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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.

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

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

$$\%\text{Removal} = \frac{C_0 - C_F}{C_0} \times 100 \tag{2}$$

Table 1
Detailed experimental conditions.

Parameters	Range
pH	2–10
Initial concentration of heavy metals	0.5–20 mg/L
Contact time	0-6 h
Particle size of DPL and RPL	30-70 mesh
Temperature	20-40 °C
Test 1 (Effect of initial concentration)	Dose of adsorbent 3 g/L, temperature 25 °C, pH 6, particle size 50 mesh and contact time 60 min
Test 2 (Effect of pH)	Dose of adsorbent 3 g/L, temperature 25 °C, particle size 50 mesh, initial concentration 5 ppm and contact time 60 min
Test 3 (Effect of contact time)	Dose of adsorbent 3 g/L, temperature 25 °C, pH 6, particle size 50 mesh and initial concentration 5 ppm
Test 4 (Effect of adsorbent dose)	Temperature 25 °C, pH 6, particle size 50 mesh, initial concentration 5 ppm and contact time 60 min
Test 5 (Effect of temperature)	Dose of adsorbent 3 g/L, pH 6, particle size 50 mesh, initial concentration 5 ppm and contact time 60 min
↓	
The set fraction was sampled at a fixed time while stirring at 120 rpm on a Shaking Incubator	
↓	
The collected samples were centrifuged at 6000 rpm for 20 min and filtered using 0.45 μm (Whatman filter)	
↓	
The amount of heavy metals was measured using an Atom Absorption Spectrometer (AAS Perkin Elmer, AAS 3300)	

3. Results and discussion

3.1. Characteristics of persimmon leaf

3.1.1. Elemental analysis (wt.% of dried material) and physical properties of persimmon leaves

The surface area is used for evaluating the performance of the adsorbent and is an indicator of the space in which the adsorption can actually take place by determining the total pore surface area per 1 g of adsorbent. It is generally known that the adsorption amount increases as the surface area increases (Choi, 2015b). The pore size affects the adsorption rate of contaminants and the specific surface area increases as the size of the micropores increases, and the adsorption amount increases (Choi, 2017). However, if the pore size is too small, it is difficult to penetrate the adsorbed material through the pores to the inside of the adsorbent, so that the number of available pores for adsorption is reduced (Choi et al., 2016). Therefore, when adsorbing and removing a single substance, it is preferable that the pore distribution is concentrated on a specific pore. However, when various substances are to be removed, such as in water treatment, a variety of pore distributions may be advantageous (Choi, 2015a; Shaheen et al., 2013). Table 2 presents the physical properties of persimmon leaf. The specific surface area and pore size of persimmon leaf are 0.853 m^2/g and 1.475 nm, respectively, and no difficulty is expected in adsorbing and removing heavy metals.

The elemental analysis of persimmon leaf is shown in Table 3. Tannin is a generic term for a substance that are widely found in plants and that hydrolyze to produce polyphenol acid, but it is not a constant compound. Tannins dissolve in water, alcohol, and aceton. However, it is almost insoluble in benzene, chloroform, and ester, and forms insoluble matter by binding with metals (Yurtsever and Sengil, 2009). Tannin adsorbs and bonds with metal ions via two mechanisms (Bacelo et al., 2016; Zhan and Zhao, 2003). In the first mechanism, 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. In the second mechanism, the metal ion is chelated in the catechol ring of the phenolic monomer. The adsorption process of tannin is not a physical bond but a bond by chemical ion exchange, and it has a high bond strength (Pangeni et al., 2014; Sengil and Ozcar, 2009). However, due to the nature of tannin, which is water-soluble, the tannin elutes into water in the case of RPL, which may lower the removal ability of heavy metals. A previous study reported that the maximum adsorption capacity of Pb was 0.56, 0.42, and 0.67 (mmol/g) when using wattle tannin gel, quebracho tannin resin, and valonia tannin resin, respectively, and Cu was 0.71 and 0.69 (mmol/g) for valonia tannin resin and mimosa tannin gel, respectively (Sengil and Ozcar, 2008, 2009; Yurtsever and Sengil, 2009; Zhan and Zhao, 2003).

The DPL, the dried persimmon leaves, is present in an organic bond form, a tannin form, an exchangeable form, a carbonate form, or a sulfide form, in which tannin is believed to be difficult to easily elute (Heras et al., 2014). Due to this phenomenon, the tannin contained in DPL is expected to help the adsorption effect of heavy metals compared with RPL. However, the shape of DPL can also change gradually by chemical reaction during heavy metal adsorption over a long period of time. In particular, it is necessary to pay attention to the control of the pH, the cation, the anion, the heavy metal concentration, and the temperature of the aqueous solution containing DPL. Typically, in plant leaves, tannin is usually in the range of 3%–25% (Bacelo et al., 2016). Persimmon leaves have many hydroxyl groups (−OH) and contain 13.03% of tannin and catechin, which are effective in removing heavy metals. The amount of tannin in the persimmon leaves was higher than the amounts of platanus (5.12%) and ginkgo (2.02%) (Xie et al., 2015).

3.1.2. Fourier transform infra-red (FT-IR) spectra and scanning electron microscope (SEM)

The persimmon leaf contains high quantities of tannin and catechin. FT-IR spectra analysis of RPL and DPL is shown in Fig. 1(a). RPL and DPL basically contained N-containing bioligans from 480 to 650 cm^{-1}, PO_4^{3-} stretching and bending of OH groups from 950 to 1150 cm^{-1}, CO stretch from 1300 to 1500 cm^{-1}, Carboxylic group and NH bending from 1500 to 1600 cm^{-1}, Carboxylic groups at 1670 cm^{-1}, C=O carbonyl groups from 1680 to 1740 cm^{-1}, CH stretching and OH carboxylic acids from 2800 to 2900 cm^{-1}, and

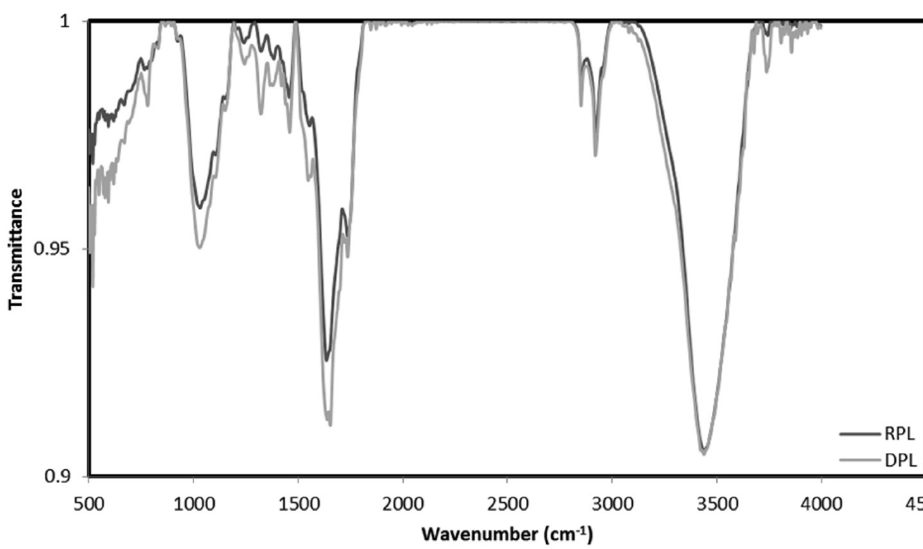
Table 2
Physical properties of persimmon leaves.

Parameters	Surface Area					Pore volume (m^3/g)	Pore size (nm)
	Single point at p/p_o (m^2/g)	BET (m^2/g)	Langmuir (m^2/g)	t-Plot Miscropore (m^2/g)	t-Plot External (m^2/g)		
Persimmon leaves	0.2010	0.8530	1.1395	1.1663	−0.3133	0.0543	1.4753

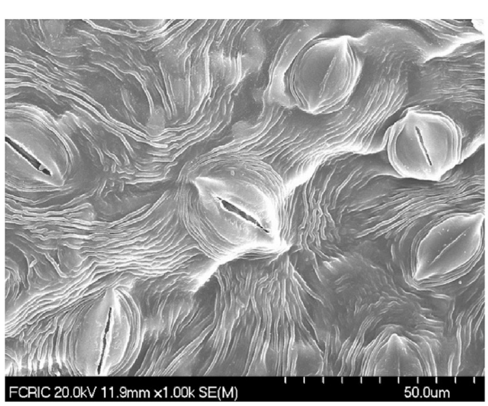
Table 3
Elemental analysis (wt.% of dried material).

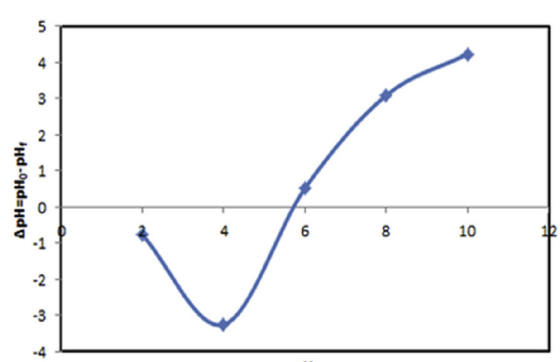
Elements		Caffeine		Catechin	Theanine		Tannin	Sulfur
wt. (%)		2.58		6.38	1.11		6.65	0.05
Elements	C	H	N	S	Moisture residual	Volatile matter	Ash	Fixed carbon
wt. (%)	57.8 ± 0.2	5.4 ± 0.1	0.83 ± 0.01	0.03 ± 0.0	1.4 ± 0.1	17.4 ± 0.1	3.23 ± 0.1	37.63 ± 4.12

bonded −OH groups from 3000 to 3500 cm^{-1}. Among them, the largest and widest peak was 1670–1740 cm^{-1} and 3000-3600 cm^{-1}. In particular, the peak of 1670–1740 cm^{-1} and 1150 cm^{-1} for DPL was deeper than that of RPL. This indicates that DPL contains more −OH, carboxylic, and carbonyl groups than RPL. In addition, the tannin component of persimmon leaves has a large number of phenolic hydroxyl groups (hydroxyl groups, −OH) and has heavy metal adsorption capacity (Bacelo et al., 2016; Pangeni et al., 2014). In general, the functional group with the highest heavy metal adsorption capacity is known as the carboxyl group. The carboxyl group dissociates to $-COO^-$ and H^+ in aqueous solution, and when it is above a certain pK, most of it transforms to $-COO^-$, and the cationic heavy metal is efficiently adsorbed (Ali et al., 2016; Choi, 2015b; Pangeni et al., 2014). The mechanism of adsorption of heavy metals by biomaterials is not well known, but the reason for the adsorption is that the functional groups in the polymeric materials in the cell tissues are coordinated with heavy metals. These functional groups are known to include −COOH, NH_2^-, $-PO_4$, $-SO_4$, $C_6H_5^-$, >CO, $(NH_2)_3C-NH-$, and −OH. Of the substances in the living body, carbohydrates and proteins have these functional groups (Hu et al., 2017; Wang and Chen, 2009; Yurtsever and Sengil, 2009). In addition, cell walls consist of cellulose,



(a)





(b) (C)

Fig. 1. (a) FT-IR spectra of persimmon leaf, (b) SEM image of persimmon leaves, and (c) pH at zero point of charge (pH_{PZC}) of persimmon leaf.

galactan, etc., and it has been stated that the $-OH$, $-CH_2OSO_3^-$, etc. contained in the molecules of galactan, $-COOH$, and $-OH$, which are mainly contained in cellulose, are involved in coordination bonding with heavy metals (Gu et al., 2008; Heras et al., 2014). The nature of RPL and DPL IR spectra did not significantly differ since both the samples contained with identical chemical components. However, the relative intensities of IR peaks differ for the DPL and RPL solids. It was noted that the relative peak intensity for the carbonyl group (1080 cm^{-1}–1160 cm^{-1}) and the carboxylate groups (1500 cm^{-1}-1800 cm^{-1}) are found increased in case of DPL than RPL. This possibly indicates that DPL possessed with enhanced functional group density than RPL which eventually facilitate the higher percentage adsorption of heavy metals. Therefore, DPL is expected to have higher heavy metal adsorption efficiency than RPL.

A scanning electron microscope (SEM) image of persimmon leaf is shown in Fig. 1(b). The surface of the persimmon leaf is very irregular and porous in nature. These porous and irregular surfaces are believed to be very helpful for adsorbing heavy metal ions (Choi et al., 2016). In addition, the surface of the persimmon leaf is composed of multiple layers of thin films. This can be useful to adsorb heavy metals.

3.1.3. Analysis of point of zero charge pH (pH_{PZC})

The pH_{PZC} was measured to confirm the adsorbent surface charge and the results are shown in Fig. 1(c). The pH affects the form of heavy metals in aqueous solution and the interaction of heavy metal and adsorbent, which is an important factor that can affect the adsorption capacity. The pH with a net total particle charge of zero is called the point of zero charge (pH_{PZC}), which is one of the most important parameters used to account for adsorbent surface adsorption (Choi, 2017). That is, the effect of pH on the adsorption of heavy metal ions when adsorbing heavy metals on the adsorbent surface in an aqueous solution can be explained based on pH_{PZC} (Appel et al., 2003; Choi, 2015b). pH_{PZC} is a convenient index to determine whether the surface of the adsorbent is positively or negatively charged (Kosmulski, 2014). The result showed that the pH of the persimmon leaf was 5.6 and the pH of the heavy metals used in the experiment was lower than the pH_{PZC} of the persimmon leaf in which Cu was pH 4, Cd was pH 3, and Pb was pH 3–4. In the case of $pH < pH_{pzc}$ for the surface of the persimmon leaf, the leaf is positively charged as a whole (Appel et al., 2003). Thus, the electrostatic attraction mechanism can be easily excluded. The sudden increase in adsorption with increasing pH appears to be related to this ion exchange mechanism (Choi, 2017). At low pH values (4.0), high concentrations of H^+ ions compete with Cu, Pb, and Cd for exchangeable cations on the adsorbent surface, inhibiting the adsorption of Cu, Pb, and Cd on to DPL surface. However, as the pH value increases, more of the exchangeable cations on the adsorbent surface are exchanged for Cu, Pb, and Cd due to the weak competitive adsorption of H^+ ions, resulting in a rapid increase in adsorption. Therefore, the pH of the aqueous solution is expected to show a high heavy metal adsorption rate of above 5.6.

3.2. Effect of different parameters on heavy metal removal

3.2.1. Effect of initial heavy metal concentration

To investigate the effect of initial concentration of heavy metals on the removal rate, the concentration of heavy metals was controlled to 0.5–20 ppm and the results are shown in Fig. 2 (a) and (b). Since the amount of adsorbent and the adsorption time must be determined according to the initial concentration of heavy metals, the effect of the initial concentration of heavy metal on the removal rate is determined via a basic experiment for deriving the optimum condition of the adsorption process. Experimental results show that both RPL and DPL have higher removal efficiencies of Cu, Pb, and Cd than 98%, at a concentration of Cu, Pb, and Cd of below 1 mg/L. It should be noted that when RPL was used, the removal efficiency was more than 90% at a concentration of below 2 mg/L. However, when DPL was used as the adsorbent, the removal efficiency was more than 90% at a concentration of up to 4 mg/L of Cu, Pb, and Cd. This is because DPL has a larger specific surface area than RPL, and thus the adsorption capacity for adsorbing heavy metals is larger.

As the concentration increased, the adsorption removal rate decreased. The removal efficiency of RPL for Cu, Pb, and Cd was found to be 27.6%, 31.6%, and 20.6%, and that of DPL was 40.6%, 54.6% and 34.6%, respectively. The decrease of the removal efficiency as the concentration of heavy metals increased was less in DPL than in RPL. The experimental results showed that the removal efficiency of Cd and Pb, Cu was affected by the initial concentration of heavy metals and reaching the equilibrium point was dependent on the initial concentration. As the initial concentration of Cd and Pb, Cu increased, the rate of removal also reached the equilibrium point quickly. That is, as the concentration of heavy metals was reduced, the adsorption efficiency increased. This is because, as the concentration was reduced, the probability of adsorption to the adsorbent per ion increased. Both RPL and DPL had the highest removal efficiency for Pb, followed by Cu and Cd. Pb forms stronger metal hydroxides ($MeOH^+$) than Cd or Cu under neutral pH conditions, and these hydroxides strongly bind to the functional groups on the persimmon surface. Adsorption by this bond is known to be stronger than adsorption by simple electrostatic attraction, and it is known that Pb adsorbs more strongly on the surface of persimmon leaves and oxides than Cu or Cd.

3.2.2. Effect of pH

Temperature, pH, alkalinity, and static materials are the main influential factors for adsorbing and removing organic and inorganic materials in aqueous solution (Ajitha et al., 2017). In particular, the pH in the aqueous solution has a significant influence on the removal of organic and inorganic matter (Kosmulski, 2014). To investigate the effect of pH on Cu, Pb, and Cd removal by RPL and DPL, the pH was adjusted to 2–10. The experimental results show that Cu has a high removal rate up to pH 6, while Pb and Cu have a high removal rate above pH 5 (Fig. 2). The effect of the pH of the solution on metal ion adsorption can be explained based on the pH at the point of adsorption (pH_{PZC}). The rapid increase in adsorption efficiency 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, Cu, and Cd for exchangeable cations on the adsorbent surface, inhibiting the adsorption of heavy metals on the persimmon surface. However, as the pH value increases, the exchangeable cations on the adsorbent surface become less competitive with the adsorption of H^+ ions, so the heavy metals are exchanged with $Me(OH)_2$ and $Me(OH)_3$, and the adsorption increases significantly (Barsbay et al., 2017). In general, heavy metals in aqueous solution exist in the form of hydroxides of Cu(OH), Cd(OH), and Pb(OH), and the heavy metals are precipitated in the form of $Cu(OH)_2$, $Cd(OH)_2$, and $Pb(OH)_2$ in neutral or alkaline conditions (Deniz and Karabulut, 2017; Hu et al., 2017). Therefore, the increasing of pH can affect the removal efficiency for Cd, Pb, and Cu. On the other hand, the removal efficiency for Pb, Cu, and Cd was 20%–45% at low pH values (pH 2.0–3.0). It can be seen that the components of the surface of the adsorbent according to the FT-IR analysis play an important role in the adsorption of heavy metals. The removal efficiency for Pb was similar in both RPL and DPL, but the removal efficiency of DPL for Cu and Cd was about 10% higher than that of RPL. This suggests that the surface of the smooth

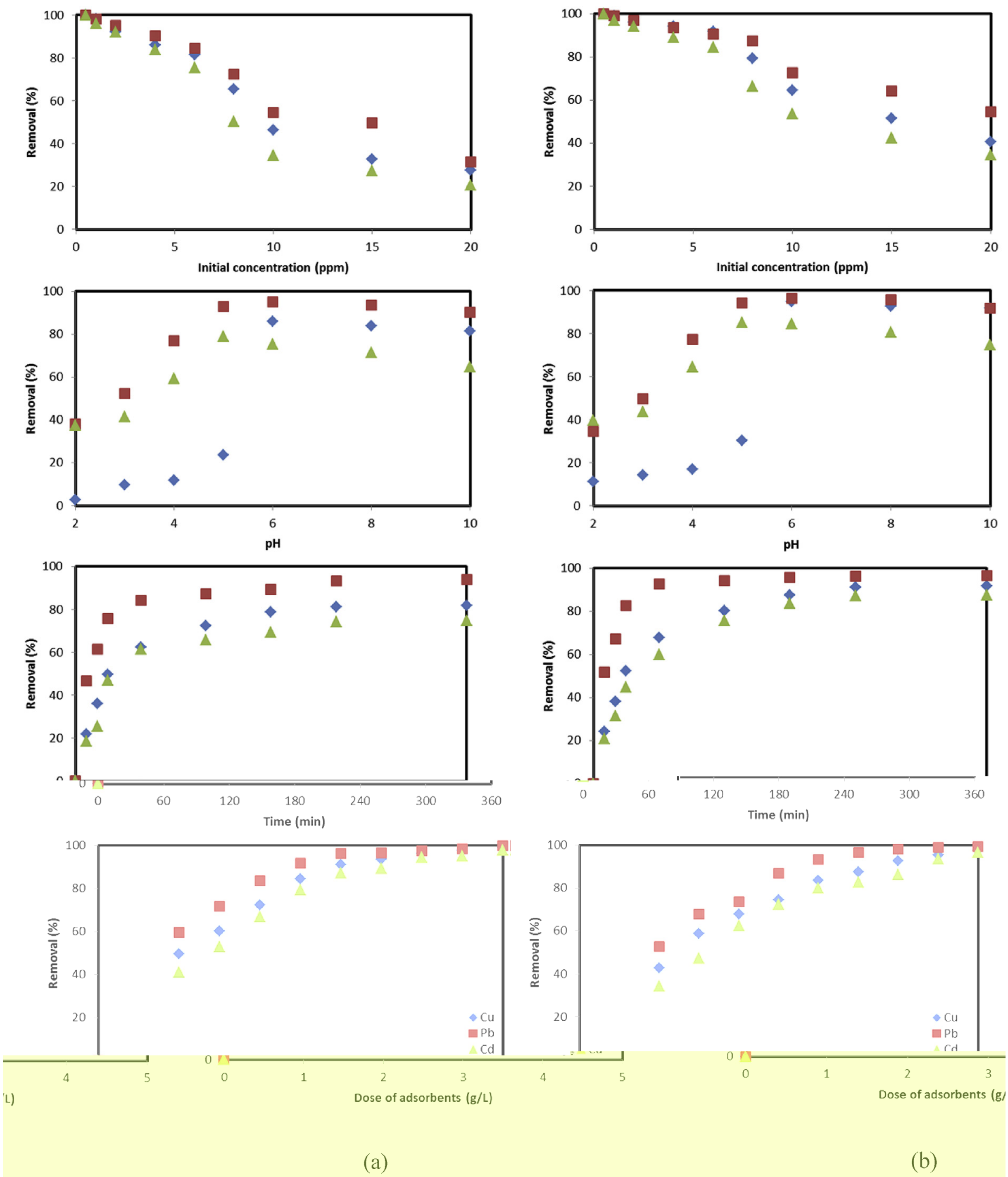


Fig. 2. Effect of initial concentration, pH, contact time and adsorbent dose of Cu, Pb, and Cd by (a) RPL and (b) DPL.

adsorbent changed to a rough and voluminous surface as the RPL changed to DPL, which made it easier to adsorb Pb, Cu, and Cd. In general, the surface adsorption mechanism of heavy metals is affected by the pH of the reaction medium, the surface characteristics of the adsorbent, and the characteristics of heavy metals. As a result, Pb, Cd, and Cu showed high removal efficiency above pH 6. Considering that the pH of general wastewater is about 6–8, when the persimmon leaves are adsorbed and the heavy metals are adsorbed in the aqueous solution, they can be applied to the field without controlling the pH. When persimmon leaf is used as a bioadsorbent, it is eco-friendly because it does not require a chemical agent, and it is very useful in resource recycling.

3.2.3. Effect of adsorbent dose

The ability to adsorb large quantities of harmful substances with an inexpensive, eco-friendly adsorbent is very important both economically and environmentally. The initial concentration of Pb, Cu, and Cd was fixed at 5 ppm and the removal efficiency was determined through experiment by increasing the concentration of adsorbent. The result is shown in Fig. 2 (a) and (b). The removal efficiency for Cd, Pb, and Cu were more than 90% in the adsorbents amount by 4 g/L of RPL and 3 g/L of DPL. The amount of adsorption depends on the state of the adsorption surface. As the persimmon leaves dry, the water contained in the persimmon leaves escapes. As a result, the surface of the persimmon leaves becomes rough and uneven. Then, the specific surface area of DPL increased more than that of RPL, and the change of surface of the adsorbent was assumed to have facilitated the adsorption of heavy metal ions. As the amount of adsorbent increased, the adsorption amount of the heavy metal increased. This is because, as the adsorbent increases, the surface area where heavy metals can be adsorbed increases, and the probability of adsorption to the adsorbent per ion increases. Therefore, when adsorbing and removing heavy metals using persimmon leaves, the amount of adsorbent is recommended to be 4 g/L for RPL and 3 g/L for DPL.

3.2.4. Effects of contacts time

To investigate the effect of contact time on the removal rate for Cu, Pb, and Cd by RPL and DPL, the removal rate was observed for 360 min. As shown in Fig. 2, Pb showed the fastest adsorption rate compared to Cu and Cd, and showed the highest adsorption efficiency. For RPL, the removal rate of Pb was 84.2% and for DPL was 92.5% in 60 min. In addition, Pb was removed by DPL, and the adsorption equilibrium was almost reached at about 60 min. In contrast, Cu and Cd showed slower adsorption rate and lower adsorption efficiency than Pb by RPL and DPL, indicating 62.5% and 61.5% onto RPL, and 67.8% and 59.8% onto DPL for Cu and Cd in 60 min, respectively. Cu and Cd reached adsorption equilibrium after 240 min. According to the percentage of adsorption, the selectivity sequence of the investigated heavy metals using RPL and DPL was given as Pb > Cu > Cd. Moreover, the adsorption rate of Cu, Pb, and Cd was faster and the removal rate of DPL was 10%–15% higher than that of RPL. This is related to the analysis of FT-IR. According to FT-IR analysis, DPL contains more –OH groups, carboxylic, carbonyl, and the carboxylate group than RPL. Moreover, DPL contains more tannins than RPL. In general, the functional group with the highest heavy metal adsorption capacity is known as the carboxyl group. In general, the carboxyl group is effective for heavy metal adsorption (Sun et al., 2014; Tan et al., 2010). Furthermore, the tannins contained in persimmon leaves are known to be effective for heavy metal adsorption, so heavy metal adsorption using DPL has dual effects. Therefore, it is considered that these components act more effectively on the adsorption of heavy metals.

3.3. Adsorption kinetics

As a result of the removal of Pb, Cd, and Cu using RPL and DPL, DPL showed about 20%–30% higher removal rate than RPL. Therefore, for adsorption kinetic analysis, we analyzed the adsorption removal data of Pb, Cd, and Cu using DPL. Pseudo-first order, pseudo-second order, and Intra-particle diffusion were applied to investigate the adsorption and diffusion rates. The pseudo-first order depends on the concentration of only one reactant, that is, the unimolecular reaction (Ali et al., 2016). The pseudo-second order depends on the concentration of one secondary or two primary reactants. Therefore, when analyzing the adsorption rate of various adsorbents in aqueous solution, it is often more appropriate to use pseudo-second order than pseudo-first order (Ho and McKay, 1999; Hu et al., 2017). Table 4 shows the parameter values obtained by calculating the experimental data. The correlation coefficients (R^2) of Cu, Pb, and Cd using DPL were determined as 0.981, 0.9879, and 0.9822, respectively, for the pseudo-first order and 0.9991, 0.9994, and 0.9989, respectively, for pseudo-second order. Therefore, the adsorption process of Cu, Pb, and Cd using DPL is a better fit in the pseudo-second order than in the pseudo-first order. Intra-particle diffusion applied data showed no linear relationship and did not cross the origin. This result suggests that Cu, Pb, and Cd adsorbed on DPL represent a complex mechanism due to the external mass transfer and internal particle diffusion. Therefore, mass transfer takes place in the initial region of adsorption ($t^{1/2}<1.7$), and in the subsequent linear region (linear region of $t^{1/2}>1.7$), the adsorption process by internal particle diffusion occurs. The internal particle diffusion rate constants of Cu, Pb, and Cd from the slope were 0.0918, 0.1085, and 0.0672 mg/g/min$^{0.5}$, respectively (Fig. 3(a) and (b)). In addition, the internal particle diffusion rate constants increased in the order of Cd, Cu, and Pb, indicating that the adsorption by persimmon leaves was the fastest in the reaction rate of Pb compared to Cu and Cd.

3.4. Adsorption isotherms

In general, the adsorbent performance is evaluated using adsorption isotherms based on adsorption equilibrium (Hu et al., 2017). The adsorption isotherm expresses the relationship between the equilibrium concentration of the adsorbate and the equilibrium adsorption amount per unit gram of adsorbent at a constant temperature (Kabbashi et al., 2009). Numerous models such as the Langmuir, Freundlich, Elovich, Dubinin-Radushkevich (D-R), and Temkin isotherms have been proposed to characterize the adsorption mechanism using adsorption isotherms. These models are currently used to identify the adsorption performance and adsorption mechanism of adsorbents or adsorbates (Murugesan et al., 2011; Redlich and Peterson, 1959).

The isothermal adsorption experiments were applied to the Langmuir, Freundlich, and D-R isotherms. The parameter values obtained by applying to the isothermal adsorption equations are shown in Table 4. Isothermal adsorption experiments were carried out with varying initial heavy metal concentrations ranging from 10 to 200 mg/L to investigate the adsorption capacity of DPL depending on the concentration of Cu, Pb, and Cd. Experimental results showed that the adsorption capacity of the three heavy metals (Cd, Pb, Cu) increased with increasing initial concentration of heavy metals, and then reached equilibrium. These results suggest that the surface of the biomaterial is gradually filled with the adsorbate, the heavy metal, and the effective adsorption area is decreased. In addition, the isothermal adsorption line appears nonlinear because the energy of the adsorption site is not uniform in the state where the adsorption site is saturated by the adsorbate, and is due to the electrostatic repulsion between the adsorbent and adsorbate. Due to the heterogeneity of these adsorbate surfaces, the rate of increase of the adsorption amount decreases. This tendency is frequently observed in the adsorption reaction where ion exchange reaction is predominant. Conversely, competitive adsorption occurs between the solutes on the adsorption site when the adsorption is linear, when it is known that non-competitive adsorption occurs.

When the heavy metal adsorption reaches equilibrium, the amount of adsorbed per unit weight of the adsorbent is the equilibrium concentration constant of the residual heavy metal ion, which is usually followed by the Freundlich or Langmuir isothermal adsorption model. The application of the Freundlich model is suitable when the energy of the adsorbed surface is unevenly distributed, such as for activated carbon (Kabbashi et al., 2009; Pangeni et al., 2014). In the Freundlich model, the K_F value is a function related to adsorptivity, and $1/n$ is the function of adsorption strength between particles and contaminants. As the value of $1/n$ decreases, the strength of the bond by adsorption increases (Choi, 2015b; Pawar et al., 2016). In the Freundlich adsorption isotherm, adsorption is good when $1/n$ value of adsorption strength

Table 4
Adsorption kinetics and isotherms constant and correlation coefficient for the adsorption of Cu, Pb, and Cd onto DPL.

Models	Parameters	Cu	Pb	Cd
Pseudo-first-order	$k_1(min^{-1})$	0.0434	0.0501	0.0401
$\ln(q_e - q_t) = \ln q_e - k_1 t$	R^2	0.981	0.9879	0.9822
	χ^2	5.6131	5.2463	6.8659
Pseudo-second-order	k_2(mg/g/min)	0.0376	0.0482	0.0305
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	R^2	0.9991	0.9994	0.9989
	χ^2	0.0142	0.0148	0.0215
Intra-particle diffusion	$k_{id}(mg/g/min^{1/2})$	0.0918	0.1085	0.0672
$q_t = k_d t^{\frac{1}{2}} + Z$	R^2	0.9412	0.9433	0.9387
	χ^2	0.0346	0.0523	0.0815
Elovich	a (mg/g/min)	1.3218	0.8514	2.4216
$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t + t_0)$	b (g/mg)	2.8769	2.2036	3.5862
	R^2	0.9867	0.9919	0.9862
	χ^2	4.3652	6.2598	3.5317
Langmuir isotherm	q_m (mg/g)	19.4217	22.5863	18.2561
$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	K_L (L/mg)	0.0254	0.0261	0.0247
	R^2	0.9217	0.9136	0.9147
	χ^2	3.1621	2.4327	3.4389
Freundlich isotherm	K_F(mg/g)	0.6816	0.7962	0.6742
$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$	n	2.1514	2.1526	2.1478
	R^2	0.9962	0.9975	0.9946
	χ^2	0.5866	0.6772	0.6015
Temkin isotherm	K_T	0.8645	0.9431	0.7765
$q_e = b_T \ln K_T + b_T \ln C_e$	b_T	2.7121	2.8021	2.5183
	R^2	0.8489	0.8537	0.8786
	χ^2	5.2387	6.9572	4.1863
Dubinin-Radushkevich isotherm	$q_m x10^4$	8.7562	11.0532	8.4327
$\ln q = \ln q_m - \beta\varepsilon^2 \quad E = \frac{1}{\sqrt{2\beta}}$	E (kJ/mol)	9.1562	8.9687	9.2678
	R^2	0.9952	0.9961	0.9937
Thermodynamic parameters				
ΔG° (kJ/mol)	303 K	−2.1648	−7.2377	−1.1761
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_L$	313 K	−2.7728	−8.2617	−1.5881
$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$	323 K	−3.3808	−9.2857	−2.0001
ΔH° (kJ/mol)		16.2576	23.7895	11.3075
ΔS° (J/mol·K)		0.0608	0.1024	0.0412

is in the range of 0.1–0.5, and adsorption is weak when it is more than 2. Also, when the adsorption strength ($1/n$) value is greater than 1, it has S-type isothermal adsorption characteristics, when the adsorption strength is less than 1, it has L-type isothermal adsorption characteristics, and when it is 1, it has C-type isothermal adsorption characteristics (Hu et al., 2017; Li et al., 2006). As a result of adsorption experiments on heavy metals in DPL, the n value was higher than 2 regardless of dose, indicating that the adsorption was easy. In particular, Pb has a lower $1/n$ value than Cu and Cd, which means that the adsorption strength of Pb is higher than that of other heavy metals. Moreover, the adsorption constant K_F of Cu, Pb, and Cd was 0.6816, 0.7962, and 0.6742, respectively, indicating that Pb had the highest adsorption constant. Generally, as the value of the adsorption constant K_F increases, the adsorbing ability of the adsorbent also increases (Murugesan et al., 2011). The results of applying this experiment to the Freundlich model show that the correlation coefficient (R^2) of Cu, Pb, and Cd is 0.9962, 0.9975, and 0.9946, respectively, which is relatively higher than that of the Langmuir model. From the above results, it can be concluded that the adsorption of persimmon leaves is compatible with the Freundlich isothermal adsorption, resulting in an ion exchange reaction in the uneven adsorption surface layer. The maximum adsorption capacity (q_m) of DPL was 22.59, 19.42, and 18.26 mg/g for Pb, Cu, and Cu, respectively. The difference of adsorption capacity is due to the difference in the molecular size, affinity, and electronegativity of heavy metal ions. The heavy metal adsorption of bioabsorbable materials is due to the heavy metal selectivity of the functional groups of the bioabsorbable material (Garg et al., 2008; Kim et al., 2015). In this study, the adsorption of Pb has more affinity than Cu and Cd onto DPL.

Table 5 presents the results of previous studies in which heavy metals were adsorbed and removed using a biomaterial adsorbent. The maximum adsorption capacity of heavy metals by persimmon leaf was lower than with modified corncob, jatropha oil cake, and sugarcane bagasse. However, the amount of adsorption was significantly higher than that of rice husk, sawdust, and peanut husk. In addition, the use of persimmon leaves containing tannin was at least 4 to 40 times more effective in removing heavy metals than using tannin alone to make gels. The use of persimmon leaf confirmed the possibility of adsorption of heavy metals. It is considered that the adsorption capacity of heavy metals will be much higher when the persimmon leaf is modified.

3.5. Thermodynamic parameters

The adsorption isotherm is the thermodynamic equilibrium between the heavy metal adsorbed on the surface of the DPL and the heavy metal in the aqueous solution, and is temperature dependent. To investigate the effect of temperature on heavy metal adsorption on DPL, the temperature was controlled from 20 to 40 °C and at pH 5. Adsorption energy is important for understanding the thermodynamic properties and the adsorption process such as the adsorption isotherm in the adsorption reaction. From D-R adsorption isotherms, adsorption energy show that the adsorption process is physical adsorption or ion exchange (Choi, 2017). D-R developed a theory that the adsorption process in very fine pores is not the adsorption layer formation in the pore walls but the filling in the pores. He also developed the potential theory of Polanyi (Arshadi et al., 2014; Cerofolini, 1982). Adsorption energy is 1–10 kJ/mol for physical adsorption, 8–16 kJ/mol for ion exchange adsorption,

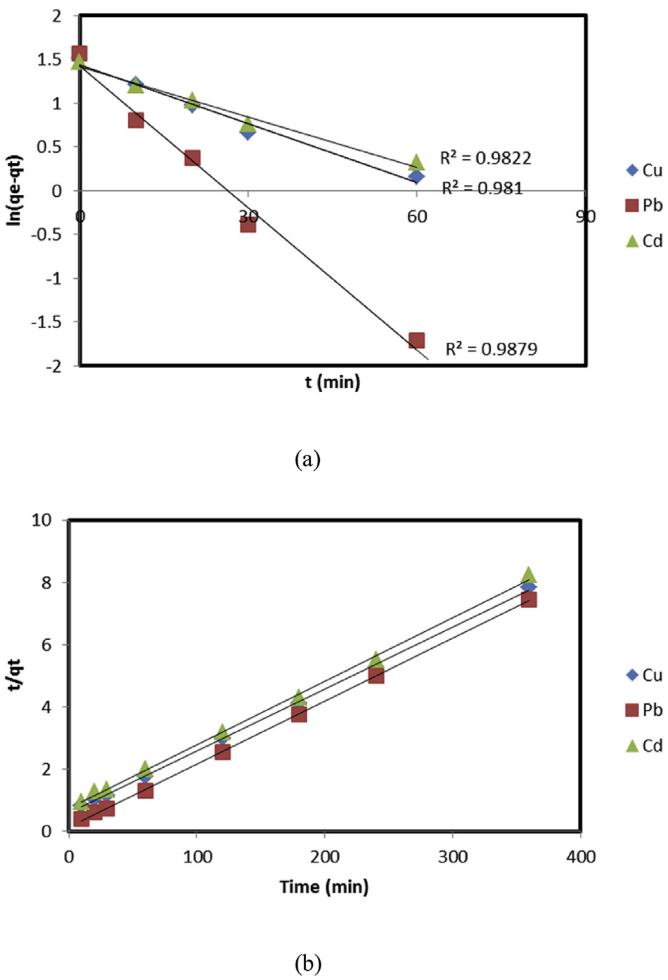


Fig. 3. (a) Pseudo-first kinetic model and (b) pseudo-second kinetic model for Cu, Pb, and Cd onto DPL.

and 20–40 kJ/mol for chemisorption (Hu et al., 2017). As shown in Table 4, the adsorption energy values of DPL were 9.16, 8.97, and 9.27 kJ/mol for Cu, Pb, and Cd, respectively. Therefore, the adsorption process of Cu, Pb, and Cd by DPL seems to be closer to selective ion exchange adsorption than chemical adsorption.

The ΔG° is a measure of useful work in chemical reactions. It is also a state function that determines the direction of the spontaneous change process for a chemical reaction, and is independent of the path of change. In the adsorption experiments carried out in this study, ΔG° decreased with increasing temperature in all investigated heavy metal ions (Cu, Pb, and Cd) (Table 4). In addition, ΔG° was negative, indicating that the adsorption process was spontaneous in nature. The values of ΔH° were all positive values of Cu, Pb, and Cd of 16.26, 23.79, and 11.31, respectively. It can be seen that the heavy metal adsorption reaction using DPL was an endothermic process and the adsorption was more likely to occur with higher temperature. Moreover, ΔS° showed positive values of Cu, Pb, and Cd of 0.06, 0.10, and 0.04, respectively. It can be seen that the adsorption process of heavy metals has a very good affinity to DPL. The positive value of ΔS° might indicate that adsorbate molecules gain at least one degree-of-freedom when they lose adsorption on the DPL. It also validates that randomness at the solid-liquid interface is increased during the adsorption process. Taking all results into consideration, Cu, Pb, and Cd removal using persimmon leaf is more likely to be performed by ion exchange adsorption than by chemical adsorption. The bio-waste adsorbent, persimmon leaves, can effectively remove Cu, Pb, and Cd in small quantities, and is environmentally friendly because it does not use chemicals. In addition, it is cheaper to reuse bio-wastes, and recycling resources is a huge advantage.

4. Conclusions

Batch experiments were conducted to adsorb and remove Cu, Pb, and Cd heavy metals in aqueous solution using RPL and DPL. Persimmon leaves include many hydroxyl groups (–OH) and contain 13.03% of tannin and catechin, which are effective in

Table 5
Comparison of the maximum adsorption capacities of heavy metal onto biomaterial adsorbents.

Adsorbent	Heavy metal	q_m (mg/g)	Reference
Sericite	Cu(II)	1.674	Tiwari et al., 2007
	Pb(II)	4.697	
Activated bentonite	Cu(II)	3.787	Pawar et al., 2016
	Pb(II)	6.535	
Mg-zeolite	Cd(II)	36.88	Choi, 2016
	Cu(II)	15.21	
	Pb(II)	58.46	
Valonia tannin gel	Cu(II)	0.71	Sengil and Ozcar, 2009
	Pb(II)	0.67	
Mimosa tannin	Cu(II)	0.60	Sengil and Ozcar, 2008
Wattle tannin gel	Pb(II)	0.56	Zhan and Zhao, 2003
Persimmon tannin gel	Cd(II)	5.27	Bacelo et al., 2016
Persimmon waste gel	Cu(II)	7.18	Bacelo et al., 2016
Sawdust (*Pinussylvestris*)	Pb(II)	9.78	Taty-Costodes et al., 2003
Peanut husk	Cu(II)	10.15	Li et al., 2006
modified corncob	Pb(II)	43.4	Tan et al., 2010
Maize corncob	Cd(II)	105.6	Garg et al., 2008
Jatropha oil cake	Cd(II)	86.96	Garg et al., 2008
Sugarcane bagasse	Cd(II)	69.09	Garg et al., 2008
Cinnamomum camphora leaves	Pb(II)	75.82	Chen et al., 2010
Dried persimmon leaves	Cd(II)	19.42	This study
	Cu(II)	22.59	
	Pb(II)	18.26	

removing heavy metals. Moreover, according to the FT-IR analysis, RPL and DPL had a structure which facilitates the adsorbtion of heavy metals because it has Carboxylic group, C=O carbonyl groups, CH stretching, O–H carboxylic acid, and bonded –OH groups. The removal of heavy metals by using RPL and DPL resulted in 10%–15% removal efficiency of DPL than RPL. The removal rates were in the order of Pb > Cu > Cd. The heavy metal adsorption experiments using RPL and DPL were more suitable for the pseudo-second order than the pseudo-first order depending on the coefficient of determination. The adsorption of Cu, Pb, and Cd by DPL was more suitable for Freundlich isothermal adsorption than Langmuir isothermal adsorption. The adsorption of Cu, Pb, and Cd was concluded to be ion exchange reaction on an uneven adsorption surface layer. The maximum adsorption capacity (q_m) of DPL by Langmuir was determined to be 22.59 mg/g, 19.42 mg/g, and 18.26 mg/g for Pb, Cu, and Cd, respectively. As a result of the adsorption experiments on heavy metals in DPL, the n value was higher than 2 regardless of dose, indicating that the adsorption was easy. The adsorption constant K_F of Cu was 0.6816, Pb was 0.7962, and Cd was 0.6742, indicating that Pb had the highest adsorption constant. That is, the adsorption rate of PB was faster than that of Cu and Cd in heavy metal adsorption experiments using DPL. In the thermodynamic experiment, ΔG° exhibited a negative value and decreased as the temperature increased, resulting in a spontaneous process. ΔH° and ΔS° showed positive values, and heavy metal adsorption reaction using DPL was an endothermic process. Therefore, it can be seen that, as the temperature increases, the adsorption improves, and the affinity of heavy metal to DPL in the adsorption process is very good. Based on these experimental results, we conclude that DPL is an inexpensive, efficient, and commercially viable new eco-friendly adsorbent for removing heavy metal ions from the polluted water. In addition, bio-adsorbent, DPL, is very economical because it can be easily applied without remodeling existing sewage treatment plants and could be employed as a low-cost alternative to commercial activated carbon in the removal of heavy metal ions from wastewater.

Conflict of interest

The author(s) confirmed that this article content has no conflict of interest.

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Nomenclature

a: Elovich constant which gives an idea of the adsorption rate constant (mg/g/min)
b: Elovich constants and represents the rate of chemisorption at zero coverage (g/mg)
b_T: Temkin constant
C_o: initial concentration of heavy metal ion (mg/L)
C_e: equilibrium concentration of heavy metal ion (mg/L)
C_F: final concentration of heavy metal ion (mg/L)
C_t: concentration of heavy metal ion at time t (mg/L)
DPL: dried persimmon leaves
E: sorption energy (kJ/mol)
ΔG°: Gibbs free energy (kJ/mol)
ΔH°: 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_{id}: intra-particle diffusion rate constant (mg/g/min$^{1/2}$)
k_L: Langmuir constant (L/mg)
k_F: Freundlich constants referring to the adsorption capacity (mg/g)
K_T: Temkin isotherm constant
m: amount of persimmon leaves (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: amount of heavy metal ions adsorbed at time t (mg/g)
q_m: Langmuir monolayer maximum adsorption capacity (mg/g)
q_{tm}: amount adsorbed per gram of adsorbent from the model (mg/g)
R: ideal gas constant, 8.314 (J/mol/K)
R^2: correlation coefficient
RPL: raw persimmon leaves
ΔS°: entropy (J/mol·K)
t: time (min)
T: absolute temperature (K)
V: the volume of solution (L)
Z: intraparticle diffusion constant
β: activity coefficient related to the mean sorption energy
ε: polanyi potential
χ^2: chi-square value $\chi^2 = \sum \frac{(q_{t-q_{tm}})2}{q_{tm}}$