Application of novel hybrid bioadsorbent, tannin/chitosan/sericite, for the removal of Pb(II) toxic ion from aqueous solution

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Abstract−We addressed the development of a novel, low-cost, and high-efficient material from hybrid materials, known as microcapsules. Microcapsules are a composite adsorbent made of a mixture of tannin, sericite and chitosan. The FT-IR analysis showed that the microcapsules contain hydroxyl, carboxyl, carbonyl, and amino groups, which play an important role in the adsorption of heavy metals. The microcapsules were able to remove 99% of Pb(II) in 30 min, and obtained a removal efficiency of more than (13-50)%, compared with the single adsorbents of tannin, chitosan, and sericite. In adsorption kinetic analysis, pseudo-second-order adsorption was more suitable than pseudo-first-order adsorption, and chemical adsorption did not limit the adsorption rate of Pb(II) ion. In isothermal adsorption, Langmuir adsorption was more suitable than Freundlich adsorption, and the maximum Langmuir adsorption capacity was 167.82 (mg/g). Furthermore, desorption and reusability studies, as well as the applicability of the material for wastewater treatment, demonstrated that microcapsules offer a promising hybrid material for the efficient removal of significant water pollutants, i.e., Pb(II) from aqueous solutions.

Keywords: Biosorption, Chitosan, Heavy Metal Removal, Hybrid Materials, Sericite, Tannin

INTRODUCTION

The adsorption process is relatively simple, and is widely used for removing pollutants because it can effectively remove various contaminants from aqueous solution or industrial wastewater [1]. In general, the adsorbents used in wastewater treatment are mainly clay minerals, zeolites, oxides, biopolymers, and activated carbon [2,3]. Research using these materials has been vigorous over the past few years. Low-cost adsorbents, i.e., adsorbents using bioabsorbents, agricultural by-products, industrial wastes, etc., have emerged as new alternative adsorbents which have been applied to waste water treatment [4,5]. To minimize the environmental impact of the adsorption process, the adsorbent must be highly adsorptive and reproducible, and the pretreatment for use must be inexpensive and simple.

Biosorption, a new, environmentally friendly adsorbent, can achieve this goal. Biomaterial adsorption utilizes adsorbents of specific biomolecules or bioadsorbents to bind or concentrate ions or molecules selected from aqueous solutions [6,7]. The mechanism of biomaterial adsorption is generally based on physico-chemical interactions between the adsorbent and the functional groups present on the biomass surface, such as electrostatic interaction, ion exchange, metal ion chelation, or complex compounds [8]. As a result, biomaterial adsorption using seaweed, agricultural waste, forest byproducts, and industrial byproducts, has over the last several years proven to be a promising technology for adsorbing heavy metals and organic contaminants in aqueous solutions in natural or modified form [9]. In particular, the adsorbent using lignocellulosic biomass, tannin, seaweed, and chitosan can adsorb and recover the metal that needs to be recovered, and thus the added value is very high.

Among the various types of biomaterial adsorbents, tannin is a natural, high molecular substance present in the leaves, roots, stems, etc. of ordinary plants, and a very inexpensive and highly efficient adsorbent that can easily be obtained everywhere [10]. Tannin is a type of polyphenol that gives a very tangy flavor, and refers to the substance originally used as a preservative when the skin of an animal was made into leather [11]. However, at present, polyphenolic compounds having strong hydroxyl groups are strongly bonded to proteins and other polymers [12]. Tannins have a large number of OH groups, which can bind reversibly to molecules, such as polysaccharides, proteins, alkaloids, and heavy metals [13]. Chitosan is a linear polysaccharide that is composed of D-glucosamine and N-acetylglucosamine [14]. It is usually obtained by treating the shell of shrimp and crustacea with a sodium hydroxide base. Unlike celluloses, chitosan is a natural polymer flocculant that absorbs harmful substances that have negative ionic amino groups [15,16]. In addition, sericite, which is one of the clay minerals that are abundant and widely distributed in soil, is inexpensive. Also, hydroxyl groups are distributed on the surface, so that various pollutants can be easily adsorbed and removed [17]. The basic crystal structure of sericite, an aluminum silicate clay mineral with potassium as its main cation, is composed of three layers comprising two tetrahedral layers and one octahedral layer, and mainly contains K^+ and Mg^{2+} between the layers. The K^+ existing between the sericite layers has a cation exchange ability [2,18]. When Al^{3+} is substituted for Si^{4+}

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at the octahedral position, the cation binds to the electron, because it is electronegative [17]. Therefore, the surface of sericite will have (−) charge, and attracts ions having charges of opposite sign, resulting in various phenomena.

However, problems arise when using such a biomaterial sorbent, such as the separation of wastewater and the generation of secondary wastes [19]. When a single material is used, the removal efficiency of heavy metals or contaminants is low, due to diffusion limitation or the reduction of surface active sites [20]. In recent years, this process has been applied to the wastewater treatment field, by applying composite adsorbents combined with various natural material adsorbents [4,8]. These complex adsorbents have various electric charges, so that toxic heavy metals and nutrients can be adsorbed and removed at the same time, and a synergetic effect on the removal rate can be obtained [21]. In other words, tannin has a negative charge on the surface, because it contains OH- on the surface, while chitosan contains numerous amino groups, so the surface charge is positive [4]. In addition, sericite has many hydroxyl groups on its surface, and thus has a negative charge [2]. Therefore, the composite adsorbent, i.e., the microcapsules, is mixed with negatively charged tannins, clay minerals, and positively charged chitosan layers, which can strongly adsorb and remove the positively charged heavy metals. Pb(II) is a toxic heavy metal and the most abundant in industrial wastewater. The aim of this study was thus to remove Pb(II) using microcapsules, a natural composite adsorbent having many advantages. For this purpose, the removal efficiency of Pb(II) was investigated in terms of the initial concentration, pH, and temperature. In addition, the adsorption kinetics, adsorption isotherms, mass transfer, and internal particle diffusion were also determined using experimental data and thermodynamic analysis was carried out.

MATERIALS AND METHODS

1. Materials

The major components of the sericite are SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO; in particular, sericite contains about (68-80)% SiO_2 and Al_2O_3, depending on the production area of the sericite [2,17]. In this experiment, the sericite (Ohken Co., Ltd., Japan) used as clay mineral was in the form of 325 mesh powdered Sericite. The sericite powder was washed several times with distilled water, and then dried at 80 °C for 24 h to remove moisture. The dried sericite was stored in a desiccator for use in experiments.

The yield of tannin extracted from vegetable raw materials depends on the type and composition of the material, the time of extraction of the tannin, the temperature, the solid-liquid ratio, and the condition of the material. Among the various methods of extracting tannins from plant materials, they can be used as extraction solvents for compounds by exploiting the polar nature of water. In this study, tannins were extracted from chestnut shells. The chestnut shells were boiled at (50-110) °C for 8 h under constant pressure. The ratio of water to chestnut shell was (2-2.4) : 1. To prevent oxidation, the extracted tannin was completely evaporated under vacuum, and stored in a desiccator.

For the production of chitosan, crab shells were immersed in hydrochloric acid (HCl) (about 5%) for 24 h to remove the car-

bonic acid. After the carbonated crabs were removed, the crab shells were washed with distilled water, added to NaOH (5%) solution, and then boiled for 5 h to decompose the proteins. The crab shells were then washed again with distilled water, and the remaining pigment was decomposed with potassium permanganate to prepare chitin. Chitin is generally insoluble in organic acids or acidic solvents, which makes it difficult to use [22]. Therefore, to facilitate dissolution, chitosan was prepared. To make chitin as monomolecular as possible, it was added to 50% sodium hydroxide solution, and boiled at 80 °C for 7 h to remove the acetyl groups of chitin, to prepare chitosan. Pb (Pb $(NO_3)_2$; Duksan Pure Chem. Co. Ltd., Korea, purity ≥99%) was GR-grade and three-times distilled water were used to prepare the concentrations required for the experiments.

2. Tannin/Chitosan/Sericite Microcapsules Preparation

Microcapsules were prepared as follows. First, tannin and sericite were mixed at a ratio of 1 : 1 in dry weight. 1.50 g of tannin+sericite was added to 150 mL of the prepared chitosan solution, and the mixture was stirred at 22 °C for 3 h, until homogeneous. The chitosan+tannin+sericite mixture was transferred to a burette, and then dropped into alkaline coagulating mixture (mixture of 200 mL of water, 300 mL of methanol, and 60.0 g of NaOH), to prepare the microcapsules. The microcapsules contained in the coagulating mixture were incubated for 24 h in the incubator, until the coagulating mixture turned yellowish brown and completely gelated. The aged microcapsules were washed several times with distilled water, until the filtrate became neutral, and the yellowish-brown color disappeared. The wet microcapsules were filtered to remove the water, and were placed in a cross-linking agents (90 mL of methanol+0.9 mL of glutaraldehyde solution) to maintain the spherical morphology of the microcapsules, and refluxed at 70 °C for 6 h. Finally, the cross-linked microcapsules were recovered, washed with ethanol, and then washed several times with water to remove unreacted glutaraldehyde molecules. The prepared microcapsules were dried at room temperature for 5 h, and stored in a desiccator for use in experiments.

3. Experimental Design and Analytical Methods

Experiments were carried out in a batch-test. Tannin, chitosan, sericite, and microcapsules were added to 1 L of each heavy metal according to the experimental plan. The pH, initial concentration of heavy metals, contact time and temperature were controlled, and the mixture was stirred at 120 rpm. The heavy metals mixed with tannin, chitosan, sericite, and microcapsules were centrifuged at 2,500 rpm for 20 min, and the supernatant was sampled and filtered (0.45 μm, Whatman filter). The pH was adjusted to (2-7) using NaOH and HCl, and the temperature was controlled to (20-50) °C.

Qualitative and quantitative analysis of the inorganic components contained in tannin, chitosan, sericite, and microcapsules were performed using X-ray diffraction (XRD; XRF-1500, Shimadzu, Japan), while surface analysis was performed using scanning electron microscopy (SEM; SM-300, Topcon, Japan). The specific surface area, pore volume, and pore diameter of tannin, chitosan, sericite, and microcapsules 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). The particle size of sericite was measured using

a particle size analyzer (Laser Diffraction Master class 3 & 4, Malvern, England). The amounts of tannin, chitosan, sericite, and microcapsules were measured using an electronic balance (XP26, Mettler Toledo, Swiss). The pH was measured with a pH meter (SevenGO pro, Mettler Toledo), and the concentration of heavy metals in the solution was analyzed by atom absorption spectrometry (AAS). The experiment was repeated five times, and the average data were used. The adsorption amounts and removal efficiencies of the heavy metals adsorbed on tannin, chitosan, sericite, and microcapsules were calculated as follows:

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

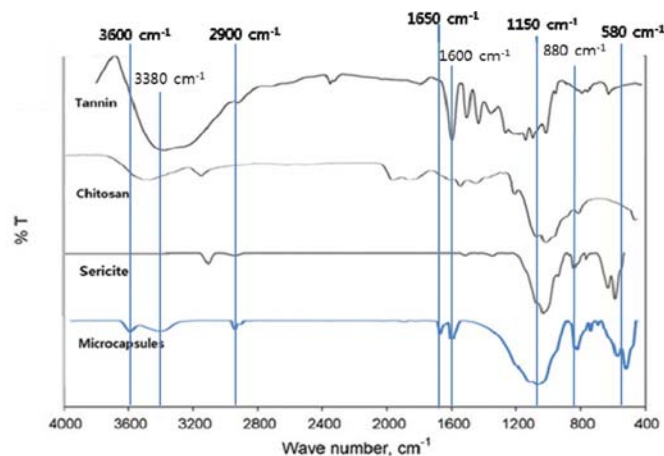$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

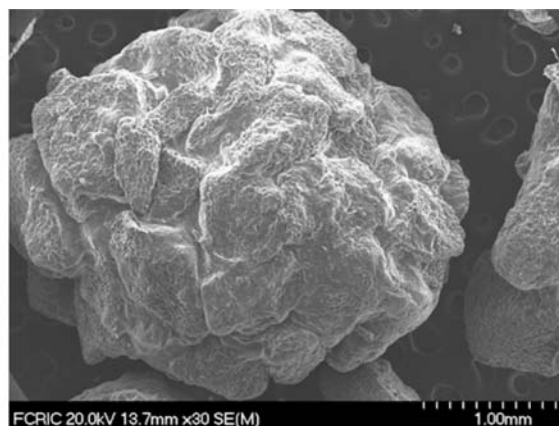## RESULTS AND DISCUSSION

1. Characterizations of Adsorbents
1-1. Characterizations of Sericite, Tannin, Chitosan, and Microcapsules

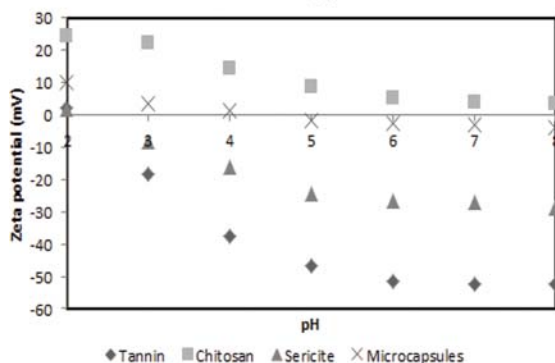Fig. 1(a) shows the results of the FT-IR analysis of tannin, chitosan, sericite, and microcapsules. The FT-IR spectra show many absorption peaks in accordance with the complex characteristics of the adsorbent, and the adsorbent can be analyzed through analysis of these peaks [1]. The adsorption of heavy metals by chitosan is mostly due to the use of amino groups, and most of the heavy metals adsorbed by tannin and sericite are due to hydroxyl groups. In the microcapsules, the peak between (400-800) cm^{-1} shows a large vibration, especially N-containing bioligands at (480-650) cm^{-1}. A peak near 800 cm^{-1} indicates C-H bending, and a broad peak near (1,000-1,300) cm^{-1} indicates a C-O stretch. The (1,500-1,600) cm^{-1} peak corresponds to the carboxylic groups and N-H bending, the (1,640-1,670) cm^{-1} peak refers to carboxylic groups, and the (1,680-1,740) cm^{-1} peak corresponds to the C=O carbonyl groups, presumably due to the lignin aromatics. In particular, the distinct peaks of (1,650 and 1,596) cm^{-1} correspond to amide N-C=O and aromatic C=C, respectively. The newly emerged (2,800-2,900) cm^{-1} peak represents C-H stretching, while that at (3,300-3,600) cm^{-1} represents bonded -OH groups. A peak near 3,400 cm^{-1} indicates the presence of free and intermolecularly bonded hydroxyl groups. The -OH stretching mode, carbonyl, and carboxylic groups, which are mainly found in microcapsules, are known to be directly involved in the adsorption of cationic nutrients and heavy metals. In particular, C-O stretching and C-H bending, which are shown as broad

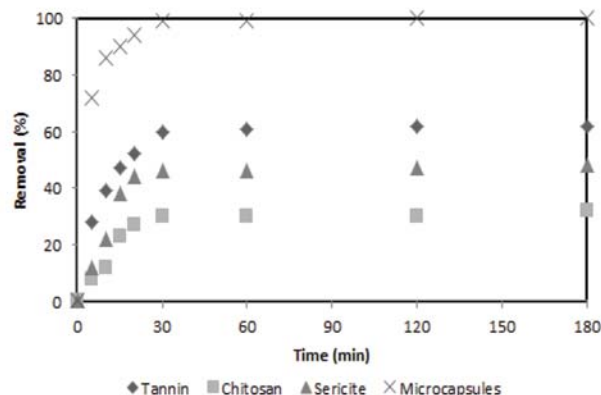Fig. 1. (a) FT-IR spectra of tannin, chitosan, sericite, and microcapsules. (b) A SEM image of microcapsules. (c) Zeta potential of tannin, chitosan, sericite, and microcapsules. (d) Removal of Pb(II) onto tannin, chitosan, sericite, and microcapsules.

and strong peaks, are believed to be involved in the adsorption of Pb(II) [23]. The results of the FT-IR analysis indicate that the mechanism of adsorption of cationic heavy metals by microcapsules may be surface adsorption, including physical processes, and ion exchange. That is, possible adsorption with such an adsorbent may be due to physical adsorption, complex formation with functional groups, ion exchange, surface precipitation, and chemical reaction with the surface region. An SEM image of the microcapsule is depicted in Fig. 1(b). It can be seen that the microcapsules contain many pores. Many of the pores contained in microcapsule are to help the adsorption of heavy metals in the aqueous solution.

Fig. 1(c) shows the change of zeta potential according to the pH of tannin, chitosan, sericite, and microcapsules. It is generally reported that the adsorption power is best when the zeta potential of the adsorbent is ±10 [24]. If the adsorbent in the aqueous solution has a large negative charge, or a zeta potential with a large positive charge, the adsorbent will have a repulsive force to lower the adsorption power [25]. However, when the zeta potential is low, the particles will not have a repulsive force, and the adsorption power increases [7,26]. According to the zeta potential analysis, the surface charge of tannin and sericite was negative, and the negative charge became stronger with increasing pH. Chitosan showed a positive zeta potential at low pH, but decreased to less than +10 as pH became neutral. In contrast, the zeta potential of the microcapsules, which are complex adsorbents, showed ±10 within the pH values of between (2 and 8). In particular, at pH (5 and above), the zeta potential of the microcapsules showed from -1.58 to -3.89 mV, indicating optimum zeta potential for the removal of cationic heavy metals and toxic substances.

1-2. Removal of Pb(II) Using Various Materials

Tannin, sericite, and chitosan reached (61, 46, and 30)% of Pb(II) removal efficiency in 60 min, respectively (Fig. 1(d)). However, the microcapsule showed 99% of Pb(II) removal efficiency in 30 min, and reached the equilibrium of removal efficiency faster than that of tannin, sericite, and chitosan. According to the FT-IR analysis of tannins, chitosan, sericite, and microcapsules, the functional groups of each adsorbent vary, and the number of active surfaces and charges on the surface differ. The hydroxyl, carboxyl, carbonyl, and amino groups of adsorbents play an important role in heavy metal adsorption [27]. The presence of these functional groups means that the adsorbent exchanges hydrogen ions with metal ions or a pair of electrons forms a complex with the metal ion, allowing it to bind with heavy metals [28]. However, the presence of these functional groups on the surface of the adsorbent does not guarantee effective removal of heavy metals, because the adsorption of heavy metals is affected by a number of complex factors, such as the number of active surfaces, the possibility of adsorbed material accessibility on the adsorbent surface, the chemical state of the adsorbent surface, and the affinity of the adsorbent surface with the metal ion to be adsorbed [18].

2. Parametric Studies of Microcapsules

2-1. Effect of pH

The pH is an important factor in determining the dissolution profile of metals in aqueous solutions. Since the size and sign of the charge varies depending on the dissolved metal ion, the pH affects the adsorption process of the metal ion [19]. The pH of the medium

has a considerable influence on the adsorption process because the hydrogen ion itself is strongly competitive with the cationic heavy metals and the chemical differentiation of the metal ions under the influence of the solution pH [29]. The adsorption of metal ions depends on the characteristics of the adsorbent surface and the species distribution of metal ions in the aqueous solution [5]. The hydrolyzed Pb(II) exists in various concentrations, depending on the concentration of Pb(II) and the solution pH [30]. To determine the effect of pH on the removal of Pb(II), pH was controlled to (2-7), using NaOH and HCl. The concentration of Pb(II) was fixed at 10 mg/L, and the quantity of microcapsules was fixed at 1 g/L. According to the experimental results, the removal process of Pb(II) was influenced by pH, and Fig. 2(a) shows the results. The adsorption capacity of microcapsules increased with increasing pH. They
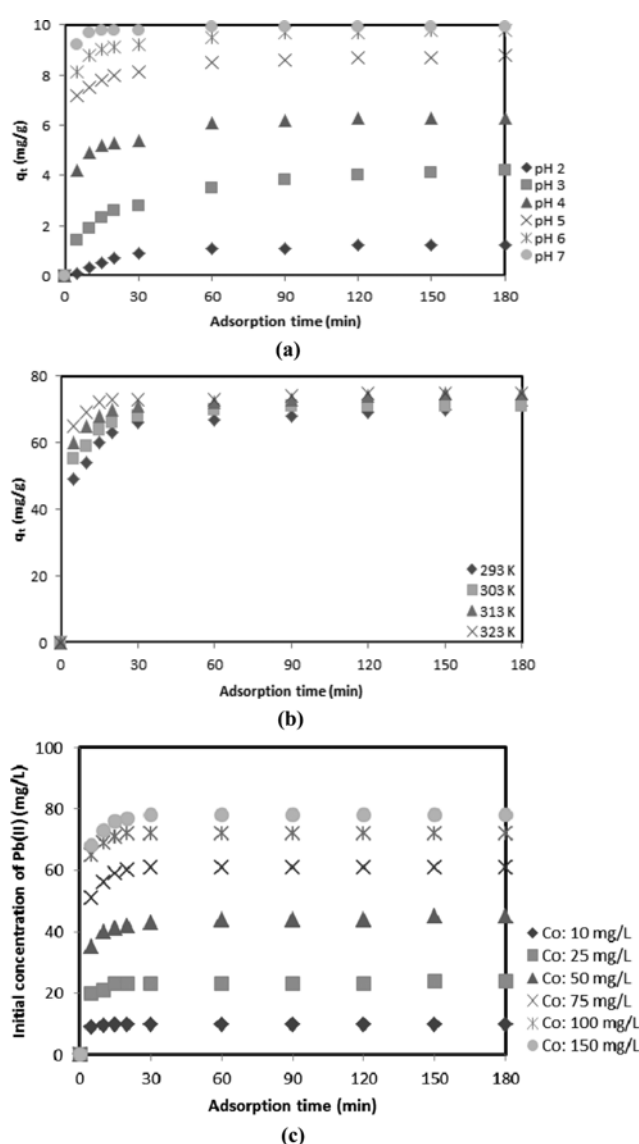

Fig. 2. (a) Effect of pH for Pb(II) uptake onto microcapsules. (b) Influence of temperature for Pb(II) uptake onto microcapsules. (c) Influence of initial concentration for Pb(II) uptake onto microcapsules (C_o: 10 mg/L, T: 293 K, pH 6, and adsorbent dose: 1 g/L).

showed 100% removal efficiency at pH 6 or higher, and little change was observed in removal efficiency. This was dominated by positively charged Pb(II) species at low pH (<4). However, at high pH values (pH=(6-11)), various types of lead were found with different charges, such as Pb(OH)$^+$ and Pb(OH)$_2$ [1]. As the pH increased, the quantity of H$^+$ ions decreased and the quantity of OH$^-$ ions increased, while the metal cations were adsorbed and removed by electrostatic attraction on the surface of the microcapsules [1]. A zeta potential from 0 to ±5 mV indicates rapid adsorption/coagulation [2,25]. A similar tendency can be seen in experiments in which tannins are modified to remove Pb(II). Yursever and Sengil [31] reported very low Pb(II) removal efficiency due to strong repulsion between cationic factors at low pH (below 4), but the electrostatic repulsion between particles decreased remarkably at pH>6, and a high removal of Pb(II) ion was obtained.

2-2. Effect of Temperature

Changes in the aqueous solution temperature affect not only the diffusion rate of heavy metal ions, but also the solubility of heavy metal ions [1]. Depending on the functional groups on the surface of the adsorbent, the temperature has a considerable effect on the adsorption efficiency [32]. However, many studies have concluded that the effect of this temperature is only observed within a limited specific temperature range [4]. The adsorption process of heavy metals in the adsorbent is divided into an exothermic reaction and an endothermic reaction, depending on the temperature [25]. Generally, as the temperature increases, the adsorption rate increases, to become endothermic. In contrast, when the adsorption rate decreases as the temperature increases, it is exothermic [1]. In this experiment on the adsorption of Pb(II) using microcapsules, as the temperature increased, the adsorption rate slightly increased, indicating that an endothermic reaction had occurred (Fig. 2(b)). This suggests that as the temperature increases, the removal of Pb(II) may be enhanced by increasing the activity of the microcapsule surface, and increasing the kinetic energy, or decreasing the thickness of the microcapsule boundary layer.

Similar results have been reported by García-Rosales and Colin-Cruz [20]; the removal efficiency of Pb(II) from corn sponges increased by (1-1.8)-times as the temperature increased from (20 to 40) °C. On the other hand, El-Sayed and Nada [33] reported that the removal efficiency of Pb(II) was reduced from (52 to 28)% as the temperature of the aqueous solution increased from (25 to 55) °C. The adsorption state can be changed depending on the active state of the adsorbent, the pH of the aqueous solution, or the competitive adsorption effect of other heavy metals, when adsorbing heavy metals using various adsorbents [16]. In this experiment, the adsorption efficiency of Pb(II) by microcapsules increased rapidly with increasing temperature, but after 30 min of adsorption, the removal efficiency of Pb(II) by temperature did not show any difference. In general, it is important to show the optimum adsorption efficiency at room temperature, because the physical damage or properties of the adsorbent can change at high temperatures.

2-3. Effect of Initial Metal Concentration

The initial concentration of metal ions in the solution plays an important role in overcoming the mass transfer resistance between the aqueous solution and the adsorbent (solid) phase [34]. Pb(II) was varied from (10 to 150) mg/L to investigate the effect of the ini-

tial concentration of heavy metals on the adsorption efficiency, at pH 6, temperature 293 K, and the quantity of microcapsule fixed at 1 g/L. Fig. 2(c) shows the effect of Pb(II) on the initial adsorption efficiency. As the initial concentration increased from (10 to 150) mg/L, the adsorption amount increased from (9.9 to 78) mg/L, but the adsorption efficiency of Pb(II) decreased from (99 to 52)%. This may be because the adsorption surface reached saturation as the initial concentration of Pb(II) increased, and the driving force to the adsorbent surface decreased, due to mass transfer resistance. In similar studies, Yustsever and Sengil [31] reported that the removal efficiency of Pb(II) using tannin decreased with increasing of initial concentration. To overcome this problem, a new method is needed to overcome the mass transfer resistance at high concentrations. Experiments on the optimum adsorption time indicate the rate at which the adsorption of heavy metals reaches equilibrium, which is an important factor in designing the adsorption process.

Experimental results showed that there was almost no change in the adsorption amount after 30 min, regardless of the initial concentration of Pb(II). Therefore, it can be seen that the adsorption equilibrium was reached after 30 min (Fig. 2(c)). The Pb(II) heavy metal content of general industrial wastewater was less than 10 mg/L. It is very efficient to remove 99% of Pb(II) of less than 10 mg/L contained in general industrial wastewater by using microcapsules.

3. Kinetic Studies

Adsorption kinetics can be used to determine the adsorption rate, adsorption mechanism, and associated rate limiting steps [2]. To further understand the adsorption process of Pb (II) in microcapsules, the experimental results were applied to pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. The correlation coefficient (R^2) of Pb (II) removal using microcapsules was measured from (0.723 to 0.942) for pseudo-first order and (0.9900 to 1.0000) for pseudo-second order, based on various concentrations of Pb(II). However, the correlation coefficient of the intraparticle diffusion model is (0.6795 to 0.9012), which is significantly lower than that of the pseudo-first-order and pseudo-second order, indicating that diffusion inside the particle is not a speed-limiting step in the adsorption process. Pseudo-first-order adsorption is controlled by diffusion and mass transfer of adsorbate to the adsorption site, whereas in the pseudo-second-order model, chemical adsorption is the rate-limiting step [22]. Moreover, the intraparticle diffusion model suggests that the diffusion inside the particle is the rate-limiting step [35]. The adsorption rate constant of the pseudo-second order (k^2) decreased with the increasing amount of Pb(II). This means that the reaction rate gradually decreased with increasing Pb(II) concentration. In general, the adsorption process consists of a complex mechanism of external mass transfer and internal particle diffusion [36]. Even though the concentration of the surface particles is kept constant, the concentration distribution changes as the particles diffuse into the inside, and the diffusion coefficient changes, depending on the type of substance and particle [3].

It can be seen that the internal particle diffusion rate constant (k_{id} (mg/g·min$^{1/2}$) increased from (0.0542 to 1.4567), as the concentration of Pb(II) increased from (10 to 150) mg/L. It was found that the internal diffusion rate of the adsorbent increased with increasing Pb(II) concentration. The Elovich equation is suitable for

Table 1. Textural properties of sericite, tannin, chitosan and microcapsules

Materials	BET specific surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	CEC (meq/g)	pH$_{PZC}$
Sericite	11.45	3.45	3.48	1.87	2
Tannin	17.05	3.62	3.67	2.16	2
Chitosan	11.20	3.7	67.04	3.24	-
Microcapsules	28.65	4.01	68.26	4.53	4.5

Table 2. Kinetic, isotherm and thermodynamic parameters for the Pb(II) onto microcapsules

Kinetic parameters

Initial concentration	q$_e$ (mg/g)	Pseudo-first-order $\ln(q_e-q_t)=\ln q_e-k_1 t$		Pseudo-second-order $\dfrac{t}{q_t}=\dfrac{1}{k_2 q_e^2}+\dfrac{1}{q_e}t$		Elovich $q_t=\dfrac{1}{\beta}\ln(\alpha\beta)+\dfrac{1}{\beta}\ln t$			Intra-particle diffusion $q_t=k_i t^{1/2}$	
		k$_1$	R^2	k$_2$	R^2	α	β	R^2	K$_i$	R^2
10	9.978	0.0281	0.942	0.3138	0.9987	3.25E+15	3.7856	0.8972	0.0542	0.8356
25	24.623	0.0254	0.859	0.1831	1.0000	4.63E+17	3.9642	0.9768	0.0578	0.9012
50	45.269	0.0194	0.809	0.0232	0.9998	1.89E+08	0.7862	0.8752	0.7265	0.7546
75	61.645	0.0236	0.928	0.0128	0.9997	3.23E+03	0.3045	0.9634	1.6458	0.7782
100	72.561	0.0211	0.782	0.0087	0.9996	3.15E+04	0.3371	0.9182	1.6027	0.7716
150	78.346	0.0207	0.723	0.0064	1.0000	2.23E+05	0.3423	0.8982	1.4567	0.6795

Parameters of isotherm constants

Adsorbents	Langmuir $\dfrac{C_e}{q_e}=\dfrac{1}{K_L q_m}+\dfrac{C_e}{q_m}$				Freundlich $\ln q_e=\dfrac{1}{n}\ln C_e+\ln K_F$			Tempkin $q_e=B\ln A+B\ln C_e$		
	K$_L$	q$_m$	Q$_0$	R^2	K$_F$	n	R^2	B	A	R^2
Pb(II)	34.403	0.205	167.82	0.9994	35.316	3.306	0.828	14.834	6.685	0.9419

Thermodynamic parameters

ΔH^o (kJ/mol)	ΔS^o (J/mol·K)	ΔG^o (kJ/mol)$=\Delta H^o-T\Delta S^o$			
		293 K	303 K	313 K	323 K
29.83	114.18	−3.62	−4.73	−5.98	−7.02

K$_F$ and n can be determined from the linear plot of lnq$_e$ vs. lnC$_e$. A plot of q$_e$ versus lnC$_e$ enables the determination of the constants A and B

systems with nonuniform adsorption surfaces [14]. The initial adsorption rate, α, decreased as the initial concentration of Pb(II) increased, and the β values related to the range of surface coverage and activation energy for chemical adsorption also increased as the initial Pb(II) concentration increased, respectively. As a result of this experiment, the Pb(II) adsorbed and removed using microcapsule pseudo-second-order adsorption was more suitable than the pseudo-first-order adsorption, and chemical adsorption did not limit the adsorption rate of Pb(II) ion.

4. Isotherm Studies

The Langmuir isothermal adsorption model is based on single layer adsorption on a homogeneous surface on homogeneously dispersed adsorption sites, and the Freundlich isotherm adsorption model is utilized to understand the adsorption on heterogeneous surfaces with multiple adsorption layers [34]. The Temkin isothermal adsorption model assumes linearity instead of reducing the heat of adsorption, ignoring very low and very high concentrations [37]. This model also assumes a uniform distribution of boundary energy,

up to the maximum binding energy. The obtained correlation coefficient (R^2) of Pb(II) removal using microcapsules was 0.9993 for Langmuir and 0.8863 for Freundlich. The adsorption removal of Pb(II) using microcapsules was more suitable for Langmuir isothermal adsorption than the Freundlich model (Table 2). The Langmuir constant K$_L$ was 34.403 L/g, and the q$_m$ was 0.205 (L/mg). The maximum adsorption amount of Langmuir was 167.82 (mg/g). In the Freundlich isothermal adsorption equation, the function 1/n indicating the adsorption strength between adsorbent and adsorbate was 0.302 and the K$_F$ value was found to be as high as 35.316 (L/g). This indicates that the adsorption strength of microcapsules and Pb(II) is very high, and the adsorption affinity is good. The interaction between the adsorbent and the adsorbent can be determined using the Temkin isothermal adsorption equation. The Temkin isotherm constants B and A obtained by the slope of q$_e$ and lnC$_e$ were 6.685 (L/g) and 14.834, respectively, and the correlation coefficient was high, indicating that the indirect interaction of Pb(II) with microcapsule was very high.

Table 3. Comparison of the Langmuir adsorption capacity for Pb(II) with various adsorbents

Adsorbent	Adsorption capacity of Pb(II) ions (mg/g)	Conditions	Reference
Sericite	4.70	pH (5.5-5.8), 298 K	[18]
Kaolinite	2.35	pH 6, 303 K	[34]
Activated bentonite	6.54	pH 5, 293 K	[28]
Chitosan bead	100.00	pH 5, 303K	[30]
Aliquat 336 functionalized chitosan	143.30	pH 5, 298 K	[14]
Chitosan nanofibril	118.00	pH 6, 303 K	[35]
Chitosan-4-(pyridin-2-ylimino methyl) benzaldehyde	104.16	pH 6, 323 K	[38]
EGTA-modified Chitosan	103.60	pH 6, 313 K	[39]
Mimosa Tannin	13.81	pH 6, 298 K	[36]
Modified quebracho tannin resin	86.94	pH 5, 296 K	[31]
Tannin-nanocellulose composite	49.53	pH 6, 293 K	[13]
Condensed Wattle tannin	114.9	pH 4.2, 298 K	[10]
Modified rubber leaf powder	109.95	pH 5	[37]
Microcapsules	167.82	pH 6, 293 K	Present study

Table 3 shows the maximum absorption capacity of the Langmuir model using various adsorbents. In general, the adsorption capacity of the modified adsorbents was (3-9)-times higher than that of the unmodified adsorbents, and the hybrid adsorbent had a higher adsorption capacity than the single adsorbent [22]. The hybrid adsorbent, the microcapsules, showed a higher adsorption capacity of Pb(II) than did the unmodified clay minerals or modified tannins and chitosan. This is because tannin, clay minerals, and chitosan are integrated to produce a synergistic effect on the adsorption of heavy metals, thereby increasing the adsorption capacity.

5. Thermodynamic Studies

The effects of various temperatures, 298, 308, and 318 K by Pb(II) adsorption onto microcapsules were analyzed based on the thermodynamic parameters of Gibbs, and Table 2 shows the results. The value of ΔG decreased with increasing temperature, indicating that it was a spontaneous endothermic process [5]. Also, the decrease in ΔG with increasing temperature was more effective at an adsorption at higher temperatures than at lower temperatures [25]. The enthalpy (ΔH) and the entropy (ΔS) were positive, and were 29.83 kJ/mol and 114.18 J/mol·K, respectively. The positive value of ΔH indicates an endothermic reaction. Moreover, due to the adsorption removal of Pb(II) by microcapsules, ΔH was found to be less than 40 kJ/mol, which was a physical reaction, rather than a chemical reaction. In addition, the positive value ΔS indicates a high affinity between microcapsules and Pb(II) during the adsorption process, and increased randomness of adsorption.

6. Desorption and Reusability

Finding inexpensive and efficient adsorbent treatment eluents for reuse of adsorbents is economically very important. In this study, we investigated the desorption and reuse of microcapsules using HCl and NaOH, in order to find an inexpensive and effective solution. Desorption experiments were carried out by varying the concentrations of HCl and NaOH from (0 to 0.2) mol/L. Experimental results show that the desorption efficiency of Pb(II) was 73.56% by 0.05 mol/L NaOH, and 54.26% by 0.05 mol/L of HCl in 2 h contact time. The desorption efficiency of Pb(II) using HCl was lower than that of NaOH (Fig. 3(a)). In general, compounds tend to produce
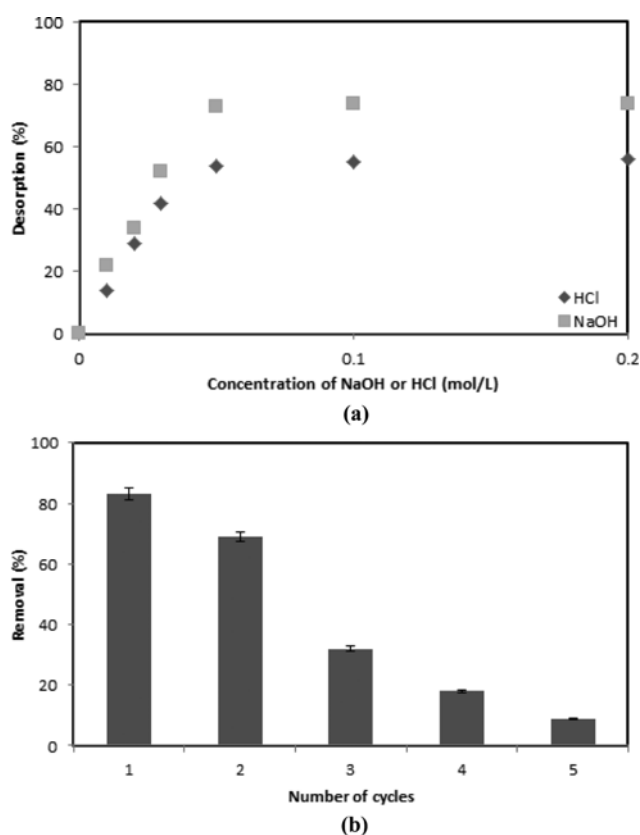

Fig. 3. (a) Desorption of Pb(II) from NaOH or HCl. (b) Percentage removal of Pb(II) in sequential adsorption-desorption.

more stable materials, and under desorption conditions with NaOH, OH⁻ easily bonds ≡M- to $HPbO_4^-$ in the ligand exchange reaction [1,40]. That is, OH- has a higher desorption efficiency than HCl, because NaOH behaves similarly to $HPbO_4^-$ in alkaline conditions, and forms stronger and more stable forms with the hydroxyl groups of Fe^{2+} and Al^{3+} [23].

The desorption efficiency of Pb(II) was 74.68% by 0.2 mol/L

NaOH concentration and 56.33% by 0.2 mol/L HCl, and Pb(II) did not significantly differ from that of 0.05 mol/L concentration. Therefore, for the reuse of microcapsules and desorption of adsorbed Pb(II), we recommend 0.05 mol/L of NaOH, rather than HCl. Fig. 3(b) shows the results of the reuse experiment for the Pb(II) adsorption of microcapsules regenerated with 0.05 mol/L NaOH. The removal efficiency of Pb(II) decreased as the adsorption-desorption cycle was repeated. In addition, Pb(II) showed about 69% removal efficiency, when second adsorption-desorption cycles were repeated. As the adsorption-desorption cycle was repeated, the removal efficiency decreased significantly, showing a very low removal efficiency of 18% in the fourth adsorption-desorption, and 9% in the fifth adsorption-desorption cycle. Therefore, it is considered that Pb(II) can be reused as adsorbent up to two-times by using microcapsules as an adsorbent. Microcapsules used as heavy metal adsorption in aqueous solution can be reused after drying at 80 °C and washing with 0.05 mol/L NaOH, and the recovered heavy metals can be reused, which is very economical. Tannins from plants can be extracted very easily, and the produced tannins are (2-8) USD/ton, depending on the type of raw materials extracted, while chitosan is (1-10) USD/ton, depending on the molecular weight. Sericite is a clay mineral that is easily available, and the price is also very cheap. Therefore, microcapsules, which are a mixture of tannin, chitosan, and sericite, are much less expensive than activated carbon, and can be used as a high efficiency adsorbent in small amounts. In addition, microcapsules can easily be applied to a sewage plant.

CONCLUSIONS

Microcapsules were prepared by mixing sericite, chitosan, and tannin in an optimum ratio, which is inexpensive, efficient, and environmentally friendly, and were then applied to remove Pb(II) from the aqueous solution. The FT-IR analysis showed that the microcapsules contain hydroxyl, carboxyl, carbonyl, and amino groups, which plays an important role in the adsorption of heavy metals. The removal efficiency of Pb(II) was higher at a higher pH (above 6) than at a lower pH. The microcapsules were able to remove 99% of Pb(II) in 30 min, and obtained a removal efficiency of more than (13-50)%, compared with the single adsorbents of tannin, chitosan, and sericite. In adsorption kinetic analysis, pseudo-second-order adsorption was more suitable than pseudo-first-order adsorption, and chemical adsorption did not limit the adsorption rate of Pb(II) ion. In isothermal adsorption, Langmuir adsorption was more suitable than Freundlich adsorption, and the maximum Langmuir adsorption capacity was 167.82 (mg/g). In thermodynamic analysis, ΔH and ΔS showed positive values, indicating that the adsorption process was endothermic. In addition, ΔH was 29.83 kJ/mol, and the adsorption process with Pb(II) removal using microcapsules was physical adsorption. Moreover, the decrease of ΔG due to the increase of temperature was more effective at higher temperatures than at lower temperatures, and was a spontaneous endothermic process with a negative value. For the desorption of adsorbed Pb(II) for the reuse of microcapsules, the use of 0.05 mol/L NaOH, rather than HCl, is recommended. Microcapsules, a mixture of tannin/chitosan/sericite, are much less expensive than acti-

vated carbon, are environmentally friendly, and can be used as high-efficiency sorbents in small quantities. In addition, the difference compared to the conventional single-charge adsorbent is that microcapsules have a variety of charges. These hybrid adsorbents have the advantage of being able to simultaneously remove various heavy metals and nutrients very efficiently by applying them to the actual industrial wastewater or polluted water in a field of various electric charges.

NOTES

The authors declare no competing financial interest.

NOMENCLATURE

A : Temkin isotherm constant
B : 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]
ΔG^o : Gibbs free energy [kJ/mol]
ΔH^o : 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_i : intra-particle diffusion rate constant [mg/gh$^{0.5}$]
k_L : Langmuir constant [L/g]
k_F : Freundlich constants referring to the adsorption capacity [mg/g]
M : amount of adsorbent [mg]
n : Freundlich isotherm constants, intensity of sorption [(mg/g)/(mg/L)$^{1/n}$]
Q_0 : Theoretical monolayer capacity [mg/g] $Q_0 = K_L/q_m$
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]
R : Removal [%]
R : ideal gas constant, 8.314 [J/mol/K]
R^2 : correlation coefficient
ΔS^o : entropy [J/mol·K]
t : time [min]
T : absolute temperature [K]
V : the volume of solution [L]
α : Elovich constant which gives an idea of the adsorption rate constant [mg/g·min]
β : Elovich constants and represents the rate of chemisorption

at zero coverage [g/mg]

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