Applicability of Composite Beads, Spent Coffee Grounds/Chitosan, for the Adsorptive Removal of Pb(II) from Aqueous Solutions

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Abstract

An experiment was conducted to evaluate the adsorptive removal of Pb(II) from an aqueous solution using a mixture of spent coffee grounds and chitosan on beads (CC-beads). Various parameters affecting the adsorption process of Pb(II) using CC-beads were investigated. Based on the experimental data, the adsorption kinetics and adsorption isotherms were analyzed for their adsorption rate, maximum adsorption capacity, adsorption energy and adsorption strength. Moreover, the entropy, enthalpy and free energy were also calculated by thermodynamic analysis. According to the FT-IR analysis, a CC-bead has a very suitable structure for easy heavy metal adsorption. The process of adsorbing Pb(II) using CC-beads was suitable for pseudo-second order kinetic and Langmuir model, with a maximum adsorption capacity of 163.51 (mg/g). The adsorption of Pb(II) using CC-beads was closer to chemical adsorption than physical adsorption. In addition, the adsorption of Pb(II) on CC-beads was exothermic and spontaneous in nature. CC-beads are economical because they are inexpensive and also the waste can be recycled, which is very significant in terms of the continuous circulation of resources. Thus, CC-beads can compete with other adsorbents.

Keywords: Adsorption, Chitosan, Spent coffee grounds, Hybrid bead, Heavy metal, Lead

1. Introduction

Many heavy metals released from industrial processes have an adverse effect on ecosystems and living organisms, so there is no dispute that they must be removed[1]. Therefore, various studies on removing harmful heavy metals by using various methods have been continuously conducted[2]. Among the various methods studied so far, the adsorption method is one of the most widely used methods for wastewater treatment because it is relatively inexpensive, applicable to a wide range of pollutant removals and has a high efficiency[3]. A variety of adsorbents have been developed using the advantages of this adsorption method; although some adsorbents have been shown to be efficient, they are not expensive or environmentally friendly and have a limited range of applications[4]. Thus, the industry is constantly demanding less expensive and more environmentally friendly materials for a broader range of adsorbents. In response to these industry demands, researchers are continuing to research new, low-cost, high-efficiency, environmentally friendly adsorbents. Currently, activated carbon, zeolite, etc., are the main adsorbents materials; however, new adsorbents have been recently developed using inexpensive and environmentally friendly biomaterials[5]. In particular, in order to simulta-

neously adsorb various heavy metals contained in wastewater, studies on composite adsorbents containing various functional groups are actively being conducted[6]. Therefore, this study was conducted to remove heavy metals in aqueous solutions by using composite beads prepared by mixing spent coffee grounds (SCG) and chitosan. It is expected that the various functional groups of SCG and chitosan will be very helpful in removing heavy metals in aqueous solution.

Coffee is now one of the most consumed beverages in the world. Coffee beans are mainly grown in over 70 countries in equatorial Latin America, Southeast Asia and Africa, and green coffee beans (green beans before roasting) are one of the most traded agricultural products in the world[7]. The coffee industry has expanded rapidly since 2000[8]. In 2016, worldwide coffee production was approximately 8.6 million ton/year, of which Brazil produced 30.16% (2.59 million ton/year) and Vietnam produced 19.18% (1.65 million ton/year)[7,9]. As coffee consumption increases, SCG also increases. SCG are the fine powder left behind after making coffee, which contain a high humidity (80~85%), organic load and acidity[7,10]. Approximately 60% of the world's coffee is made from soluble coffee, resulting in an enormous amount of SCG of approximately 6 million tons per year[11]. SCG are being used in the production of biodiesel, fuel pellets and compost, as well as animal feed[7]. SCG are small particles (> 20 mm) of organic material composed of fibers (> 50%) and complex lignin structures with a large surface area[12]. SCG also contain an embedded tannin material that provides a polyhydroxy-polyphenol functional group that is suitable for heavy metal adsorption[11,13]. Chitosan is a natural cationic polysaccharide that is obtained via alkaline N-deacetylation of chitin, which

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can be extracted from the shells of shrimp, crab and shellfish[14]. The matrix structure of this natural polymer contains many amine (-NH$_2$) and hydroxyl (-OH) functional groups[15]. Thus, chitosan can easily adsorb heavy metal ions in an aqueous solution.

The adsorption of heavy metals using biomaterials is environmentally friendly and has the advantage of a low cost of adsorbent[6]. However, since the adsorption amount of heavy metals is low and post-treatment is required after the adsorption step, it is not widely used in the wastewater treatment field[5,16]. Therefore, in order to compensate for the various disadvantages of the adsorption of heavy metals using biomaterials, this study has made hybrid adsorbents using SCG and chitosan, and applied Pb(II), which is widely used in industrial processes, to be removed from aqueous solution. Moreover, to the best of our knowledge, this is the first study that reports on the preparation of SCG and chitosan composite beads (CC-bead) for the adsorption of heavy metals. The experimental results were analyzed via adsorption kinetics and adsorption isotherms, and thermodynamic analyses were conducted through an adsorption experiments with temperature changes.

2. Materials and Methods

2.1. Adsorbent and adsorbate

The SCG were collected at the coffee shop of company 'A' in Korea. The SCG were washed several times with distilled water to remove any contaminants. The washed SCG were then placed in a large porcelain dish and dried in an oven at 80 ℃ for 48 h. The dried SCG were then pulverized using mixer and sieved. Only particles smaller than 150 mesh (0.104 mm) were used. This is because the smaller the particle size, the larger the specific surface area of the adsorbent. Additionally, the smaller particle size, the easier it is to form the hybrid adsorbent with chitosan and spherical particles[1]. Chitosan is a linear amino polysaccharide consisting of approximately 20% β 1, 4-linked N-acetyl-D-glucosamine (GlcNAc) and approximately 80% β 1, 4-linked D-glucosamine (GlcN). It is prepared by partial deacetylation of chitin in hot alkali[14]. In this experiment, chitosan extracted from crab shell (Sigma Aldrich, Japan) was used.

The composite CC-beads were prepared by mixing SCG and chitosan as follows. Approximately 2.0 g of chitosan was dissolved in 50 mL of a 5% (v/v) acetic acid solution and allowed to stand overnight to form a yellow viscous chitosan acetate solution. The CC-beads were prepared by mixing 3.0 g of SCG in 50 mL of chitosan-containing acetate solution and stirring at 24 ℃ for 5 h until the mixture became homogeneous. The SCG and chitosan mixture was transferred to a pipette and dropped into a coagulant solution to prepare the spherical beads. The CC-beads in the clotting solution were then incubated until the clotting solution turned yellowish brown. The fully gelled CC-beads were washed several times with distilled water until the yellowish brown color of the coagulation solution disappeared. The dehydrated CC-beads were then placed in a cross-linking reaction and refluxed at 70 ℃ for 6 h to maintain their morphology spherically. Finally, the crosslinked CC-beads were recovered, washed with ethanol, and then washed several times with distilled water to remove any remaining glu-

taraldehyde molecules. The prepared CC-beads were dried at 35 ℃ for 5 h and stored in a desiccator for experiments. The Pb(II) selected as heavy metal solution was GR grade Pb(NO$_3$)$_2$ (Duksan Pure Chem., Co. Ltd. Korea, purity $\geq$ 99%). Pb(II) was prepared at a concentration of 1,000 mg/L, diluted with distilled water, and used as a solution at the required concentration.

2.2. Experimental design and analytical methods

The experiment was conducted in a batch-test. An amount of CC-beads was added to a 1 L aqueous solution containing Pb(II) according to the experimental plan. The experimental conditions for the various parameters were pH 3~10, initial concentration 1~500 mg/L of Pb(II), contact time 0~60 min, amount of adsorbent 0.1~3 g/L and temperature 25~55 ℃, which were controlled according to the experimental design and then sampled at a predetermined time while stirring at 120 rpm using a multi-magnetic stirrer. The collected samples were filtered using a 0.45 μm (Whatman filter), and the amount of heavy metals was measured using ICP-MS (inductively coupled plasma with mass spectrometer, Perkin Elmer, NexloN 2000). The pH was adjusted with NaOH and HCl, and the temperature was controlled using a thermostat of a multi-magnetic stirrer. All experiments were fixed with one parameter in order to test one parameter. The weight of samples was measured with an electronic balance (XP26, Mettler Toledo, Swiss) and the pH was measured with a pH meter (SevenGO pro, Mettler Toledo).

The molecular structure and composition of the sample's surface were analyzed via FT-IR (Jasco, FT-IR 4100). BET (Brynauer-Emmett-Teller) was analyzed using a nonsurface analyzer (Model ASAP, 2020). The particle size of the SCG was measured with a particle size analyzer (Laser Diffraction Master Class 3 & 4, Malvern, England) and the CEC (cation exchange capacity) of the samples was measured using the Kjeldahl method. The amount and efficiency of the Pb(II) adsorption onto the CC-beads were calculated using Equations 1 and 2[1].

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

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

Table 1 summarizes the models used for adsorption kinetics, adsorption isotherms, and thermodynamic interpretations.

3. Result and Discussions

3.1. Characteristics of the hybrid bead

The adsorption process contains all the processes that take place with the interaction of the adsorbate with the adsorbent on the surface of the adsorbent[16]. The adsorption capacity of the adsorbent depends on the physicochemical properties of the adsorbent, the chemical characteristics of the adsorbent, the experimental conditions, and the affinity between the adsorbent and the adsorbate[26]. Among them, the

Table 1. Adsorption Isotherms, Kinetic Models and Thermodynamic Models[5,11,18-24]

Isotherms	Nonlinear form	linear form	Plot	Reference
Langmuir	$q_e = \dfrac{q_m k_l C_e}{1 + k_L C_e}$	$\dfrac{C_e}{q_e} = \dfrac{C_e}{q_m} + \dfrac{1}{q_m k_L}$	$\dfrac{C_e}{q_e}$ vs C_e	[18]
Freundlich	$q_e = k_F C_e^{1/n}$	$\log q_e = \log k_F + \dfrac{1}{n} log C_e$	$\log q_e$ vs $\log C_e$	[19]
Tempkin	$q_e = B\ln(A) C_e$	$q_e = B\ln(A) + B\ln C_e$	q_e vs $\ln C_e$	[20]
Dabinin-Radushkevich	$q_e = q_0 \exp(-\beta \epsilon^2)$	$\ln q_e = \ln q_0 - \beta \epsilon^2$	$\ln q_e$ vs ϵ^2	[21]

Kinetic order	Equations	Straight line plot	
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \left(\dfrac{k_1}{2.303}\right)t$	$\log(q_e - q_t)$ vs t	[22]
Pseudo-second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{t}{q_e}$	$\dfrac{t}{q_t}$ vs t	[22]
Elovich	$q_t = \beta \ln(\alpha\beta) - \ln t$	q_t vs $\ln t$	[23]
Intraparticle diffusion	$q_t = k_{id} t^{1/2} + C$	q_t vs $t^{1/2}$	[24]

Thermodynamic		
$\triangle G = \triangle H - T\triangle S = -RT\ln K_c$ $\ln K_c = -\dfrac{\triangle H}{RT} + \dfrac{\triangle S}{R}$		[25]

* Nomenclature

A: Tempkin constant (L/g), B: Tempkin constant (J/mol). The constant B is related to the heat of adsorption, C_o: Initial concentration of Pb(II) (mg/L), C_e: Equilibrium concentration of Pb(II) (mg/L), C_t: Concentration of Pb(II) at time t (mg/L), $\varDelta G^o$: Gibbs free energy (kJ/mol), $\varDelta H^o$: 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_{id}: Intraparticle diffusion rate constant (mg/g · h$^{0.5}$), 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_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, $\varDelta S^o$: Entropy (J/mol · K), t: Time (min), T: Absolute temperature (K), V: Volume of solution (L), α: Elovich constant, which gives an idea of the adsorption rate constant (mg/g · min), β: Elovich constants, which represents the rate of chemisorption at zero coverage (g/mg).

Table 2. A Physical Property of Chitosan, Spent Coffee Ground and CC-beads

Sample	pH$_{pzc}$	C	N	O	O / C	(O + N) / C	Surface area	CEC
		Wt (%)					m^2/g	cmol/kg
SCG	5.1 ± 0.3	55.28	16.35	28.31	0.51	0.81	0.34 ± 0.1	9.48
Chitosan	7.14 ± 0.5	47.62	19.42	32.82	0.69	1.09	0.186 ± 0.1	20.08
CC-bead	6.73 ± 0.4	69.41	5.23	23.94	0.34	0.42	10.82 ± 0.2	36.54

physicochemical properties of the adsorbent essentially correspond to the functional group (FT-IR), which influences the particle diameter, cation exchange capacity (CEC), zeta potential, pH$_{pzc}$ and solid adsorption efficiency[27]. In general, when the particle diameter is small and the specific surface area is large, therefore the adsorption force is improved[4]. This is because the larger the pores, the more the interface of the solid required for adsorption increases[5]. Additionally, the higher the measured value of the cation exchange capacity, the greater the adsorption capacity of the solids in the aqueous solution.

3.1.1. BET surface and CEC

The BET surface area had the order of CC-bead > SCG > chitosan. The CC-bead had a BET surface area that was 10-fold larger than the SCG (Table 2). In the SEM image, the CC-bead has more pores compared to SCG and chitosan. When the adsorbent contains more pores, the specific surface area increases (Figure 1). In addition, the CEC in-

creased in the order of SCG < chitosan < CC-bead, and the CC-bead was approximately 4-fold higher than the CEC. The adsorption amount in the adsorption process is proportional to the surface area of the adsorbent, where the larger the surface area, the larger the adsorption amount[4]. As a result, the CC-bead showed a higher CEC and BET surface area compared than that of SCG and chitosan. Additionally, it a showed higher performance for the adsorption of Pb(II) in an aqueous solution than individual adsorbents, such as SCG or chitosan. Therefore, according to the above analysis, the adsorption amount of Pb(II) in the CC-bead is expected to be higher than that of SCG and chitosan.

3.1.2. pH$_{pzc}$

The pH at which the adsorbent surface charge assumes that a value of zero is defined as the point of zero charge, pH$_{pzc}$[28]. At pH values higher than pH$_{pzc}$, the surface charge of the adsorbent has a negative
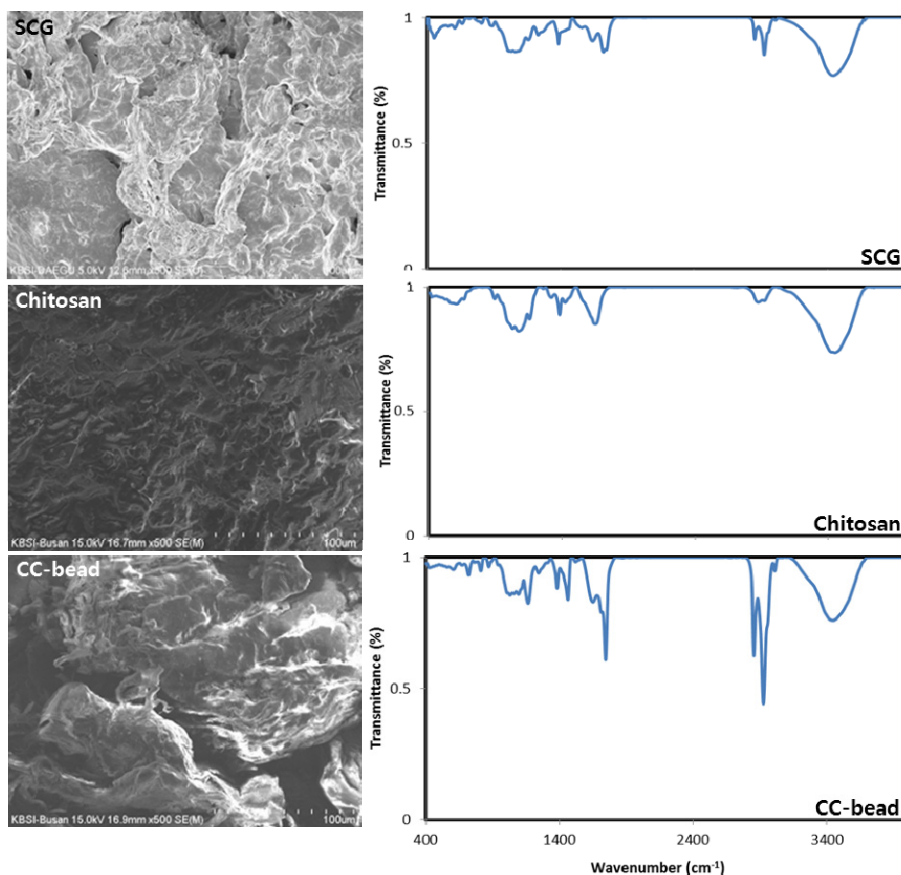
Figure 1. SEM and FT-IR spectra of chitosan, coffee and a CC-bead.

charge and interacts with the cation species to adsorb, but at a pH lower than pH_{pzc} the adsorbent surface is positively charged and can interact with the anion species[2]. Thus, pH_{pzc} is useful for understanding the adsorption mechanism by understanding the proton/deprotonation behavior of the adsorbent material. The pH_{pzc} value of the CC-bead was approximately 4.73, indicating that it would be advantageous to remove Pb(II) from the aqueous solution. Heavy metal ions-containing industrial wastewaters discharged from industrial processes are, in general, weakly acidic[1]. Thus, the low pH_{pzc} of the CC-bead keeps the surface charge of the CC-bead negative and makes Pb(II) favorable for adsorption.

3.1.3. Carbon content

The carbon content of the CC-bead was increased while the contents of N and O were decreased compared to SCG and chitosan. The reduction of oxygen (O) is the result of the reduction of various acidic functionalities present on the CC-bead adsorbent surface. This indicates that the surface of the CC-bead adsorbent is more basic[5]. Additionally, the O/C ratio of the CC-bead was lower than that of SCG and Chitosan. This indicates a direct bond between the hydroxyl group (-OH) and the polarized carbon[7]. In addition, the reduction in the O/C ratio due to the oxygen removal is to make the CC-bead surface hydrophobic[14]. There are various compounds on the surface of the adsorbent, which are oxygen complexes containing oxygen, mainly carboxyl groups, car-

boxyl groups in which carbonyl groups and lactone groups are bonded, phenols group, and a carbonyl group[16]. The oxygen compounds contained in these groups cause the adsorbent to have polarity properties such as hydrophobicity, acidity and negative charge, which makes it possible to adsorb ionic substances other than organic substances[7]. This pulling force and adsorption force of the surface of the adsorbent remove the organic substances present in the water[8]. According to the above analysis, the CC-bead has an easy structure for heavy metal adsorption compared with individual SCG and chitosan, which is a main reason for using a CC-bead composite adsorbent to remove heavy metals from an aqueous solution.

3.1.4. SEM and FT-IR spectra

The surface morphologies of SCG, chitosan and the CC-bead were observed via SEM images, as shown in Figure 1. The CC-bead increased the micropores and showed a smooth intermediate surface between the chitosan and SCG. These observations were in good agreement with the increased BET surface area of the CC-bead. There are many different techniques for characterizing adsorbents. Among them, FT-IR analysis is a very useful analytical method to know how much the adsorbent contains the functional groups that are capable of interacting with the adsorbed material[1,4]. Essentially, the functional groups possessed by SCG, chitosan and CC-bead were similar, although there were differences in the size of their peaks. The main functional groups

of SCG and chitosan and CC-bead are bonded-OH groups (3,000~ 3,500 cm^{-1}), CH stretching (2,800~2,900 cm^{-1}), C=O carbonyl groups (1,680~1,740 cm^{-1}), Carboxylic groups (1,640~1,670 cm^{-1}), CO stretch (1,300~1,450 cm^{-1}) and PO_4^{3-} streching (1,000~1,150 cm^{-1}). The CC-bead showed a large peak at CH stretching (2,800~2,900 cm^{-1}), C=O carbonyl groups (1,680~1,740 cm^{-1}) and CO stretch (1,300~1,450 cm^{-1}) compared to SCG and chitosan. The bonded-OH groups (3,000~3,500 cm^{-1}) showed wide and large peaks in all SCG, chitosan and CC-bead samples. In general, the functional groups with the highest heavy metal adsorption capacity are known as carboxyl and carbonyl groups[4]. Both groups dissociate into -COO- and H^{+} in an aqueous solution, and above a certain pK value, they mostly become -COO-, effectively adsorbing the cationic heavy metals[27]. There is no precise literature on the mechanism of heavy metal adsorption by various biomaterials. However, it is considered that the functional groups contained in the polymer material in the cell are coordinated with heavy metals[14]. Therefore, -COOH, -OH, a large amount of carboxyl group and the carbonyl group, which are involved in the coordination bond with the heavy metals contained in the CC-bead, will have a great influence on the removal of heavy metals.

3.2. Different parametric studies

The adsorption experiment conditions using various parameters play an important role in the evaluation of the adsorption process. The main experimental conditions affecting the adsorption capacity of the adsorbent are the initial concentration, the pH of the aqueous solution, the contact time, the temperature, the amount of adsorbent and the coexistence of other contaminants[2,27]. The initial concentration and adsorption amount are generally correlated with the amount of adsorbent, except when the initial concentration is significantly increased[4,5]. The effect of Pb(II) adsorption on the CC-bead was investigated using various parameters that have major influences.

3.2.1. Effect of the initial pH

The pH of the aqueous solution, which has a significant effect on the adsorption process, plays an important role in controlling the surface charge of the adsorbent, the degree of ionization of the adsorbed material in the solution, and the dissociation of various functional groups on the active site of the adsorbent[16]. The removal efficiencies were 32.3 and 25.5% at pH 3 and 4, respectively. However, the removal efficiency increased with an increasing pH, which was 70.6 and 96.6% at pH 5 and 7, respectively. This observation is in agreement the pH_{pzc} value of the CC-bead. At pH 9 and 10, the removal efficiency decreased slightly, but nevertheless maintained a high removal efficiency of over 91% (Figure 2(a)).

The adsorption of metal ions by the CC-bead is also greatly influenced by the pH, and the adsorption capacity decreases at a low pH[27]. The behavior of the CC-bead in the aqueous solution depends on pH_{pzc} ($_{pzc}$: permanent charge point). If the pH in the aqueous is higher than pH_{pzc} (pH > pH_{pzc}), the CC-bead surface is negatively charged due to the deprotonation of the carboxyl group and the hydroxyl group[28]. When the CC-bead surface is negatively charged,

(a)

(b)

(c)
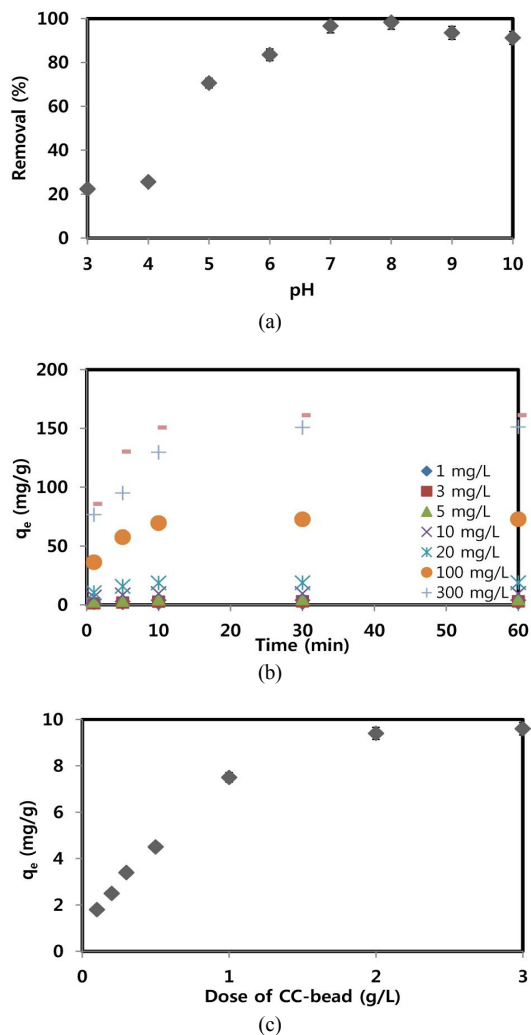
Figure 2. (a) Removal of Pb(II) by various pH in an aqueous solution (contact time: 30 min, Pb(II) concentration: 10 mg/L, CC-bead 2 g/L and 25 ℃), (b) Adsorption amount of Pb(II) with various initial concentrations (contact time: 60 min, pH 7, CC-bead 2 g/L and 25 ℃), (c) Effect of CC-bead dosage for Pb(II) adsorption (Pb(II) concentration: 10 mg/L, contact time: 60 min, pH 7 and 25 ℃).

electrostatic bonding with metal ions strongly occurs, which in turn improves the adsorption ability[29]. By contrast, when the pH in an aqueous solution is lower than pH_{pzc} (pH < pH_{pzc}), the CC-bead is positively charged and electrostatic bonding is greatly attenuated due to charge repulsion[2,8]. In a similar manner, the pH also affects the charged nature of the adsorbate. Depending on the pH, metal ions can form hydroxides, which have a lower adsorption power than metal ions. A similar observation was made by Ahmad *et al.*[29]. Moreover, the difference in the adsorption efficiency of heavy metals depending on the pH is due to the change in the ionic form of the heavy metals in the aqueous solution depending on the pH[1,10]. As the pH of the aqueous solution increases (> 5.8), Pb(II) is present in the form of Pb(OH) or Pb(OH)$_2$, thereby the adsorption amount of Pb(II) onto the CC-bead rapidly increases. Considering that the pH of industrial wastewater containing heavy metals is approximately 6~7, it can be applied

Table 3. Kinetic Parameters for Sorption of Pb(II) on CC-beads

Pb(II) C_o (mg/L)	$q_{e.cal}$ (mg/g)	Pseudo-first-order		Pseudo-second-order		Intraparticle diffusion		Elovich		
		k_1 (1/min)	R^2	k_2 (g/mg · min)	R^2	k_{id} (mg/g · h$^{0.5}$)	R^2	α (mg/g · min)	β (mg/g)	R^2
1	1.00	-0.0933	0.9290	9.98×10^{-1}	0.9996	0.0233	0.8882	0.0280	3.0864	0.7708
3	2.95	-0.1577	0.9698	3.78×10^{-2}	0.9991	0.2535	0.7511	0.0212	1.8028	0.9006
5	4.90	-0.0998	0.4918	8.45×10^{-3}	0.9995	0.2505	0.6544	1.9229	1.6731	0.8684
10	9.63	-0.166	0.7713	1.12×10^{-3}	0.9999	0.3562	0.6071	12.1199	1.1130	0.8417
20	19.12	-0.1315	0.7116	1.43×10^{-4}	0.9998	1.0742	0.6314	0.6997	0.3765	0.8568
100	74.07	-0.1845	0.8926	2.46×10^{-6}	0.9998	4.8671	0.6894	0.3898	0.0869	0.8928
300	156.25	-0.1809	0.7844	2.62×10^{-7}	0.9986	11.929	0.8432	0.2789	0.0423	0.9259
500	163.93	-0.2276	0.9995	2.27×10^{-7}	0.9999	10.613	0.7115	1.9256	0.0411	0.8931

to the field without controlling the pH when adsorbing heavy metals in an aqueous solution using a CC-bead adsorbent.

3.2.2. Initial concentration and contact time

The initial concentration of heavy metals in an aqueous solution is a major factor influencing the adsorption process. Since the amount of adsorbent and the adsorption time are determined according to the initial concentration of heavy metals, this is closely related to the economics and commercialization of the adsorbent[4,7]. Therefore, the effect of the initial concentration of heavy metals on the removal rate is the basic experiment for deriving the optimal condition of the adsorption process. To investigate the effect of the initial concentration of Pb(II) on the removal efficiency, the concentration of Pb(II) was varied from 1 to 500 mg/L and pH 7 ± 0.4, with the results shown in Figure 2(b). As the initial Pb(II) concentration increased, the removal efficiency decreased from 95% at 10 mg/L to 53% at 300 mg/L. This is because the surface of the adsorbent that can be adsorbed is limited due to the amount of adsorbent being constant. Contrary to the adsorption efficiency, the final adsorption amount increased, and the initial adsorption amount gradually decreased as the concentration of Pb(II) increased. The adsorption amount of Pb(II) on the CC-bead was 72.7, 160.8 and 163.51 mg/g for 100, 300 and 500 mg/L of Pb(II), respectively. The adsorption amount of Pb(II) on the CC-bead was affected by the initial concentration, and an adsorption equilibrium was reached at 163.51 mg/g.

Regarding the contact time, two steps should always be identified during the sorption process: (i) fast and quantitatively superior; and (ii) slow and quantitatively insignificant. During the first step, the adsorption process is accelerated due to the high solubility of the active sites on the bioadhesive, whereas in the second step the process is decelerated until equilibrium is reached[3,16]. The adsorption of Pb(II) using CC-beads increased continuously until contact time of 10 min, but increased slowly after 10 min. The reaction between the adsorbate and the adsorbent was very rapid, and after 30 min the adsorption equilibrium was reached. The most basic condition of a good adsorbent is to adsorb a large amount of contaminants in a short period of time, and strongly adsorb the adsorbent material over time so that it does not desorb[27,30]. CC-beads, which are inexpensive adsorbents made from waste, can adsorb heavy metals in a short time.

3.2.3. Adsorbent dosage

As the dosage of the adsorbent increases, the surface area of the adsorbent available to the adsorbate increases. As the surface area of adsorbent increases, the adsorption amount increases, so the adsorption capacity and the amount of adsorbent are correlated[4]. Therefore, the amount of adsorbent is also a good parameter for evaluating the economics of the adsorbent, such as the initial concentration of the adsorbate in an aqueous solution[1,26].

If a large amount of heavy metal ions can be adsorbed on a small amount of adsorbent, this is useful not only in an economic sense but also in an environmental protection aspect. The effect of the adsorbent amount on the removal efficiency of Pb(II) was investigated by varying the CC-beads from 0.1 to 3 g/L, with the results shown in Figure 2(c). The amount of adsorption until 2 g/L of CC-beads was continuously increased, but the adsorption amount was insignificantly changed at more than 2 g/L. This is probably because the adsorbing capacity of the bioabsorbent does not increase further due to agglomeration/aggregation of the adsorbent and the adsorbate after a certain period of time[1]. In this experiment, the removal efficiency was over 95% at 2 g/L of CC-beads. Therefore, when adsorbing Pb(II) using CC-beads in an aqueous solution, a CC-bead amount of 2 g/L is recommended.

3.3. Adsorption kinetics

Studies on adsorption kinetics play an important role in predicting optimum conditions in the adsorption process. Modeling the adsorption kinetics provides information on possible adsorption mechanisms and possible rate control steps, such as mass transfer or chemical reaction processes[31]. Adsorption kinetics can use several kinetics models, such as pseudo-first and pseudo-second order (linear or nonlinear), intraparticle diffusion and Elovich. Thus, experimental data was analyzed using pseudo-first and pseudo-second order, intraparticle diffusion and Elovich, with the results summarized in Table 3.

As the initial concentration of Pb(II) increased, the rate constants of the pseudo-first and pseudo-second models, k_1 and k_2, and the number of adsorbable sites of Elovich decreased. In addition, Elovich's initial

Table 4. The Parameters of Langmuir, Freundlich and D-R Isotherms for Adsorption of Pb(II) CC-bead (CC-bead: 2 g/L, pH: 7, T: 25 ℃)

Models	Parameters	Pb(II)
Langmuir isotherm	q_m (mg/g)	163.51
	K_L (L/g)	0.00408
	R^2	0.991
Freundlich isotherm	K_F (L/g)	1.630
	n	1.194
	R^2	0.9891
Tempkin	A (L/g)	0.328
	B (J/mol)	28.219
	R^2	0.8673
Dabinin-Radushkevich	β (mole^2/J^2)	-0.0921
	ε (KJ/mole)	0.41528
	Xm	67.6083
	R^2	0.8492

adsorption rate constant (α) and the internal diffusion coefficient constant (k_{id}) decreased. It can be seen that as the initial concentration of Pb(II) increases, and the adsorption rate and the number of adsorbable sites of the CC-beads decrease. In contrast, the diffusion of internal particles became active and the amount of initial adsorption to CC-beads increases. The pseudo-second model has the highest correlation coefficient (R^2) and is most suitable for Pb(II) adsorption via CC-beads. Additionally, the correlation in intraparticle diffusion was lower than the pseudo-first-order and pseudo-second-order, indicating that intraparticle diffusion is not a rate-limiting step in the adsorption process.

3.4. Adsorption isotherm

It is essential to analyze the adsorption kinematic equation in order to predict the adsorption parameters consistently by optimizing the adsorption equilibrium correlation and quantitatively comparing the behavior of the adsorbent to various adsorbent systems[27,32]. Adsorption isotherms, a common name for adsorption equilibrium relationships, are an indispensable analytical tool for the production design of adsorption systems because they explain how adsorbents and adsorbates correlate, including optimization of the adsorption mechanism path, surface properties and the capacity of the adsorbent[8,11]. The mathematical relevance of the adsorption isotherms, which play an important role in these applications of adsorption modeling analysis, operational design and adsorption systems, is generally plotted between the solid-phase and residual concentrations[4,12]. The association between the equilibrium concentration of the adsorbent and the adsorbent material is defined by the equilibrium sorption isotherm when the solute concentration does not change as a result of the zero pure transfer of the adsorbed and desorbed solute from the adsorbent surface[5,33]. The most commonly used adsorption isotherms are Langmuir and Freundlich. In this study, the adsorption process of Pb(II) on CC-beads was analyzed via Langmuir, Frundlich, Tempkin and Dabinin-Radushkevich for

(a)

(b)

(c)

(d)
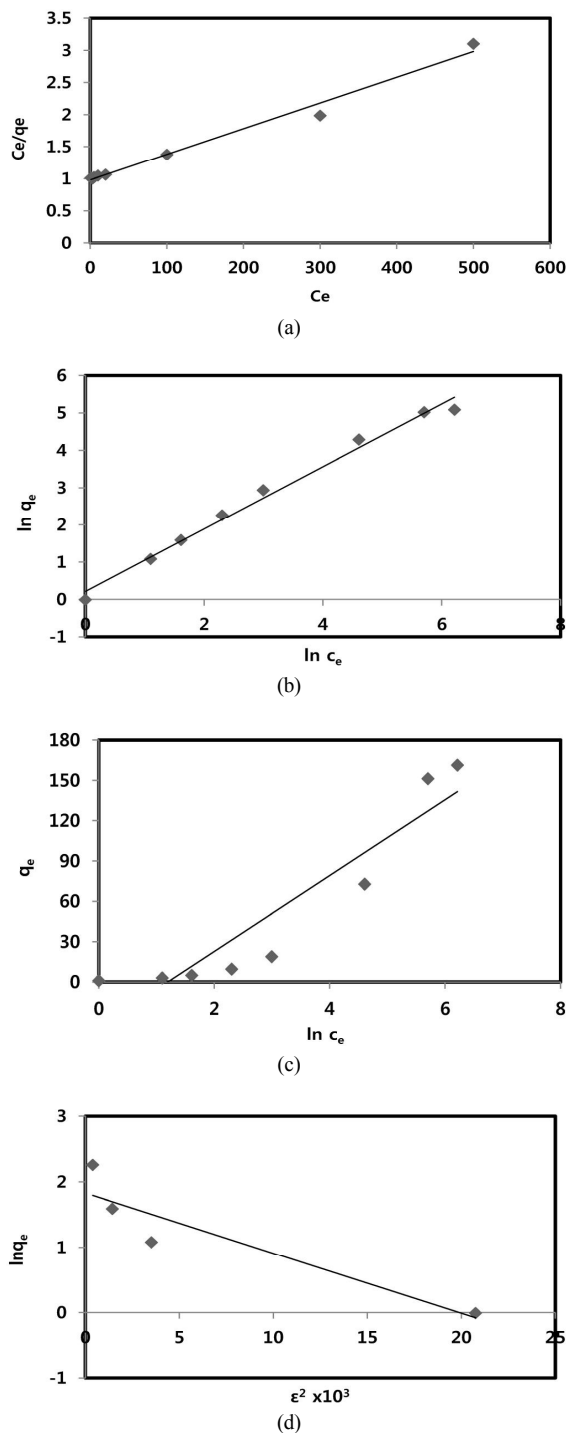
Figure 3. Plot of (a) Langmuir, (b) Freundlich, (c) Tempkin and (d) Dabinin-Radushkevich for Pb(II) removal onto CC-adsorbent.

various interactions between adsorbents and adsorbates, with the results shown in Table 4 and Figure 3(a~d).

The adsorption isotherms, according to the correlation coefficient (R^2) analysis, showed that Langmuir was 0.991 and Freundlich was 0.9891, which showed similar correlations, but Langmuir was slightly higher than Freundlich. According to the Freundlich isothermal adsorp-

Table 5. Comparison of Pb(II) Adsorption onto Various Bioadsorbents

Adsorbent	Isotherm	Kinetic	q_{max} (mg/g)	Reference
Modified spent coffee grounds	Langmuir	PS2	93.15	[10]
Coffee husks	L	PS2	37.04	[8]
Exhausted coffee grounds	L	PS2	61.60	[9]
Coffee residues	L	PS2	9.91	[35]
Coffee grounds	L	PS2	22.90	[13]
Chitosan bead	L	PS2	79.20	[36]
Chitosan-coated cotton fibers	F	PS2	86.09	[37]
Chitosan/$CoFe_2O_4$	L	PS2	151.06	[38]
Thiosemicarbazide modified chitosan	L	PS2	56.89	[39]
CC-beads (SCG-chitosan)	L	PS2	163.51	This study

L: Langmuir isotherm, F: Freundlich Isotherm, PS2: Pseudo-second-model.

tion analysis, the larger the value of K_F is, the better the adsorption capacity, and the 1/n value indicating the adsorption strength is stronger in the range between 0 and 1[1,34]. As a result, K_F was found to be as high as 4.082, and 1/n was 0.8375, which ranged between 0 and 1. This indicates that the adsorption of Pb(II) using CC-beads was excellent in adsorbability and the adsorption strength was strong. In addition, R_L = 0.3289 as calculated in Langmuir, which corresponds to 0 < R_L < 1, indicates that the adsorption process of Pb(II) onto CC-beads is favorable. A and B calculated by the Tempkin plot were 0.328 and 28.219, respectively, and R^2 was 0.8673. According to the data analyzed above, it can be seen that the Pb(II) was adsorbed strongly onto the CC-beads and the adsorption was chemisorption in nature.

In Table 5, the removal of Pb(II) using coffee and chitosan was compared with the results using CC-beads. As a result of the comparative analysis, the adsorption capacity was lower than that of unmodified coffee or chitosan modified adsorbent. In addition, the adsorption of Pb(II) using SCG and chitosan was mostly compatible with Langmuir and the pseudo-second-model, as in this experiment. In addition, the removal efficiency of Pb(II) was much higher in composite adsorbents, made by combining different materials than those adsorbed by Pb(II) using SCG and chitosan separately. This is also a good reason for the adsorption of Pb(II) using complex adsorbents in this experiment.

3.5. Thermodynamic interpretation

Since the adsorption amount is mainly due to an increase in the active surface area of the adsorbent and the increase in the porosity, it is necessary to analyze the correlation between the temperature and the adsorption amount in order to analyze the mechanism of the adsorption process. A variety of analytical opinions are presented on the relationship between the temperature and adsorbent. The effect of the temperature on the adsorption amount depends on the type of adsorbent.

Aksu[40] reported that increasing the temperature from 25 ℃ to 45 ℃ increased the adsorption capacity of the activated carbon. On the other hand, Alpat et al.[26] reported that the adsorption capacity of Ni(II) increased at a temperature of 20~40 ℃, but decreased at tem-

Table 6. Thermodynamic Parameters for the Adsorption of Pb(II) on CC-beads (C_o: 100 mg/L, pH 7, Particle Size: 50, Mixing Rate: 180 rpm)

	Temperature (K)			
	298 K	308 K	318 K	328 K
ΔG^o (kJ/mol)	-1.019	-1.621	-2.255	-2.671
ΔH^o (kJ/mol)	-25.73			
ΔS^o (J/mol·K)	14.43			

peratures of 40~60 ℃. This reduction may be due to the inactivation of the bioadhesive surface or the destruction of some active sites on the bioadhesive surface. In contrast, Horsfall and Spiff[41] have shown that at high temperatures metal ions tend to escape from the surface of the adsorbent, which reduces the thickness of the boundary layer, limiting the adsorption process while the metal is in the solution phase. In particular, biomass adsorbents change the surface texture as the temperature increases, which decreases the adsorption capacity. That is, heavy metal adsorption via biomass is greatly influenced by temperature due to the high variability of potential binding sites[27]. In this study, the adsorption amount of Pb(II) on the CC-beads increased with an increase in the temperature. ΔG^o showed negative values at all temperatures, indicating that the adsorption process of Pb(II) to the CC adsorbent was spontaneous in nature (Table 6) and that the decrease in ΔG^o with an increasing temperature is more advantageous for the adsorption at high temperatures[5]. The positive values of ΔS^o demonstrate a high affinity between the CC-beads and Pb(II), indicating that the randomness of Pb(II) adsorbed on the CC-beads over time has increased. In addition, ΔH^o of the negative value indicates that the adsorption process was exothermic.

3.6. Sustainable environmental circulation

Cost is an important parameter for the selection of an adsorbent[1]. The adsorption of heavy metals using waste not only reduces the waste disposal costs but also has a great significance in terms of resource recycling. Moreover, the production cost of CC adsorbent is about

0.05~0.3 \$/kg, which is less than half of that of commonly used activated carbon (1.0~10 \$/kg). Therefore the CC adsorbent can compete with the conventional adsorbent, despite their lower adsorption capacity. These waste-based adsorbents are accessible for environmental conservation and sustainable environmental circulation and are suitable for use in wastewater treatment to improve wastewater management.

4. Conclusions

The adsorption of the heavy metal Pb(II) in an aqueous solution was performed using CC-beads mixed with SCG and chitosan. According to the FT-IR analysis, the CC-bead has a structure that can easily adsorb heavy metals because it has a carboxy-carbonyl group, O-H carboxylic acid and a bound -OH group as the main functional groups. As the initial concentration of Pb(II) increased, the rate constants of the pseudo-first and pseudo-second models, Elovich's initial adsorption rate constant (α) and the internal diffusion coefficient constant (k_{id}) decreased. The adsorption process of Pb(II) using CC-beads was suitable for pseudo-second-order kinetic and Langmuir, where the maximum adsorption amount of Langmuir was 163.51 (mg/g) for Pb(II). The analysis of the values of the adsorption energy from Dabinin-Radushkevich and B from Tempkin showed that the adsorption of Pb(II) by CC-beads was a chemisorption, and ΔG^o was a spontaneous process with a negative value. In addition, ΔS^o and ΔH^o were calculated as positive and negative values, respectively. This indicates that the randomness of Pb(II) adsorbed on the CC-bead increased with time, and the adsorption process was exothermic. CC-beads, made from a mixture of SCG and chitosan, are inexpensive and can be recycled, which is very significant in terms of the recycling of resources; thus, CC-beads can compete with other adsorbents.

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