Application of hybrid bead, persimmon leaf and chitosan for the treatment of aqueous solution contaminated with toxic heavy metal ions

Sung-Whan Yu and Hee-Jeong Choi

ABSTRACT

In this study, hybrid beads, which are made by mixing persimmon leaf and chitosan, was used to remove Pb(II) and Cd(II) from aqueous solution. According to the Fourier transform infrared spectrometry (FT-IR) analysis, the hybrid bead has a structure that enables the easy adsorption of heavy metals because it has carboxylic, carbonyl groups, O-H carboxylic acid, and bonded -OH groups. The adsorption of Pb(II) and Cd(II) by hybrid beads was more suitable with the Langmuir isothermal adsorption and showed an ion exchange reaction which occurred in the uneven adsorption surface layer. The maximum adsorption capacity of Pb(II) and Cd(II) was determined to be 278.68 mg/g and 87.91 mg/g, respectively. Furthermore, the adsorption removal process of Pb(II) and Cd(II) using hybrid beads is a spontaneous exothermic reaction and the affinity of the adsorbed material for the adsorbent is excellent. Hybrid beads are inexpensive, have a high removal efficiency of heavy metals, and are environmentally friendly.

Key words | adsorption, chitosan, heavy metal, hybrid bead, persimmon leaf, tannin

NOMENCLATURE

- $C_o$: Initial concentration of heavy metal ions (mg/L)
- $C_e$: Equilibrium concentration of heavy metal ions (mg/L)
- $C_t$: Concentration of heavy metal ion at time $t$ (mg/L)
- $E$: Sorption energy (kJ/mol)
- $\Delta G^0$: Gibbs free energy (kJ/mol)
- $\Delta H^0$: Enthalpy (kJ/mol)
- $k_1$: Adsorption rate constants of the pseudo-first-order model (1/min)
- $k_2$: Adsorption rate constants of the pseudo-second-order model (mg/g/min)
- $k_L$: Langmuir constant (L/mg)
- $k_F$: Freundlich constants referring to the adsorption capacity (mg/g)
- $m$: Quantity of adsorbent (g)
- $n$: Freundlich isotherm constants, intensity of sorption (mg/g)/(mg/L)$^{1/n}$
- $q_e$: Amount adsorbed per unit weight of adsorbent at equilibrium (mg/g)
- $q_t$: Quantity of heavy metal ions adsorbed at time $t$ (mg/g)
- $q_m$: Langmuir monolayer maximum adsorption capacity (mg/g)
- $R$: Removal efficiency (%)
- $R$: Ideal gas constant, 8.314 (J/mol/K)
- $R^2$: Correlation coefficient
- $\Delta S^0$: Entropy (J/mol-K)
- $t$: Time (min)
- $T$: Absolute temperature (K)
- $V$: Volume of solution (L)
- $\beta$: Activity coefficient related to the mean sorption energy
- $\varepsilon$: Polanyi potential

INTRODUCTION

Toxic heavy metal contaminants cause physical or chemical changes in aquatic environments, altering the quality of the aquatic environment, while the use of contaminated water has a crucial negative impact on living organisms (Choi et al. 2016).

In particular, Pb(II) and Cd(II) can have a fatal effect on living organisms in aquatic ecosystem with small amounts (He et al. 2014; Lee & Choi 2018). Various processes such...
as adsorption, coagulation-flocculation, membrane filtration, membrane separation, electrochemical operations, ion-exchange, biosorption, etc., have been studied for heavy metal removal and applied directly in the field (Choi & Lee 2015; Ali et al. 2016; Bacelo et al. 2016; Barsbay et al. 2018). Some of these methods are costly and inefficient in controlling the concentration of heavy metal ions in wastewater (Lee & Choi 2018). Other processes are also not highly efficient or environmentally friendly, and some processes are also necessary for secondary treatment (Abdelfattah et al. 2016).

In recent years, many studies have been conducted to adsorb and remove heavy metals by using agricultural by-products or biological materials, which are inexpensive and highly efficient in removal (Garg et al. 2008; Chen et al. 2010; Abdelfattah et al. 2016; Ali et al. 2016; Bacelo et al. 2016; Lee & Choi 2018). However, adsorbents using agricultural by-products or biomaterials are problematic due to the separation of wastewater and the generation of secondary wastes caused by the reduction of the removal rate of heavy metals due to the diffusion limitation and the decrease of the surface-active sites (Xu et al. 2017). In order to overcome this problem, we attempted to remove Pb(II) and Cd(II) by using an environmentally friendly, low-cost adsorbent using deciduous agricultural byproducts, persimmon leaves, and chitosan.

Persimmon is mainly produced in Asia, especially China, Japan, and Korea, accounting for more than 90% of the world’s production (Lee & Choi 2018). In Korea, persimmon is a fruit tree commonly found in rural areas, which have favorable conditions for a variety of persimmon species because of the moderate climatic conditions. The persimmon leaves used in this study are byproducts of persimmon trees and are natural adsorbents easily obtainable from Korean farms. Persimmon leaves are known to be able to bind and remove toxic substances such as heavy metals and alkaloids because they contain a large amount of tannin, a polyphenol compound that binds to metal ions by chelation (Shen et al. 2004; Martínez-Las Heras et al. 2016). However, according to the literature, maximum adsorption capacities of Pb(II) and Cd(II) were 53.37 mg/g and 51.85 mg/g using natural tannin (Xu et al. 2017) and 80.23–118.00 mg/g and 60.85 mg/g using chitosan (Li et al. 2016), respectively.

Generally, chitosan is a natural cationic polysaccharide obtained by the alkali N-deacetylation of chitin, which can be extracted from shells of shrimp, crab, shellfish, etc. (Sargin et al. 2016). Since the matrix structure of this natural polymer contains many free amine (-NH2) and hydroxyl (-OH) functional groups, chitosan can adsorb and remove efficiently heavy metal ions from wastewater (Liu et al. 2014). Chitosan is a highly efficient adsorbent for cationic pollutants. However, chitosan is a cationic natural polymer. Thus, the adsorption capacity of its cations is lower than the adsorption capacity of anions (Zhao et al. 2015; Sargin & Arslan 2015). In addition, when heavy metals are adsorbed and removed by using tannin without modification, the time required to reach adsorption equilibrium is considerable (Yurtsever & Sengil 2009; Bacelo et al. 2016). On the other hand, the phenol groups of tannin can ion-exchange with metal ion, and amino and hydroxyl groups of chitosan can act as chelation sites coordinate with metal ion. Moreover, the increase of pH values enhances efficiency of both ion-exchange and coordination. The adsorption process of heavy metals in aqueous solution is greatly affected by pH. Adsorption of Pb(II) in the aqueous solution can be facilitated at higher pH region than that of lower pH. Due to these properties, the binding of tannin-containing persimmon leaves to chitosan can increase the adsorption efficiency of heavy metals. Therefore, the aim of the present study was to improve the adsorption removal efficiency of Pb(II) and Cd(II) in aqueous solution using hybrid beads with persimmon leaves, which contain an anionic polymer tannin and chitosan. Experimental results were applied to Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherms, and thermodynamic analyses were carried out through adsorption experiments with temperature changes. Pseudo-first-order, pseudo-second-order, and intra-particle diffusion have been analyzed in many works using chitosan and tannin; therefore, in this paper, the results of the analysis are summarized using a simple figure.

MATERIALS AND METHODS

Adsorbent and adsorbate

Persimmon leaves were collected from persimmon farms in Gangneung city, Gangwon province, Korea. The washed persimmon leaves with deionized water to remove organic substances and contaminants were cut into squares of 0.5 cm (width) × 0.5 cm (length) size, placed in a large porcelain dish, and then dried in an oven at 80 °C for 72 h (Lee & Choi 2018). The dried persimmon leaves were powdered for the experiment and stored in a desiccator. The hybrid beads used in the experiments were prepared as follows.

One and a half grams of persimmon leaf powder was added to 150 mL of chitosan acidic solution, and the
mixture was stirred at 24 °C for 4 h until the mixture became homogeneous. The mixture of chitosan and persimmon leaf was transferred to a burette and then dropping it in a coagulation solution (a mixture of 200 mL of water, 300 mL of methanol, and 60.0 g of NaOH). The hybrid beads in the clotting solution were incubated for 24 h in the incubator until the coagulation solution turned yellowish-brown. The hybrid beads were washed several times with distilled water until the filtrate became neutral and the yellowish-brown color disappeared. The wet hybrid beads were filtered to remove water and the cross-linking agents (90 mL of methanol + 0.9 mL of glutaraldehyde solution) were added to maintain the spherical shape of the hybrid beads. The mixture was allowed to age at 70 °C for 6 h in an incubator. Finally, the cross-linked hybrid beads were recovered, washed with ethanol, and then washed several times with water to remove unreacted glutaraldehyde molecules. The produced hybrid beads were dried at room temperature for 5 h and then stored in a desiccator for use in experiments. A Pb(II) and Cd(II) stock solution of 1,000 mg/L was prepared by dissolving Pb(NO₃)₂ (Duksan Pure Chem., Co. Ltd, Korea, purity ≥ 99%) and Cd(NO₃)₂·H₂O (Sigma Aldrich, Japan, purity ≥ 99%) in deionized water, respectively. The stock solution diluted with distilled water, and then used as a solution at a required concentration.

Experimental design and analytical methods

The experiment was carried out by batch-test and hybrid beads were added to 1 L of each heavy metal. The effect of initial Pb(II) and Cd(II) concentration from 0.5 to 50 mg/L, contact time from 0 to 120 min, pH from 2 to 10, dose of adsorbent from 0.5 to 20 g/L, particle size of persimmon leaf from 50–70 mesh and temperature from 25 to 45 °C on the adsorption of heavy metals onto hybrid beads were investigated. The pH was adjusted to 2–10 using NaOH and HCl and the temperature was controlled using a Shaking Incubator Thermostat. The mixed sample solution was stirred at 120 rpm in a shaking incubator and sampled at a predetermined time. The collected samples were centrifuged at 3,000 rpm for 20 minutes, filtered using a 0.45 μm Whatman filter, and the quantity of heavy metals was measured using an atomic absorption spectrometer (AAS, Perkin Elmer, AAS 3500). All experiments were repeated five times and the mean values were used as experimental results. The specific surface area and pore volume of persimmon leaf, chitosan and hybrid beads were measured using a Brunauer–Emmett–Teller (BET) specific surface analyzer (Model ASAP, 2020), and the molecular structures and components of the surface functional groups were analyzed by Fourier transform infrared spectrometry (FT-IR; Jasco, FT-IR 4100) (Lee & Choi 2018). The particle size and amount of persimmon leaf, chitosan, and hybrid beads was measured using a particle size analyzer (Laser Diffraction Masterclasses 3 and 4, Malvern, UK) and using an electronic balance (XP26, Mettler Toledo, Switzerland), respectively (Lee & Choi 2018). The other parameters were fixed to test each parameter separately. The quantity of persimmon leaves was measured with an electronic balance (XP26, Mettler Toledo, Switzerland). The adsorption amount (qt) and removal efficiency (%) of the heavy metals adsorbed on the hybrid beads were calculated using Equations (1) and (2) below (Lee & Choi 2018).

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  
\[ R = \frac{C_0 - C_t}{C_0} \times 100 \] 

RESULTS AND DISCUSSION

Characteristics of hybrid bead

Physical properties of persimmon leaves, chitosan, and hybrid bead

Determining the surface area is one of the methods used for evaluating the performance of the adsorbent, which is the index of the space in which the adsorption can actually occur by calculating the total pore surface area per 1 g of the adsorbent (Choi & Lee 2015; Lee & Choi 2018). Therefore, it is generally recognized that as the size of the surface area increases, the adsorption amount also increases (Liu et al. 2014; Bacelo et al. 2016). The pore size affects the adsorption and desorption rates of contaminants, and the larger the micropores, the larger the specific surface area and the adsorption amount increases (Wan & Hanafiah 2008; Pangeni et al. 2014). However, when the pore size is too small, it is difficult to penetrate the pore adsorbing material through the pores to the inside of the adsorbent, so the number of available pores is reduced (Choi 2014). Therefore, it is preferable that the pore distribution is concentrated on the specific pore when the single substance is adsorbed and removed, but it may be advantageous to vary the pore distribution if various substances are to be removed, as it is in the water treatment (Wan & Hanafiah 2008; Bacelo et al. 2016). Table 1 shows the properties of...
persimmon leaves, chitosan, and hybrid beads. The specific surface area and the pore size of the hybrid beads are 16.65 m²/g and 4.66 nm, respectively.

According to the related literature, persimmon leaves contain a large number of hydroxyl groups (-OH), tannin, and catechin which are effective in removing heavy metals (Martínez-Las Heras et al. 2014; Lee & Choi 2018). Persimmon leaf contains 6.65% of tannin, which is a higher content than Platanus (5.12%) and Ginkgo (2.02%) (Wi et al. 2015). The mechanism by which tannin adsors and bonds with metal ions involves a process whereby the hydroxyl group in the phenolic group contained in the tannin compound releases two H⁺ and binds to the divalent metal cation to form a ring and chelates the metal ion in the catechol ring of the phenolic monomer (Liu et al. 2017; Xu et al. 2019). Therefore, the adsorption process of tannin is not a physical bond but a bond by chemical ion exchange, and its bond strength is very high.

### FT-IR spectra

The FT-IR spectra of chitosan, persimmon leaf, and hybrid beads are shown in Figure 1. Persimmon leaves are basically composed of 480 to 650 cm⁻¹ of N-containing bioligans, 950 to 1,150 cm⁻¹ of PO₄³⁻ stretching, 1,300 to 1,450 cm⁻¹ of CO stretching, 1,500 to 1,600 cm⁻¹ of carboxylic group and NH bending, 1,640–1,670 cm⁻¹ of carboxylic groups, 1,680–1,740 cm⁻¹ of C=O of carbonyl groups, 2,800–2,900 cm⁻¹ of CH stretching and OH carboxylic acids, and 3,000–3,500 cm⁻¹ of bonded -OH groups. Also, the tannin component of persimmon leaf contains a large number of phenolic hydroxyl groups (hydroxyl group, -OH-) and has heavy metal adsorption ability (Abdelfattah et al. 2016).

According to FT-IR analysis of chitosan, peaks at 3,500 to 3,500 cm⁻¹ are bonded -OH groups, peaks at 1,640 to 1,670 cm⁻¹ are carboxylic groups, and peaks at 1,500 to 1,600 cm⁻¹ are bending carboxylic and N-H bending groups. Moreover, the peaks at 1,424 and 1,380 cm⁻¹ indicate C-H bending of alkyl groups, and the peaks at 1,310 and 1,253 cm⁻¹ represent C-N bending and N-H groups, respectively. 1,148 and 1,027 cm⁻¹ represent the asymmetry of the C-O-C group and the C-O vibration, respectively, and the peak at 897 cm⁻¹ is attributed to the β-1,4-glycosidic bond.

The FT-IR of hybrid beads shows many carboxyl groups and carbonyl groups required for the adsorption of heavy metals by mixing the peaks of tannin and chitosan.

In general, the functional group with the highest heavy metal adsorption capacity is known as the carboxyl group (Lee & Choi 2018). The carboxyl group dissociates to -COO⁻ and H⁺ in aqueous solution, and most of the carboxyl group becomes a -COO⁻ form above a certain pK value, so that the cationic heavy metal is efficiently adsorbed (Choi 2016; Xu et al. 2016). In addition, no studies could be found that accurately identify the mechanism of heavy metal adsorption. This is the reason why the physical properties of persimmon leaves, chitosan, and hybrid beads are presented in Table 1.

### Table 1: Physical properties of persimmon leaves, chitosan, and hybrid beads

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (m³/g)</th>
<th>Pore size (nm)</th>
<th>Particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single point at p/p₀</td>
<td>BET</td>
<td>t-Plot miscropore</td>
<td></td>
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<tr>
<td>Persimmon leaves</td>
<td>0.2010</td>
<td>0.8530</td>
<td>1.1395</td>
<td>1.1663</td>
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<td>Chitosan</td>
<td>0.5162</td>
<td>2.0562</td>
<td>12.6852</td>
<td>1.8623</td>
</tr>
<tr>
<td>Hybrid bead</td>
<td>4.2632</td>
<td>16.653</td>
<td>22.6324</td>
<td>23.5637</td>
</tr>
</tbody>
</table>

Figure 1 | FT-IR spectra of persimmon leaf, chitosan, and hybrid beads (persimmon leaf data by Lee & Choi (2018)).
metal adsorption by various biomaterials (Xu et al. 2016). However, the adsorption occurs because the functional groups in the polymer substance in the cell tissue are coordinated with heavy metals (Wan & Hanafiah 2008; Chen et al. 2010). These functional groups include -COOH, NH₂, -PO₄, -SO₄, C₆H₅, >CO, (NH₃)₂C-NH, and -OH. Therefore, -OH, -CH₂OSO₂, -COOH, and -OH are involved in coordination with heavy metals in hybrid beads, and a large number of carboxyl groups and carbonyl groups are believed to have a considerable influence on the adsorption of heavy metals (Sengil & Ozacar 2009; Bacelo et al. 2016; Lee & Choi 2018).

**Parametric study**

To investigate the effects of various parameters on the adsorption efficiency of Pb(II) and Cd(II) using hybrid beads in aqueous solution, the initial concentrations of various heavy metals, the different pH of the aqueous solution, the different amounts of adsorbent, and the contact time was examined.

**Effect of initial concentration**

The effect of initial concentration on the removal efficiency was examined by controlling the concentration of heavy metals from 0.5 to 20 mg/L and the results are shown in Figure 2(a). Since the amount of adsorbent and the adsorption time are determined according to the initial concentration of heavy metals, the effect of the concentration of the initial heavy metal on the removal efficiency is a basic experiment for deriving the optimum condition of the adsorption process. As a result, Pb(II) and Cd(II) were determined to have higher removal efficiencies than the initial concentration below 2 mg/L of 98%. Adsorption efficiency decreased with increasing initial concentration of heavy metals. Removal efficiency was determined as 62.3% for Pb(II) and 40.7% for Cd(II) at a heavy metal concentration of 20 mg/L. Moreover, the removal efficiency was measured as up to 90% until 10 mg/L of Pb(II) and 5 mg/L of Cd(II). The removal efficiency of Pb(II) by hybrid beads was higher than that of Cd(II). In addition, the removal efficiency of Cd(II) was higher than that of Pb(II) as the concentration of heavy metals increased. As a result, the adsorption amounts of Pb(II) and Cd(II) were affected by the initial concentration of heavy metals. Also, as the concentration was reduced, the removal efficiency increased. This is because, as the concentration is reduced, the probability of adsorption to the adsorbent per ion increases.

**Effect of pH**

The pH of the aqueous solution has a considerable influence on the removal of heavy metals. Depending on the pH, the ionic form of the heavy metal in the aqueous solution differs. To investigate the effect of pH on the removal efficiencies of Pb(II) and Cd(II), the pH was controlled from 2 to 10. The removal efficiencies of Pb(II) and Cd(II) were obtained at 98.2% and 90.3% above pH 5, respectively (Figure 2(b)). However, the removal efficiencies of Pb(II) and Cd(II) were from 43.4% to 64.2% at low pH (2.0–3.0). From FT-IR analysis, it is considered that the carbonyl and carboxyl components on the surfaces of the hybrid beads played an important role in the adsorption of heavy metals. According to previous studies, the surface adsorption mechanism of heavy metals is generally influenced by the pH of the reaction medium, the surface characteristics of the adsorbent, and the inherent characteristics of heavy metals (Bacelo et al. 2016; Lee & Choi 2018).

The increase of heavy metal adsorption by hybrid beads from pH 2 to pH 5 seems to be related to the ion exchange mechanism. At low pH values (below pH 4.0), high concentrations of H⁺ ions compete with Pb(II) and Cd(II) for exchangeable cations on the adsorbent surface, consequently inhibiting the Pb(II) and Cd(II) adsorption on the surface of the hybrid beads. However, as the pH value is increased, the H⁺ ion decreases on the adsorbent surface, leading to competition between the exchangeable cation and the H⁺ ion on the decreased surface of the adsorbent. Pb(II) and Cd(II) are exchanged with Pb(OH)₂ and Cd(OH)₂ or Pb(OH)₃ and Cd(OH)₃ with increasing pH value and adsorption onto hybrid beads increases rapidly (Barsbay et al. 2018). In general, heavy metals form hydroxides in aqueous solution and exist in the form of Cd(OH)⁺ and Pb(OH)⁺ (Yurtsever & Sengil 2009). They also precipitate in the form of Cd(OH)₂ and Pb(OH)₂ in neutral or alkaline pH (Choi et al. 2016; Lee & Choi 2018). Therefore, the increased pH affects the removal efficiencies of Pb(II) and Cd(II). The adsorption of Pb(II) by the hybrid beads is higher than that of Cd(II). Pb(II) forms a stronger metal hydroxide (MeOH⁻) than Cd(II) above pH 5 conditions. These hydroxides strongly bond to the functional groups on the surface of the hybrid beads. The favorable selectivity of heavy metals on adsorbents is related to various factors, such as hydrated ionic radius and hydration energy of the
heavy metals. It is known that the coordination numbers of Pb(II) and Cd(II) are 6 and 4, respectively (Choi et al. 2016; Li et al. 2016). As a consequence, it is likely that the movement of hydrated Cd(II) in the pores of hybrid bead is stereo-chemically hindered (Choi et al. 2016). Moreover, pore size distribution is an important factor in determining the fraction of the total volume of a particle that is accessible to molecules of a given size and shape. The Pb(II), which was the species with the lowest hydration energy (1,481 kJ/mol) compared with Cd(II) (1,807 kJ/mol) (Choi et al. 2016), might more facilitate the entrance of hydrated Pb(II) ions into the channel of hybrid beads compared to the Cd(II) metal. Therefore, the selectivity for Pb(II) is the greater than those for the Cd(II). The results of the above experiment show that both Pb(II) and Cd(II) have high removal efficiencies above pH 6. Considering that the pH of the sewage plant is about 6–8, the hybrid bead can be applied in the field without adjusting the pH when the heavy metal ions are adsorbed in the aqueous solution using the hybrid beads as the adsorbent. This reduces the use of chemicals and does not require post-treatment due to the use of chemicals, which is very economical and very useful in resource recycling.

**Effect of adsorbent dose**

The amount of adsorbent is a very important process parameter in terms of economy and environment. Regardless of the degree of efficiency of an adsorbent, if the economy is poor, the industry is reluctant to use it. In other words, a large amount of heavy metals can be adsorbed in small quantities, and if the adsorbent is environmentally friendly, it can be obtained at the time of field application. The effect of the adsorbent amount on the removal efficiency of Pb(II) and Cd(II) was tested by increasing the amount of adsorbent after fixing the initial concentration at 5 ppm and pH 6. The experimental results demonstrated that the removal efficiency of Pb(II) and Cd(II) increased with increasing amount of adsorbent (Figure 2(c)). This suggests that the surface area with the heavy metal adsorption can be increased with the increase of the amount of the adsorbent, and thus the probability of adsorption to the adsorbent per ion is increased. The removal efficiency of Pb(II) and Cd(II) onto hybrid beads reached more than 95% and 92% for 3 g/L of adsorbent, respectively. Therefore, when Pb(II) and Cd(II) are removed by
using hybrid beads, the recommended amount of adsorbent is 3 g/L.

**Effect of contact time and adsorption kinetics**

The ability to reach adsorption equilibrium in a short time is a basic condition for good adsorbents. Therefore, it is necessary to optimize the efficiency of the adsorption of heavy metals on the adsorbent depending on the contact time. More than 90% of the Pb(II) and Cd(II) was adsorbed with the hybrid beads in 30 min contact time and adsorption equilibrium was reached in 60 min contact time (Figure 2(d)). Tannins are an excellent candidate for biomaterial sorbents as they are readily available, inexpensive, easily extracted from plants, and easily converted into insoluble (tannin gel or tannin foam) or immobilized matrices. However, the adsorption rate of tannin adsorbent is very low (Bacelo et al. 2016; Xu et al. 2017). Luzardo et al. (2017) reported that adsorption equilibrium was reached after 24 h as a result of adsorption removal of Pb(II) using mimosa tannin. To address this problem, Xu et al. (2017) modified tannin to tannin gel and adsorption equilibrium of Cr(III), Cu(II), and Pb(II) was then reached in 4 h contact time. In addition, Sargin & Arslan (2018) prepared microcapsules with chitosan/sporopollenin and the adsorption equilibrium for the removal of heavy metals was reached after 6 h. According to various researchers, while the adsorption of heavy metals by modifying tannins can reduce the adsorption equilibrium time, it still takes a long time to reach adsorption equilibrium (Zhan & Zhao 2003; Sengil & Ozacar 2008; Yurtsever & Sengil 2009; Bacelo et al. 2016; Xu et al. 2017). When the hybrid beads were used in this study, adsorption equilibrium was reached in 1 h. Therefore, hybrid beads have the advantage of being able to remove heavy metals very quickly and efficiently in aqueous solution.

Adsorption kinetics can be used to explain adsorption rate, adsorption mechanisms, and adsorption limiting rate. The pseudo-first-model ($\ln(q_e - q_t) = \ln(q_e) - k_1 t$) more readily achieves physical adsorption because it is controlled by diffusion and mass transfer of adsorbate to the adsorption site (Ali et al. 2016; Lee & Choi 2018). On the other hand, the pseudo-second-model ($t/t_q = 1/k_2 q_e^2 + t/q_e$) more readily achieves chemical adsorption because chemisorption is the rate-limiting step. The intra-particle diffusion model is used as a rate-limiting step for diffusion within the particles (Sengil & Ozacar 2009; Xu et al. 2017). According to the coefficient of determination, the adsorption removal process of Pb(II) and Cd(II) using hybrid beads was more suitable for the pseudo-second-order than the pseudo-first-order model (Figure 3(a) and 3(b)). The correlation between intra-particle diffusion using hybrid beads was 0.9779 for Pb(II) and 0.9632 for Cd(II), which was lower than that with the pseudo-first-order and pseudo-second-order models (Figure 3(c)). This indicates that diffusion in the particles is not a rate limiting step in the adsorption process. Based on the above experimental results, the removal of Pb(II) and Cd(II) using hybrid beads indicates that chemical adsorption rather than physical adsorption can be used to limit the adsorption rate of heavy metals. Both Pb(II) and Cd(II) were highly correlated with the contact time and $\ln(q_e - q_0)$. This indicates that the affinity between...
the heavy metal and the adsorbent is very high and the adsorption proceeds very rapidly in the reaction. In addition, Pb(II) had a higher correlation coefficient, reached the adsorption equilibrium more rapidly, and had a higher adsorption capacity than Cd(II). The most basic condition for a good adsorbent is that it should adsorb large amounts of contaminants in a short contact time and strongly adsorb them over time without being desorbed. Hybrid beads are environmentally friendly adsorbents capable of adsorbing large quantities of heavy metals in a short contact time.

**Adsorption isotherm**

In general, the adsorbent performance is evaluated by adsorption isotherms based on adsorption equilibrium. The adsorption isotherm expresses the relationship between the equilibrium concentration of adsorbate and the equilibrium adsorption amount per unit gram of adsorbent at a constant temperature (Zhao et al. 2013). Numerous models such as Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) have been developed and presented to identify the mechanism of adsorption. At present, these models are used to identify the adsorption performance and adsorption mechanism of adsorbents or adsorbates. In the Langmuir adsorption isotherm, the binding force of adsorption is in the monolayer, and adsorbents or adsorbates. In the Langmuir adsorption isotherm, the binding force of adsorption is in the monolayer, and adsorption does not occur in the other separated layers (Ali et al. 2013). The parameters of Langmuir, Freundlich, and D-R isotherms for adsorption of Pb(II) and Cd(II) with hybrid beads are presented in Table 2. This difference in adsorption capacity on hybrid beads is due to the difference in the molecular size of heavy metal ions, the affinity between adsorbent and adsorbate, and the electronegativity of heavy metal ions. In addition, heavy metals adsorption with bioabsorbable materials is effective due to the heavy metal selectivity of the functional groups of bioabsorbable materials (Choi 2014). The results of this study suggest that hybrid beads have more affinity for adsorption of Pb(II) than Cd(II).

According to the Langmuir adsorption isotherm, the adsorption capacity of Pb(II) and Cd(II) was 1.345 and 0.782 (mmol/g), respectively (Table 2). This difference in adsorption capacity on hybrid beads is due to the difference in the molecular size of heavy metal ions, the affinity between adsorbent and adsorbate, and the electronegativity of heavy metal ions. In addition, heavy metals adsorption with bioabsorbable materials is effective due to the heavy metal selectivity of the functional groups of bioabsorbable materials (Choi 2014). The results of this study suggest that hybrid beads have more affinity for adsorption of Pb(II) than Cd(II).

The application of the Freundlich adsorption isotherm is known to be appropriate when the energy of the adsorbed surface is unevenly distributed, such as with activated carbon. In the Freundlich model, the $K_F$ value is a function of adsorptivity and $1/n$ is the function of the adsorption strength between particles and contaminants. As the value of $1/n$ decreases, the bond by adsorption becomes stronger. Experimental results show that $1/n$ was measured as 0.475 for Pb(II) and 0.711 for Cd(II). The adsorption constant $K_F$ of Pb(II) was 14.316 and that of Cd(II) was 12.137, indicating that Pb(II) had a higher adsorption constant than Cd(II). In general, it is known that as the value of the adsorption constant $K_F$ increases, the adsorbing ability of the adsorbent also increases (Ali et al. 2016). In addition, the adsorption results of Pb(II) and Cd(II) using hybrid beads were more suitable for the Langmuir adsorption isotherm than the Freundlich model (Table 2). The D-R adsorption isotherm is most widely used to determine the adsorption energy or to understand the adsorption mechanism (Chen et al. 2010). In this study, adsorption isotherm model analysis was performed to quantitatively evaluate the sorption behavior of isothermic metal ions.

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>Pb(II)</th>
<th>Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td>$q_m (mmol/g)$</td>
<td>1.345</td>
<td>0.782</td>
</tr>
<tr>
<td>$\frac{C_e}{q_e} = \frac{C_0}{q_m} + \frac{1}{q_mK_L}$</td>
<td>$K_L (L/mmol)$</td>
<td>1.34515</td>
<td>87.93</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.982</td>
<td>0.978</td>
<td></td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>$K_F (mmol/g)$</td>
<td>14.316</td>
<td>12.137</td>
</tr>
<tr>
<td>$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$</td>
<td>$n$</td>
<td>2.102</td>
<td>1.404</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.842</td>
<td>0.826</td>
<td></td>
</tr>
<tr>
<td>Dubinin-Radushkevich isotherm</td>
<td>$q_m (mmol/g)$</td>
<td>1.928</td>
<td>1.901</td>
</tr>
<tr>
<td>$\ln q_e = \ln q_m - \beta e^{2}$</td>
<td>$k (mol^2/kJ^2)$</td>
<td>0.004</td>
<td>0.012</td>
</tr>
<tr>
<td>$E = (-2\beta)^{-0.5}$</td>
<td>$E (kJ/mol)$</td>
<td>11.215</td>
<td>8.432</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.967</td>
<td>0.942</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Parameters of Langmuir, Freundlich, and D-R isotherms for adsorption of Pb(II) and Cd(II) with hybrid beads.
8.432 kJ/mol, respectively, indicating that adsorption of Pb(II) and Cd(II) on hybrid beads seems to be close to selective chemisorption.

The results of previous studies in which heavy metals are adsorbed by using persimmon leaf or chitosan are shown in Table 3. Özmen et al. (2009) was found that the maximum adsorption capacity for Pb(II) was 9.947 mg/g using glass beads with glutaraldehyde. The adsorption capacity of modified persimmon leaf and chitosan was much higher than that of the heavy metal adsorbed with unmodified persimmon leaf and chitosan. The removal of Pb(II) and Cd(II) using hybrid beads showed a higher adsorption capacity than the modified persimmon leaf and an equivalent adsorption capacity as that of the modified chitosan. Hybrid beads made from persimmon leaf and chitosan are inexpensive, have a high removal efficiency of heavy metals, and are environmentally friendly. In addition, hybrid beads are very economical when it is used as a heavy metal adsorbent since no post treatment is required.

Thermodynamic interpretation

The adsorption process is affected by temperature because it indicates the thermodynamic equilibrium between the heavy metal adsorbed on the surface of the hybrid beads and the heavy metal in the aqueous solution. In order to investigate the effect of temperature on the adsorption of Pb(II) and Cd(II) on hybrid beads, the temperature was controlled between 25–45 °C. The experimental results were analyzed using Gibb’s free energy (ΔG°) variation.

The energy change of ΔG° is a measure of the usefulness of a chemical reaction and is a state function that determines the direction of the spontaneous change process for a chemical reaction. However, it is not related to the path of change (Choi & Lee 2015; Ali et al. 2016). In other words, when a given chemical reaction system moves from a single equilibrium state to a new equilibrium state, a condition in which ΔG° has a negative value, that is, a condition that is useful, must be established to ensure the change occurs spontaneously (Heidari et al. 2014; Lee & Choi 2018). Experimental results showed that the values of ΔG° from −7.86 to −8.17 for Pb(II) and −2.86 to −2.94 for Cd(II) decreased with increasing temperature and were negative (Table 4). Therefore, the process of adsorption of

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Heavy metal</th>
<th>q_m (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cinnamomum camphora</td>
<td>Pb(II)</td>
<td>75.82</td>
<td>Chen et al. (2010)</td>
</tr>
<tr>
<td>Glass bead</td>
<td>Pb(II)</td>
<td>9.95</td>
<td>Ozmen et al. (2009)</td>
</tr>
<tr>
<td>Dried persimmon leaf</td>
<td>Pb(II)</td>
<td>22.59</td>
<td>Lee &amp; Choi (2018)</td>
</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>18.26</td>
<td></td>
</tr>
<tr>
<td>Persimmon waste gel</td>
<td>Cu(II)</td>
<td>7.18</td>
<td>Bacelo et al. (2016)</td>
</tr>
<tr>
<td>Persimmon tannin gel</td>
<td>Cd(II)</td>
<td>5.27</td>
<td>Bacelo et al. (2016)</td>
</tr>
<tr>
<td>Modified quebracho tannin</td>
<td>Pb(II)</td>
<td>86.207</td>
<td>Yurtsever &amp; Sengil (2009)</td>
</tr>
<tr>
<td>Mimosa tannin gel</td>
<td>Cu(II)</td>
<td>43.71</td>
<td>Sengil &amp; Ozacar (2008)</td>
</tr>
<tr>
<td>Ca(II) imprinted chitosan microspheres</td>
<td>Pb(II)</td>
<td>47.10</td>
<td>Sankaramarkrishnan &amp; Sanghi (2006)</td>
</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>49.90</td>
<td></td>
</tr>
<tr>
<td>Xanthated chitosan</td>
<td>Pb(II)</td>
<td>283.00</td>
<td>He et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>420.00</td>
<td></td>
</tr>
<tr>
<td>Thiosemicarbazide modified chitosan</td>
<td>Pb(II)</td>
<td>325.20</td>
<td>Li et al. (2016)</td>
</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>257.20</td>
<td></td>
</tr>
<tr>
<td>EGTA-modified chitosan</td>
<td>Pb(II)</td>
<td>103.60</td>
<td>Zhao et al. (2015)</td>
</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>83.18</td>
<td></td>
</tr>
<tr>
<td>Hybrid bead</td>
<td>Pb(II)</td>
<td>278.68</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>87.91</td>
<td></td>
</tr>
</tbody>
</table>

Table 4 | Thermodynamic parameters for adsorption of Pb(II) and Cd(II) onto hybrid beads

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Temperature</th>
<th>Pb(II)</th>
<th>Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔG°(kJ/mol)</td>
<td>298 K</td>
<td>−7.86</td>
<td>−2.86</td>
</tr>
<tr>
<td>ΔH°(kJ/mol)</td>
<td>308 K</td>
<td>−8.01</td>
<td>−2.90</td>
</tr>
<tr>
<td>ΔS°(J/mol·K)</td>
<td>318 K</td>
<td>−8.17</td>
<td>−2.94</td>
</tr>
<tr>
<td>ΔGo(kJ/mol)</td>
<td></td>
<td>−3.64</td>
<td>−1.76</td>
</tr>
<tr>
<td>ΔHo(kJ/mol)</td>
<td></td>
<td>14.23</td>
<td>3.71</td>
</tr>
<tr>
<td>ΔSo(J/mol·K)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Pb(II) and Cd(II) using hybrid beads is a spontaneous process in nature. Moreover, the value of enthalpy (ΔH°) is −3.64 and −1.79 for Pb(II) and Cd(II), respectively. The result indicated that the heavy metal adsorption reaction using the hybrid beads was an exothermic process. However, entropy (ΔS°) shows positive values 14.23 and 3.71 for Pb(II) and Cd(II), respectively, indicating the excellent affinity with the adsorbent.

CONCLUSIONS

Batch experiments were conducted to adsorb heavy metals of Pb(II) and Cd(II) in aqueous solution using hybrid beads. According to the FT-IR analysis, the hybrid bead has a structure that enables the easy adsorption of heavy metals because it has carboxylic, carbonyl groups, CH stretching, O-H carboxylic acid, and bonded -OH groups. Experimental results showed that more than 90% of Pb(II) and Cd(II) was adsorbed with the hybrid beads at a contact time of 30 min. Pb(II) and Cd(II) adsorption processes using hybrid beads were more suitable for the pseudo-second-order model because the pseudo-second-order model was more closely correlated than the pseudo-first-order model.

In addition, the adsorption of Pb(II) and Cd(II) with the hybrid beads was more suitable for Langmuir isotherms. The maximum adsorption capacity with the Langmuir model was 278.68 mg/g for Pb(II) and 87.91 mg/g for Cd(II). The values of 1/n of Pb(II) and Cd(II) were 0.475 and 0.711, respectively. The adsorption strength of Pb(II) and Cd(II) by hybrid beads was good and Pb(II) and Cd(II) exhibited L type isothermal adsorption characteristics. In thermodynamic experiments, ΔG° and ΔH° were negative and ΔS° was positive. The adsorption removal process of Pb(II) and Cd(II) using hybrid beads is a spontaneous exothermic reaction and the affinity of the adsorbed material for the adsorbent is excellent. Hybrid beads, which are made by mixing chitosan and persimmon leaf, are inexpensive, have a high removal efficiency of heavy metals, are environmentally friendly, and can be applied in the field. Furthermore, they are very economical for use as a heavy metal adsorbent because no post treatment is needed.

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