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Adsorption of heavy metals from aqueous solutions by waste coffee residues: kinetics, equilibrium, and thermodynamics

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ABSTRACT

Waste coffee residues (WCRs) are used to remove heavy metals (Cu^{2+}, Pb^{2+}, and Zn^{2+}) from aqueous solutions. The surface characteristics of WCRs were analyzed by scanning electron microscopy, specific surface area analysis, zeta-potential analysis, and Fourier-transform infrared spectroscopy. The specific surface area, mean pore diameter, and pH_{pzc} of the WCRs were 0.19 m^2/g, 14 nm, and 3.5, respectively. Adsorption experiments are performed to evaluate the kinetics, equilibrium, and thermodynamic parameters. The percentage of Cu^{2+} that was removed from a solution increased as the pH and the WCR dose increased, but it declined as the Cu^{2+} concentration increased. The adsorption kinetics and equilibrium fit pseudo-second-order and Langmuir models, respectively. At pH 5 and 25℃, the maximum adsorption capacities of the WCRs for Cu^{2+}, Pb^{2+}, and Zn^{2+} were 8.2, 27.6, and 8.0 mg/g, respectively. The ΔH^0 values for the adsorption of Cu^{2+}, Pb^{2+}, and Zn^{2+} on WCRs were 9.73, 13.77, and 9.15 kJ/mol, respectively, and the corresponding ΔS^0 values were 109.4, 127.0, and 96.6 J/mol/K. The adsorption of Cu^{2+}, Pb^{2+}, and Zn^{2+} on WCRs is an endothermic, spontaneous physisorption process, and the adsorption kinetics is controlled mainly by surface diffusion.

Keywords: Adsorption; Coffee residues; Heavy metals; Kinetics; Equilibrium; Thermodynamics

1. Introduction

The contamination of water by heavy metals is a serious threat to global ecosystems. Mining, electroplating, and metal processing are the main sources of heavy metals in the environment. Owing to their hazardous effects, persistence, and accumulation, heavy metals pose risks to human and environmental health, and must therefore be eliminated from the discharges of these industries. Several techniques have exhibited various degrees of success in the control of heavy metal pollution. Examples include coagulation, precipitation, filtration, ion exchange, and adsorption. Among various methods for treating water, the adsorption technique is preferred because of its convenience, ease of implementation, and simplicity.

Coffee is a popular beverage globally, and enormous quantities of coffee grounds are produced daily. Some coffee grounds are recycled for soil remediation, animal feed, or odor adsorbents. However, more are

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burned as waste, generating carbon dioxide. The reuse of coffee residues for beneficial purposes would help to convert this waste into a resource.

Using waste as a low-cost adsorbent is attractive, because doing so reduces the environmental and financial costs of disposal. Coffee residues as an adsorbent have been utilized to remove organic and inorganic compounds from aqueous solutions. Chemical modification can increase the number of active binding sites in the material, improve its ion exchange properties, and form new functional groups that favor metal uptake. However, some possible modifications of green adsorbents are very costly. Therefore, the green adsorbents that can be used most profitably are those derived not only from activated carbon but also from agricultural wastes, and preferably from untreated wastes [1]. Franca et al. [2], who used spent coffee grounds to assess the adsorption kinetics and equilibrium of methylene blue, suggested that the spent coffee grounds are an effective adsorbent for the removal of cationic dyes from aqueous solutions. Boonamnuayvitaya et al. [3] investigated the use of coffee residues that are bound with clay as an adsorbent to remove heavy metal ions from solutions. Kyzas et al. [4] examined the equilibrium and thermodynamics of the adsorption of reactive and basic dyes on waste coffee residues (WCRs). The adsorption kinetics of dyes [2,4–8] and heavy metals [9–12], and the adsorption equilibrium of dyes [2,4–8,13] and heavy metals [9–12,14–16] can be found in the literature; however, few studies have evaluated the thermodynamic parameters of the adsorption of dyes [4,5,7,8] and heavy metals [12] on WCRs. Previous research has not elucidated the adsorption equilibrium and thermodynamic parameters of heavy metals on WCRs, with the exception that Azouaou et al. [12] determined the adsorption equilibrium and thermodynamic parameters for Cd^{2+}. Accordingly, this study elucidates the adsorption equilibrium of Cu^{2+}, Pb^{2+}, and Zn^{2+} on WCRs and calculates the relevant thermodynamic parameters. This investigation (i) characterizes the surface of WCRs; (ii) determines the effectiveness of WCRs in removing Cu^{2+} with reference to solution pH, Cu concentration, and WCR concentration; (iii) determines the equilibrium and thermodynamic parameters of the adsorption of Cu^{2+}, Pb^{2+}, and Zn^{2+} on WCRs; and (iv) examines the desorption and re-adsorption of Cu^{2+} on WCRs.

2. Materials and methods

2.1. Materials

Coffee was obtained from a local manufacturer of instant coffee, and WCRs were derived by the steam extraction of coffee grounds. The grounds were air-dried (50℃) for 48 h and then passed through a 100-mesh sieve. $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, HNO_3, and NaOH were purchased from Merck. Solution pH was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH. All compounds were used as received. All solutions were prepared using deionized water (Milli-Q) and reagent-grade chemicals.

2.2. Characterization of WCRs

The size and morphology of WCRs were determined by scanning electron microscopy (SEM) (JEOL JSM-6500F, Japan); their specific surface area was determined by the BET method using a surface area analyzer (ASAP 2010; Micromeritics, USA), and the pH at zero charge (pH_{pzc}) was measured using a Zeta-Meter 3.0 (Zeta-Meter, Inc., USA). The functional groups of WCRs were identified by Fourier-transform infrared spectroscopy (FTIR) using the KBr pressed-disc method with Spectrum One and Autoimagic systems (Perkin Elmer, USA).

2.3. Adsorption experiments

All adsorption experiments were performed in a sealed pyramidal 250 mL glass bottle. The adsorption and desorption kinetics were determined for Cu^{2+}, and adsorption equilibrium experiments were conducted for Cu^{2+}, Pb^{2+}, and Zn^{2+}. Adsorption and desorption kinetics were assessed over 3 h at 25℃. An initial pH of 5.0 was used in all adsorption experiments, except in those that were carried out to examine the effect of pH. In the experiments on adsorption kinetics, 0.3 g of WCRs was placed in a bottle that contained 200 mL Cu^{2+} solution with a concentration of 20 mg/L and shaken at 100 rpm. The effect of Cu^{2+} concentration on the percentage of Cu^{2+} removed by WCRs was examined using Cu^{2+} concentrations of 5, 10, and 20 mg/L and a WCR concentration of 1.5 g/L. The effect of WCR dosage on Cu^{2+} removal by WCRs was investigated using WCR concentrations of 1.5, 2.5, and 3.5 g/L at Cu^{2+} of 20 mg/L. The effect of pH on the removal of Cu^{2+} by WCRs was evaluated using initial pH values of 3, 4, and 5, a Cu^{2+} concentration of 20 mg/L, and a WCR concentration of 1.5 g/L. To obtain the thermodynamic parameters, adsorption equilibrium experiments were performed at 15, 25, and 35℃ for 24 h. After the adsorption experiments, the WCRs were collected, filtered, and dried. In each desorption experiment, 0.3 g of Cu^{2+}-loaded WCRs was placed in a bottle that contained 200 mL 0.5 M HNO_3, which was shaken at 100 rpm for 3 h. The re-adsorption and re-desorption procedures were same as the adsorption and desorption procedures, respectively. Suspended particles were separated by filtration through a 0.22 μm filter (Millipore). Heavy metal concentrations, before and after adsorption, were measured using an atomic absorption spectrophotometer (Perkin Elmer 3300, USA). All adsorption experiments were conducted in triplicate and mean values are presented.

3. Results and discussion

3.1. Surface characteristics of WCRs

Fig. 1 displays a SEM micrograph of WCRs, which shows a scraggy surface morphology with plates and several cavities, probably with a low-specific surface area. Fig. 2 plots the surface potential of WCRs. The specific surface area, mean pore diameter, and pH_{pzc} of the WCRs were 0.19 m^2/g, 14 nm, and 3.5, respectively. Boonamnuayvitaya et al. [3] and Kyzas et al. [4] indicated that the surface area of WCRs was small. Franca et al. [2] determined that the pH_{pzc} of spent coffee grounds was 3.4–3.6, and Kyzas et al. [4] determined that the pH_{pzc} of WCR was 3.4. The surface properties of WCRs herein are similar to those identified by previous studies.

Fig. 3 shows the FTIR spectra of WCRs in the range 400–4,000 cm^{-1}. The spectral peaks at 1,059, 1,124, 1,418, 1,651, 1,700, 2,911, and 3,443 cm^{-1} were associated with C–N bending at 1,030–1,130 cm^{-1} [3]; C–O stretching in acids, alcohols, phenols, ethers, and esters at 1,000–1,300 cm^{-1} [13]; C–H deformation vibrations in alkane at 1,418 cm^{-1} [17]; C=O stretching vibrations in ketones at 1,600–1,700 cm^{-1} [3] or 1,640–1,660 cm^{-1} [18]; C–H stretching vibrations in the methyl group at 2,800–3,000 cm^{-1} [17–20]; and OH stretching vibrations in carboxylic acids, alcohols, and phenols at 3,200–3,600 cm^{-1} [20].

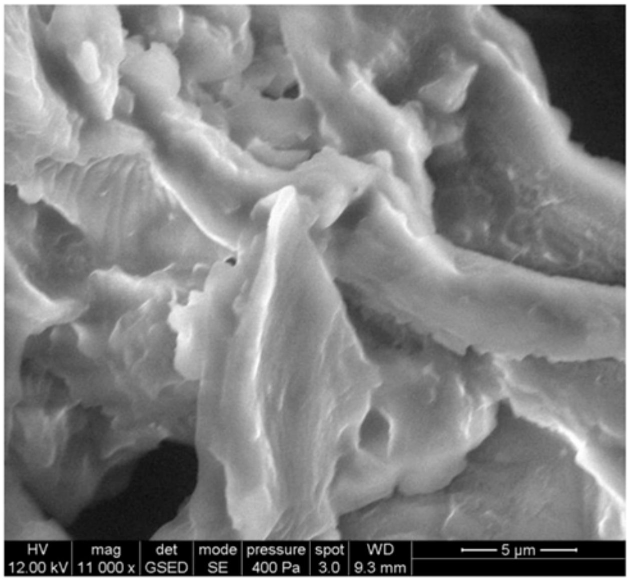

Fig. 1. SEM micrograph of WCRs.

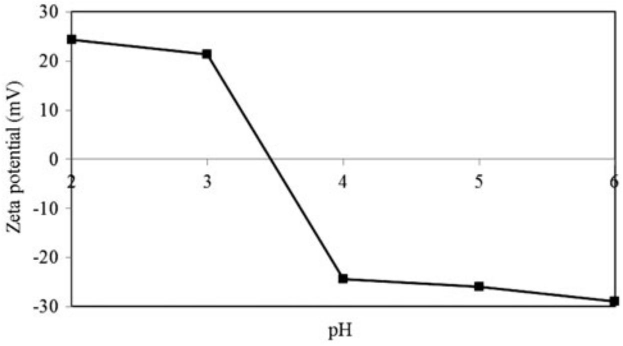

Fig. 2. Zeta potential of WCRs.

3.2. Kinetic analyses of Cu^{2+} adsorption on WCRs

Fig. 4 displays the effects of Cu^{2+} concentration, WCR dosage, and solution pH on the removal of Cu^{2+} by WCRs. The Cu^{2+} removal percentage increased with pH and the WCR dose; conversely, it decreased as the Cu^{2+} concentration increased. At pH 5, the charge on the surfaces of the WCRs was negative; at pH 3, it was positive. Therefore, the percentage of Cu^{2+} removed at pH 5 exceeded that at pH 3. The adsorption rate was high in the first 40 min and slowed rapidly thereafter. Initially, the surface sites of the WCRs were vacant, and the Cu^{2+} concentration gradient was relatively high, so the initial adsorption rate was high. This fast-phase sorption was character-

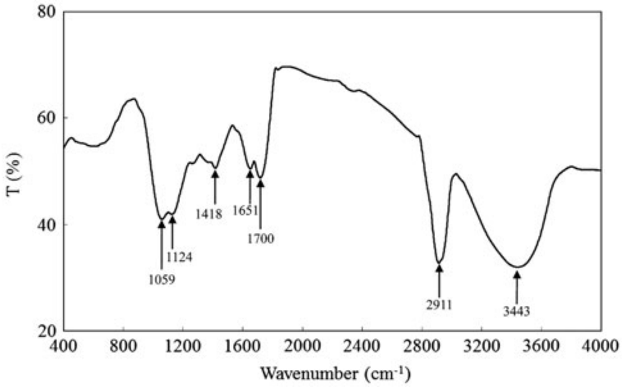

Fig. 3. FTIR spectra of WCRs.

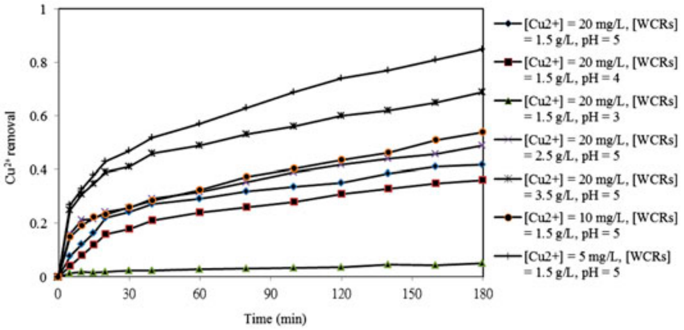

Fig. 4. Effects of Cu^{2+} concentration, WCR dosage, and solution pH on adsorption of Cu^{2+} by WCRs.

ized as passive uptake through physical adsorption or adsorbent surface ion exchange [18,21]. Increasing the WCR dosage increased Cu^{2+} adsorption. These experimental results were expected because, as the adsorbent dose increased, the increase in the number of adsorption sites caused more Cu^{2+} attaching to WCRs. The mass of Cu^{2+} adsorbed per unit mass of WCRs ($q_{e,\ exp.}$) increased with pH and Cu^{2+} concentration, but decreased as the WCR dosage increased (Table 1). The unit adsorption decreased as the adsorbent dose increased, because the adsorption sites remained unsaturated during the adsorption process. Several studies have demonstrated that the unit adsorption capacity declines as the adsorbent dosage increases [6,22,23].

Adsorption kinetics, which indicates adsorption rate, is an important characteristic of adsorbents. The pseudo-second-order model [24,25] and intraparticle diffusion model [26] were tested against the experimental data to elucidate the adsorption kinetics. The pseudo-second-order model is,

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{1}$$

where q_e and q represent the amounts of Cu^{2+} adsorbed on WCRs at equilibrium and at time t (mg/g), and k_2 is the rate constant of the pseudo-second-order model for adsorption (g/mg min). Since the application of pseudo-second-order models cannot determine the diffusion mechanism, the intraparticle diffusion model was applied to the kinetic results to identify the diffusion mechanism. In the intraparticle diffusion model, film diffusion was negligible, and intraparticle diffusion was the only rate-controlling step. The intraparticle diffusion model is

Table 1
Kinetic parameters for the adsorption of Cu^{2+} by WCRs

Pseudo-second-order model	$q_{e,\ exp.}$ (mg/g)	k_2 (g/mg/min)	$q_{e,\ cal.}$ (mg/g)	R^2
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 1.5 g/L, pH 3	0.67	0.0989	0.53	0.976
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 1.5 g/L, pH 4	4.80	0.0038	5.81	0.989
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 1.5 g/L, pH 5	5.58	0.0055	6.21	0.989
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 2.5 g/L, pH 5	3.92	0.0096	4.15	0.977
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 3.5 g/L, pH 5	3.90	0.0128	4.08	0.987
$[Cu^{2+}]$ = 10 mg/L, [WCRs] = 1.5 g/L, pH 5	3.59	0.0081	3.87	0.964
$[Cu^{2+}]$ = 5 mg/L, [WCRs] = 1.5 g/L, pH 5	2.83	0.0133	3.04	0.984

Intraparticle diffusion model	k_i (mg/g/min$^{0.5}$)	C (mg/g)	R^2
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 1.5 g/L, pH 3	0.034	0.109	0.983
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 1.5 g/L, pH 4	0.358	0.210	0.971
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 1.5 g/L, pH 5	0.370	0.829	0.950
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 2.5 g/L, pH 5	0.222	0.885	0.995
$[Cu^{2+}]$ = 20 mg/L, [WCRs] = 3.5 g/L, pH 5	0.205	1.177	0.987
$[Cu^{2+}]$ = 10 mg/L, [WCRs] = 1.5 g/L, pH 5	0.220	0.537	0.994
$[Cu^{2+}]$ = 5 mg/L, [WCRs] = 1.5 g/L, pH 5	0.167	0.614	0.995

$$q = k_i t^{1/2} + C \quad (2)$$

where C is the intercept and k_i is the intraparticle diffusion rate constant (mg/g min$^{0.5}$).

The q value ($q_{e,\ cal.}$) that was derived from the pseudo-second-order model was consistent with the experimental q value ($q_{e,\ exp.}$), suggesting that the pseudo-second-order model accurately describes the adsorption kinetics. Various researchers have found that the adsorption kinetics follows the pseudo-second-order model [6,12,27]. When the regression of q as a function of $t^{1/2}$ is linear and passes through the origin, intraparticle diffusion is the sole rate-limiting step [28]. However, although the regression herein was linear, the plot did not pass through the origin (Table 1), suggesting that the intraparticle diffusion was not the only rate-controlling step of the adsorption. Akkaya et al. [29] showed that pore diffusion and surface diffusion occur simultaneously in an adsorbent particle. Since the BET surface area of WCRs is very small, this study suggests that the adsorption kinetics is dominated by surface diffusion.

3.3. Equilibrium analyses of adsorption of heavy metals on WCRs

Fig. 5(a)–(c) shows the adsorption equilibrium of Cu^{2+}, Pb^{2+}, and Zn^{2+}, respectively, at different temperatures. Langmuir [30] and Freundlich [31] isotherms were used to describe the adsorption equilibrium. The expression for the Langmuir isotherm is

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \quad (3)$$

where q_e is the equilibrium metal adsorption capacity (mg/g); C_e is the equilibrium adsorbate concentration in a solution (mg/L), and q_{max} and K_L (L/mg) are the Langmuir constants that are related to the maximum adsorption capacity (monolayer capacity) and bonding energy of adsorption (or “affinity”), respectively.

The Freundlich isotherm, which empirically determined and used to model multilayer adsorption and adsorption on heterogeneous surfaces, is given by:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

where K_F is an adsorption equilibrium constant, which represents adsorption capacity, and n is a constant that specifies adsorption intensity.

Table 2 presents the parameters of the isotherms associated with the adsorption of heavy metals by WCRs. The high correlation coefficients (R^2) indicate that the Langmuir model accurately described the adsorption equilibrium. Some investigations have shown that the adsorption interactions between heavy metals and adsorbents are most accurately described by the Langmuir model [11,12,15]. Notably, K_L, K_F, and q_m increased with temperature, suggesting that the adsorption of heavy metals on WCRs increased with temperature (Table 2). These experimental results indicate that the affinity of binding sites for heavy metals increased with temperature, suggesting that the adsorption of heavy metals on WCRs is endothermic. The values of K_F and q_m followed the order $Pb^{2+} > Cu^{2+} > Zn^{2+}$. Ouki and Kavannagh [32] and Reddad et al. [33] found that the adsorption affinity followed the order $Pb^{2+} > Cu^{2+} > Zn^{2+}$ for clinoptilolite and sugar-beet pulp, respectively.

3.4. Thermodynamic parameters and desorption experiments

A study of the temperature dependence of adsorption provided valuable information about ΔG^0, ΔH^0, and ΔS^0. The Langmuir isotherm was applied to calculate thermodynamic parameter values via Eqs. (5) and (6).

$$\Delta G^0 = -RT \ln(K_L) \quad (5)$$

$$\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

where K_L is the Langmuir equilibrium constant (L/mol), R is the gas constant (8.314×10^{-3} kJ/mol K), and T is the temperature (K). Both ΔH^0 and ΔS^0 were determined from the slope and intercept of the van’t Hoff plot of $\ln(K_L)$ vs. $1/T$ [27]. Table 3 presents the thermodynamic parameters of the adsorption of heavy metals. The negative values of ΔG^0 at all temperatures reveal that the adsorption of heavy metals on WCRs is spontaneous. The positive ΔH^0 indicates that the adsorption process is endothermic. The positive value of ΔS^0 suggests that the randomness of adsorbate at the solid–liquid interface increased during adsorption. Although no particular criterion that is related to ΔH^0 values can be utilized to predict adsorption, adsorption heats of 20.9–418.4 kJ/mol, which are the heats at which the chemical reactions occur, are commonly assumed to be similar to those of chemisorption [34]. Additionally, Kara et al. [35] suggested that the ΔH^0 of physisorption is <40 kJ/mol. Hence, the ΔH^0 value herein suggests that the adsorption of Cu^{2+}, Pb^{2+}, and

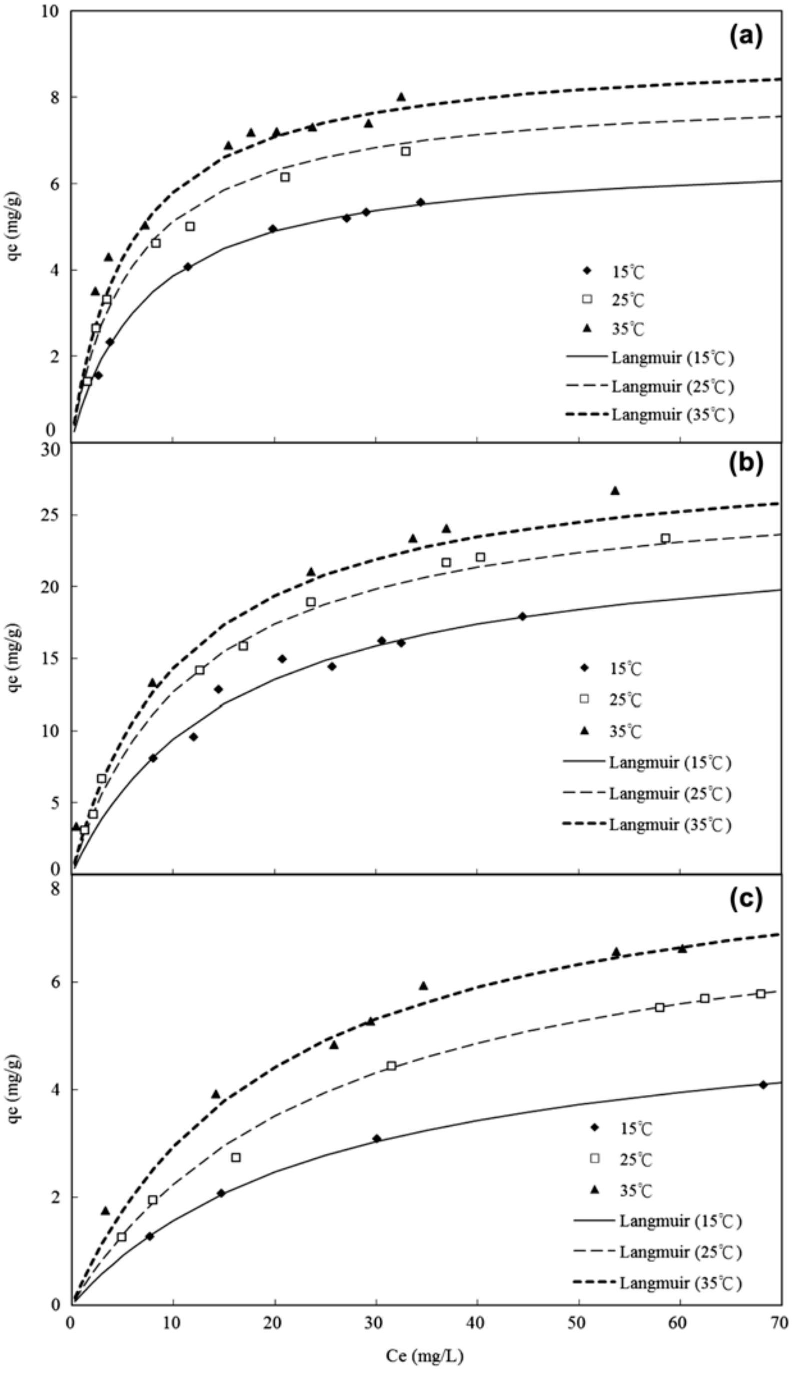

Fig. 5. Adsorption isotherm analyses of heavy metals on WCRs, (a) Cu^{2+}, (b) Pb^{2+}, and (c) Zn^{2+}.

Zn^{2+} on WCRs was driven by a physisorption process, and the adsorption affinity followed the order $Pb^{2+} > Cu^{2+} > Zn^{2+}$. The order of ΔH^0 values for heavy metals herein matched the order of maximum adsorption capacities. The hydration enthalpy of metal ions can be utilized to assess the theoretical affinity of metal ions for adsorbents. A more hydrated cation has stronger hydration enthalpy and is less able to interact with ligand [36]. The hydration enthalpy of Pb^{2+}, Cu^{2+}, and Zn^{2+} were −1,481, −2,100, and −2,046 kJ/mol, respectively [36]. Accordingly, Pb^{2+} had the highest affinity and the greatest adsorption capacity.

To evaluate the possibility of reusing WCRs and to elucidate the adsorption mechanism, the desorption

Table 2
Isotherm parameters for the adsorption of heavy metals by WCRs

Langmuir constants	K_L (L/mg)	q_m (mg/g)	R^2
Cu^{2+}			
15℃	0.136	6.7	0.999
25℃	0.166	8.2	0.997
35℃	0.176	9.1	0.999
Pb^{2+}			
15℃	0.064	24.2	0.974
25℃	0.085	27.6	0.985
35℃	0.093	29.8	0.949
Zn^{2+}			
15℃	0.039	5.7	0.999
25℃	0.040	8.0	0.999
35℃	0.050	8.9	0.948

Freundlich constants	K_F	n	R^2
Cu^{2+}			
15℃	1.110	2.097	0.960
25℃	1.540	2.144	0.900
35℃	1.955	2.571	0.954
Pb^{2+}			
15℃	3.254	2.148	0.918
25℃	3.440	1.962	0.946
35℃	4.697	2.267	0.991
Zn^{2+}			
15℃	0.476	1.922	0.976
25℃	0.559	1.762	0.986
35℃	0.936	2.032	0.967

Table 3
Thermodynamic parameters for the adsorption of heavy metals

	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol/K)
Cu^{2+}			
15℃	−21.7	9.73	109.4
25℃	−23.0		
35℃	−23.9		
Pb^{2+}			
15℃	−22.7	13.77	127.0
25℃	−24.2		
35℃	−25.3		
Zn^{2+}			
15℃	−18.8	9.15	96.6
25℃	−19.5		
35℃	−20.7		

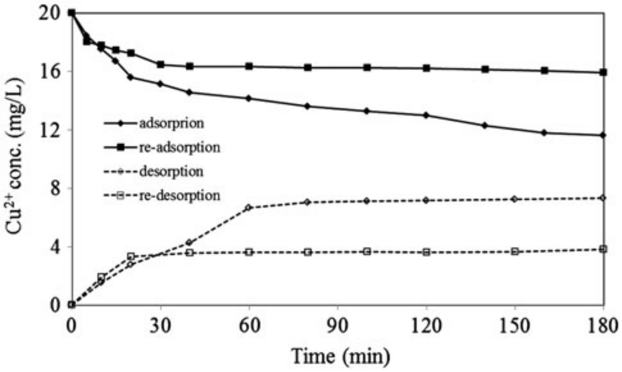

Fig. 6. Adsorption and desorption analyses of Cu^{2+} on WCRs.

process must be studied. Fig. 6 shows analyses of the adsorption and desorption of Cu^{2+} on WCRs. The Cu^{2+} on Cu^{2+}-loaded WCRs surfaces was replaced by high concentrations of H^+. The concentrations of Cu^{2+} that were removed by WCRs and released by Cu^{2+}-loaded WCRs were 8.4 and 7.3 mg/L, respectively, in the first round, and 4.1 and 3.8 mg/L in the second round, respectively. The Cu^{2+} recovery percentages in the first and second cycles were 95 and 99%, respectively, and the time to reach equilibrium in desorption and re-desorption were 60 and 20 min, respectively. Although the desorption rate increased throughout each cycle, the Cu^{2+} adsorption capacity declined significantly. The Cu^{2+}-loaded WCRs were highly desorptive, verifying the finding that adsorption proceeded by physisorption. The decrease in adsorption efficiency is attributable to (i) material degradation that is caused by the extreme pH conditions of desorption and (ii) the progressive blocking of active sites on the adsorbent by impurities, which slightly reduced adsorption potential [3,37]. Kyzas [37] demonstrated that the strong acidic conditions favor the desorption of Cu^{2+}. Furthermore, the loss of the capacity of reused coffee residues to adsorb copper is small enough to allow repeated use. The regeneration of saturated carbon by a thermal or chemical procedure is known to be expensive and results in loss of the carbon. Given that the coffee residues of the type used in this study can be obtained at nearly zero cost, and their use in bed columns or in a possible pilot-scale wastewater plant has great potential [37].

4. Conclusions

The adsorption kinetics and equilibria of Cu^{2+}, Pb^{2+}, and Zn^{2+} on WCRs were investigated. The mass of Cu^{2+} adsorbed per unit mass of WCRs increased with pH and the Cu^{2+} concentration, but it decreased as the WCR dosage increased. The adsorption kinetics was controlled mainly by surface diffusion, according to analyses using the intraparticle diffusion model.

The adsorption of Cu^{2+}, Pb^{2+}, and Zn^{2+} on WCRs was a spontaneous physisorption process, and the values of ΔH^0, ΔS^0, and maximum adsorption capacity followed the order $Pb^{2+} > Cu^{2+} > Zn^{2+}$.

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