

Cationic metal solutions were prepared by dissolving analytical grade $Cd(NO_3)_2{\cdot}4H_2O$ (Samchun, Korea) and $Pb(NO_3)_2$ (Kanto, Japan) in deionized–distilled water. Each batch experiment was performed by bringing into contact 0.4 g of biosorbent with 200 mL of a metal solution of known concentration in a 230 mL bottle. In experiment for screening a new excellent biosorbent, 2 g/L of each biosorbent was contacted with 100 mg/L of Cd(II) or Pb(II) solution at pH 4.0. Effect of pH was investigated with chestnut bur as biosorbent at pH 2, 2.5, 3, 3.5 and 4. Kinetic and isotherm studies were conducted with chestnut bur at pH 4.0. The bottles were horizontally agitated on a shaker at 200 rpm for 6 h under room temperature (20–25 °C). In all batch experiments, the solution pH was maintained at the desired value using a 1 M HCl or 1 M NaOH solution. Samples were intermittently removed from the bottles to analyze Cd(II) or Pb(II) concentration, following appropriate dilution with deionized–distilled water. It was confirmed from three independent replicates that the batch experiments were producible within at most 5% error.

2.3. Analysis

After being filtered through a 0.45 μm membrane, Cd(II) or Pb(II) concentration of the samples were measured using inductively coupled plasma-atomic emission spectrometer (ICP/IRIS, Thermo Jarrell Ash Co., USA). Infrared spectrum of native biomass of chestnut bur was obtained using a Fourier transform infrared spectrometer (Vertex 70, Bruker).

3. Results and discussion

3.1. Screening of a new efficient biosorbent from forest biowastes

Six kinds of forest biowastes, which are abundant in Korea, were tested as biosorbents for the removal of cationic metals. For comparable experiment, four kinds of agricultural biowastes were used in this study (Table 1). Uptake of cationic metal by each biosorbent was dependent on both biosorbent type and metal species. In all cases, the uptake of Pb(II) were higher than that of Cd(II). In the case of bark, it had 9.31 mg/g of Cd(II) uptake and 25.89 mg/g of Pb(II) uptake. Pine needle showed 3.9 times of Pb(II) uptake compared with Cd(II) uptake. It has been well known that Pb(II) adsorbs on biosorbents more easily than Cd(II) does (Sud et al., 2008; Vijayaraghavan and Yun, 2008). Among the forest biowastes, chestnut bur had the highest uptake values of both Cd(II) and Pb(II); the former was 16.18 mg/g, the latter 42.36 mg/g. These values were higher than those of agricultural biowastes used in this study. Rice straw was the most efficient biosorbent among agricultural biowastes (Table 1). Agricultural biowastes have been well studied by many researchers due to its low cost and availability in nature (Li et al., 2007; Salman et al., 2013; Sud et al., 2008). They have showed the high potential of agricultural biowastes as biosorbent for the removal of toxic heavy metals. However, there are relatively few studies on the use of forest biowastes as biosorbents (Park et al., 2008, 2011; Zou et al., 2013). To sum up, forest biowastes, especially chestnut bur, is a potent candidate for biosorbent because it had higher uptake value with respect to cationic metals, compared with agricultural biowastes (Table 1). This study is the first one reporting the application of chestnut bur which is abundant and cheap as biosorbent for the removal of heavy metals.

Table 1
Cd(II) and Pb(II) uptake of forest and agricultural biowastes.

Biomass		Cd(II) uptake (mg/g)	Pb(II) uptake (mg/g)
Forest biowastes	Bark	9.31	25.89
	Chestnut bur	16.18	42.36
	Sawdust	5.46	15.45
	Pinecone	4.29	15.17
	Pine needle	6.65	25.86
	Pine-nut cone	10.92	27.16
Agricultural biowastes	Corncob	5.87	23.86
	Cornhusk	5.08	23.20
	Rice husk	6.56	16.59
	Rice straw	9.34	32.66

3.2. Effect of pH on metal biosorption by chestnut bur

For evaluating the potential of biosorbent for metal removal, it is very important to investigate the removal efficiency of a given biosorbent for the target metal. Metal uptake can involve different types of biosorption processes that are affected by various physical and chemical factors, and these factors determine the overall biosorption performance of a given biosorbent (Park et al., 2010). Among various factors which affect metal uptake rate, specificity for the target metal, and the quantity of target removed, solution pH has been known to be the most important regulator of the biosorption process. The pH affects the solution chemistry of metal itself, the activity of functional groups on the biosorbent, and the competition with coexisting ions in solution (Vijayaraghavan and Yun, 2008).

Fig. 1 shows the uptake of each metal by chestnut bur according to the solution pH. The experiments were conducted below pH 4 in

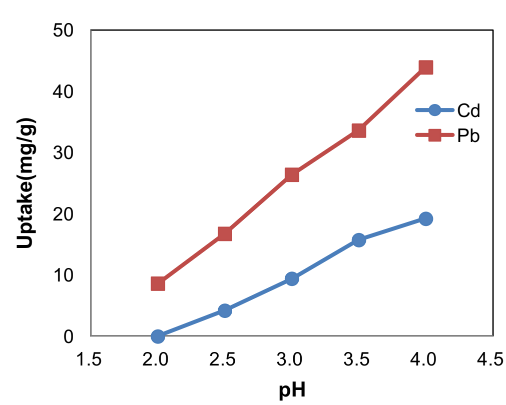

Fig. 1. Effect of pH on the removal of Cd(II) and Pb(II) by chestnut bur (experimental condition: biomass dosage = 2 g/L, metal concentration = 100 mg/L).