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Research article

Persimmon leaf bio-waste for adsorptive removal of heavy metals from aqueous solution

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ABSTRACT

The aim of this study was to investigate heavy metal removal using waste biomass adsorbent, persimmon leaves, in an aqueous solution. Persimmon leaves, which are biomaterials, have a large number of hydroxyl groups and are highly suitable for removal of heavy metals. Therefore, in this study, we investigated the possibility of removal of Cu, Pb, and Cd in aqueous solution by using raw persimmon leaves (RPL) and dried persimmon leaves (DPL). Removal of heavy metals by RPL and DPL showed that DPL had a 10%–15% higher removal than RPL, and the order of removal efficiency was found to be Pb > Cu > Cd. The pseudo-second order model was a better fit to the heavy metal adsorption experiments using RPL and DPL than the pseudo-first order model. The adsorption of Cu, Pb, and Cd by DPL was more suitable with the Freundlich isothermal adsorption and showed an ion exchange reaction which occurred in the uneven adsorption surface layer. The maximum adsorption capacity of Cu, Pb, and Cd was determined to be 19.42 mg/g, 22.59 mg/g, and 18.26 mg/g, respectively. The result of the adsorption experiments showed that the *n* value was higher than 2 regardless of the dose, indicating that the heavy metal adsorption on DPL was easy. In the thermodynamic experiment, ΔG° was a negative value, and ΔH° and ΔS° were positive values. It can be seen that the heavy metal adsorption process using DPL was spontaneous in nature and was an endothermic process. Moreover, as the temperature increased, the adsorption increased, and the affinity of heavy metal adsorption to DPL was very good. This experiment, in which heavy metals are removed using the waste biomass of persimmon leaves is an eco-friendly new bioadsorbent method because it can remove heavy metals without using chemicals while utilizing waste recycling.

1. Introduction

Wastewater produced in industrial processes generally contains inorganic contaminants and organic toxicants (Choi, 2015a). In particular, various compounds including cadmium, lead, copper, and chromium have been widely used in the chemicals industry and in the finishing processes in metals and mining. These heavy metal pollutants can cause physical and chemical changes in the water environment, altering the quality of the water environment, and the use of contaminated water can have a crucial negative impact on living organisms (Choi et al., 2016). Especially, cadmium (Cd) and lead (Pb) are harmful contaminants that can have a detrimental effect on living organisms even with small accumulations (Abdelfattah et al., 2016). Cd is a toxic heavy metal commonly present in wastewater and is very toxic. While Pb is less toxic than cadmium, it is one of the heavy metals most commonly used in industrial processes, and is therefore one of the most abundant heavy metals in wastewater (Choi, 2015b; Taty-Costodes et al., 2003). Pb has a high affinity for enzymes, phosphate ions (PO_4^{3-}), ligands, and biomolecules including thio (−SH) which affect the membrane permeability of the kidneys, liver, and brain, thereby inhibiting biosynthesis of the cells in vivo (Chen et al., 2010). It also complexes with the oxo-groups of enzymes that influence the stages of hemoglobin synthesis and porphyrin metabolism, resulting in peripheral and central nerve toxicity, renal toxicity, and digestive disorders (Kabbashi et al., 2009). Copper (Cu) is one of the dangerous heavy metals used in many industries such as mining and smelting, plating, brass manufacturing, petroleum refining, and electroplating, and is used in Cu based pesticides (Sengil and Ozcar, 2008). The released copper is not decomposed by microbial activity

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in the natural environment and causes a serious delayed action on the activity and decomposition of organic matter (Kim et al., 2015). Low levels of copper are found as minerals essential for the catalytic activity of enzymes in organisms, but excessive copper intake accumulates in the liver causing gastrointestinal problems, kidney damage, and anemia, and the higher the concentration, the greater the potential toxicity to the organism (Li et al., 2006; Murugesan et al., 2011). Accumulation of Cu, Pb, and Cd in the human body causes gastrointestinal problems, kidney damage, and anemia etc., and is more potentially toxic at higher concentrations, leading to death (Ali et al., 2016; Barsbay et al., 2017). The International Agency for Research on Cancer (IARC) classified Cu, Pb, and Cd as carcinogens, and the World Health Organization (WHO) regulates the release of Cd, Pb, and Cu to be less than 0.003 mg/L, 0.01 mg/L, and 2 mg/L, respectively (Choi et al., 2016). Therefore, these toxic heavy metals need to be removed before they are released into the water system.

Many techniques for efficiently removing heavy metals from aqueous solutions have been developed and many studies have been reported, such as adsorption, coagulation-flocculation, membrane filtration, membrane separation, electrochemical operations, solvent extraction, ion-exchange, and biosorption etc (Arshadi et al., 2014; Barsbay et al., 2017; Choi, 2015b; Feizi and Jalali, 2015; Ihsanullah et al., 2016). Some of these methods are expensive, and are inefficient in controlling the concentration of heavy metal ions in wastewater. These various methods for removing heavy metals in aqueous solutions have advantages and disadvantages in terms of effectiveness, cost, and environmental impact (Choi et al., 2016). The adsorption method is known to be suitable for the removal of heavy metals because it is easier to operate than other processes, and the cost of the process is low (Kim et al., 2015; Wang and Chen, 2009). Activated carbon, widely used as an adsorbent to date, is useful for removing various pollutants because of its relatively large specific surface area and pore development. Activated carbon, however, is expensive and requires additives in order to improve its ability to remove minerals. Recently, many studies have been carried out to adsorb and remove heavy metals by using biomaterials, such as straw, banana peel, sunflower seed, lung apricot, chaff, daily palm leaf, tea leaf, canola residue, cashew nut shell, tamarind seed, and orange peel etc (Feizi and Jalali, 2015; Garg et al., 2008; Gupta and Nayak, 2012; Kim et al., 2015; Li et al., 2006; Nguyen et al., 2013; Niazi et al., 2016; Shaheen et al., 2013; Taty-Costodes et al., 2003; Wang and Chen, 2009). These studies mainly use low-cost agricultural wastes or byproducts as an adsorbent. However, they have several problems such as poor separation of wastewater after treatment and a low removal rate of heavy metals due to diffusion limitation or reduction of surface active sites, etc (Niazi et al., 2016). Therefore, efficient research is needed to develop a new adsorbent that can recycle waste, is inexpensive, and can increase the adsorption amount of heavy metals. In order to overcome this problem, eco-friendly low cost bio-adsorbent persimmon leaves were used in this study to remove Cu, Pb, and Cd.

Currently, China produces the largest amount of persimmon in the world, followed by South Korea and Japan. China, South Korea, and Japan account for 90.4% of the world's total persimmon production (Pangeni et al., 2014). Accordingly, persimmon leaves are by-products of persimmon trees and are natural adsorbents that can be easily obtained from farms anywhere in Korea. In addition, the persimmon leaves contain a large amount of tannin, a polyphenol compound that binds to metal ions by chelation (Xie et al., 2015). Tannin is an important protective agent for plant tissue in plants, but it is known to have the ability to combine with toxic substances such as heavy metals and alkaloids (Gu et al., 2008; Yurtsever and Sengil, 2009). Therefore, in this study, we attempted to confirm the possibility of the removal of Cu, Pb, and Cd from aqueous solution using persimmon leaves, which can be easily obtained. For this purpose, adsorption kinetic was analyzed by using pseudo first-order, pseudo second-order, and internal particle diffusion. In addition, the experimental results were applied to various adsorption isotherms, and thermodynamic analysis was carried out through adsorption experiments according to temperature changes.

2. Materials and methods

2.1. Adsorbent and adsorbate

Persimmon leaves (*Diospyros kaki*, *Rojo Brillante* var.) were harvested from trees in an orchard in Gangneung, Korea. The collected persimmon leaves were washed several times with deionized water to remove the organic substances and contaminants on the surface of the persimmon leaves. The cleaned persimmon leaves were cut into 1 cm (width) x 1 cm (length) size and stored in a refrigerator for use as a raw persimmon sample (RPL). The dried persimmon leaves (DPL) were placed in a porcelain dish of the same size as that for the RPL and dried in an oven at 80 °C for 72 h. The DPL leaves were stored in a desiccator for the experiment. Cu, Pb, and Cd were selected as heavy metal solutions and were classified as GR grade $CuSO_4 \cdot 5H_2O$ (Junsei Chemical Co., Japan, purity≥99%), $Pb(NO_3)_2$ (Duksan Pure Chem., Co. Ltd. Korea, purity≥ 99%), and $Cd(NO_3)_2 \cdot H_2O$ (Sigma Aldrich, Japan) respectively. Cu, Pb, and Cd were each prepared at a concentration of 1000 mg/L, diluted with distilled water, and then used as a solution at the required concentration.

2.2. Experimental design and analytical methods

Experiments were carried out in a batch-test, and RPL and DPL were added to 1 L of each heavy metal according to the experimental plan. The detailed experimental conditions represented in Table 1.

The pH was adjusted to 2–10 using NaOH and HCl and the temperature was controlled to 10–30 °C using a thermostat in the Shaking Incubator. All experiments were repeated five times and the mean values were used as experimental results. The other parameters were fixed to test each single parameter. The qualitative and quantitative analysis of the inorganic components contained in the persimmon leaves was carried out using X-ray diffraction (XRD; XRF-1500, Shimadzu, Japan) and the surfaces of the persimmon leaves were analyzed by scanning electron microscope (SEM; SM-300, Topcon, Japan). The size of the persimmon leaf was first determined by using a sieve of 30–70 mesh, and determined using a Particle Size Analyzer (Laser Diffraction Master, classes 3 & 4, Malvern, England). The amount of persimmon leaf material was measured with an electronic balance (XP26, Mettler Toledo, Swiss) and the pH was measured with a pH meter (SevenGO pro, Mettler Toledo). The adsorption amount and percentage removal of heavy metals on RPL and DPL were calculated using Equation (1) and Equation (2) as follows.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

The percentage removal of heavy metal ions was calculated using the following equation:

$$\%\text{Removal} = \frac{C_0 - C_F}{C_0} \times 100 \quad (2)$$