Surface Modification of Phosphoric Acid–activated Carbon in Spent Coffee Grounds to Enhance Cu(II) Adsorption from Aqueous Solutions

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Abstract

The purpose of this study was to analyze the efficiency with which phosphorylated spent coffee grounds (PSCG) remove cationic Cu(II) ions from an aqueous solution. The pHpzc of the SCG was 6.43, but it was lowered to 3.96 in the PSCG, confirming that an acidic functional group was attached to the surface of the PSCG. According to FT-IR analysis, phosphorylation of the SCG added P=O, P-O-C (aromatic), P=OOH, and P-O-P groups to the surface of the adsorbent, and the peaks of the carboxyl and OH groups were high and broad. Also, the specific surface area, mesopore range, and ion exchange capacity increased significantly by phosphorylation. The adsorption kinetics and isothermal experiments showed that Cu(II) adsorption using SCG and PSCG was explained by PSO and Langmuir models. The maximum Langmuir adsorption capacity of SCG and PSCG was 42.23 and 162.36 mg/g, respectively. The adsorption process of both SCG and PSCG was close to physical adsorption and endothermic reaction in which the adsorption efficiency increased with temperature. PSCG was very effective in adsorbing Cu(II) in aqueous solution, which has great advantages in terms of recycling resources and adsorbing heavy metals using waste materials.

Keywords: Adsorption, Copper removal, Kinetic, Phosphoric acid, Spent coffee grounds

1. Introduction

During the past few decades, the amount and diversity of heavy metal pollution in wastewater caused by industrial activities have increased dramatically and done serious damage to the environment. Heavy metals generally are toxic and do not decompose. Consequently, they accumulate in living organisms and pose a risk to human health [1]. For example, heavy metals such as lead, cadmium, nickel, and copper are carcinogens and can cause nerve and kidney disease [2]. Copper (Cu(II)) is used commonly in many important industrial applications. As a heavy metal toxic to living organisms, copper can cause various diseases in the human body, such as liver and brain damage, central nervous system disorders, depression, and lung cancer [3]. According to the World Health Organization, the maximum allowable Cu(II) concentration in drinking water is 1 mg/L [4]. Therefore, to protect environmental safety and human health, it is essential to remove effectively Cu(II) from wastewater before it is discharged into natural water resources.

Copper ions in industrial wastewater can be reduced and recovered using any of several physicochemical methods such as chemical precipitation, membrane filtration, reverse osmosis, ion exchange, electrochemical treatment, and adsorption [1,2]. Among those methods, adsorption using activated carbon is a safe, effective, and economical method for removing copper ions from wastewater [5]. Recently, activated carbon derived from agricultural products and other biomass (gambir, orange peel, coconut shell, poplar sawdust, hazelnut shell, rice husk, walnut shell, etc.) has attracted increasing attention due to its low cost, environmental friendliness, and easy availability [6-9]. However, natural biosorbents have low adsorption efficiency and, in some cases, low mechanical strength and low selectivity [6]. To correct those shortcomings, researchers chemically modify biosorbents using various techniques to improve their properties [3,5,6]. In general, biomaterials are pretreated through physical and chemical methods [6]. Because the physical method is simple, it can be used to pretreat biosorbents [2]. However, because physical pretreatment has low efficiency in removing heavy metals from aqueous solutions, recent work has focused on surface modification using acids and bases to attach functional groups advantageous for adsorption of heavy metals [2,6]. For this reason, chemical treatment of biomass is more effective than physical methods in increasing the adsorption capacity for heavy metals in aqueous solutions [3,9]. Lasheen et al. [8] prepared an adsorbent based on a chemically modified orange peel adsorbent and found that increasing the number of carboxyl groups (-COOH) on the adsorbent enhanced Cu(II) adsorption. Chen et al. [10] modified the surface of granular activated carbon using citric acid and found that introducing

a carboxylic acid functional group (-COOH) to the carbon surface pro-vided a higher binding capacity for adsorbing copper ions. During Cu(II) adsorption, copper ions bind to acidic functional groups, such as phenol, carboxyl, hydroxyl and carbonyl groups, on the adsorbent surface [8]. According to Puziy et al. [11], phosphorus-containing and carboxyl groups are important for adsorption of Cu(II) in aqueous solutions. In addition, phosphorus-containing groups are most im-portant for Cu(II) adsorption in acidic solutions [15,16]. Therefore, to improve Cu(II) adsorption, an appropriate method is needed to increase the number of oxygen-containing or phosphorus-containing groups on the adsorbent surface.

Various methods have been studied to increase the number of phos-phorus-containing groups on adsorbents, but phosphoric acid activation is used most widely for activated carbon adsorbents [6,12] because a significant amount of phosphorus can be introduced into the carbon structure [13]. Phosphorus-containing activated carbon contains several specific acid groups on the surface that play an important role in Cu(II) adsorption [6]. In particular, phosphoric acid promotes bond cleavage reaction in aqueous solution and crosslinking through cycliza-tion and condensation to form a bonding layer of, for example, phos-phate and polyphosphate ester that can protect the internal pore struc-ture [5,14], producing an excellent adsorbent for aqueous solutions. According to previous studies, phosphoric acid−activated adsorbents can be recycled and have various other advantages such as low toxicity [13,15].

Various sources of biomass (microalgae, sawdust, sugar cane husk, corn stalk, crab husk, etc.) have been used to adsorb Cu(II) from aque-ous solutions, as use of biomass can reduce the amount of waste dis-charged [5,6]. For that purpose, spent coffee grounds (SCG) are a suit-able carbon-based biomass from which to create an adsorbent for Cu(II) removal. Coffee is the second most consumed beverage world-wide after water, with 6 million tons of soluble coffee produced annu-ally [6]. Therefore, a large amount of SCG is produced every year, and that amount is expected to increase steadily. SCG contain many forms of organic matter, including lignin, cellulose, hemicellulose, and other polysaccharides, that can be used as sources for other value-added products [17]. For example, SCG are being studied as an adsorbent for biodiesel production, a source of sugar, a precursor for the production of activated carbon, compost, a raw material for antioxidant extraction, and an adsorbent for metal ion removal [18]. Previous studies have demonstrated that SCG can be used to successfully reduce or remove Cu(II) from copper-contaminated solutions [17]. However, the removal efficiency is low compared with existing technology, and a large amount of SCG is required to increase the removal efficiency [19,20]. Adsorbing hazardous substances using SCG is useful in terms of re-cycling waste. Many studies have been published about using SCG to adsorb various heavy metals and dyes, but few papers have reported the phosphorylation of SCG to remove Cu(II) from aqueous solutions or analyzed the removal efficiency. Therefore, in this study, SCGs were activated using phosphoric acid to increase their efficiency in re-moving Cu(II) from an aqueous solution. The activated SCG were used to remove Cu(II), a heavy metal emitted from industrial processes,

from an aqueous solution, and the removal efficiency was analyzed. Various experiments were conducted to optimize the Cu(II) removal ef-ficiency, and the data were analyzed using adsorption kinetics and ad-sorption isotherm equations. A thermodynamic analysis was performed using Gibb's free energy equation.

2. Materials and methods

2.1. Phosphorylation of spent coffee grounds

SCG were collected from a coffee shop in Gangneung and washed several times with distilled water to remove contaminants. The washed SCG were dried at 75 ± 2 °C for 24 hours to evaporate moisture. The dried SCG were milled using an agricultural mill (SWISSMEX model Junior-r), and material that passed through 40 - 60 mesh (particle sizes of 0.25 - 0.4 mm) was recovered and stored in a desiccator until fur-ther use. The method for activating SCG into porous carbon using phosphoric acid (H_3PO_4) was as follows: 100 mL of 85% phosphoric acid and 75 g of phosphorus pentoxide were dissolved under heating and stirring. After cooling, 20 g of SCG were added to the mixture, and phosphorylation was induced by stirring at 150 rpm for 5 hours in a reaction device. The mixed sample was left at room temperature for 4 hours to allow the reaction to complete, and then 1 N sodium hydroxide was added to pH 7.5 - 8.0. The mixture was washed with distilled water until it was neutral, put in a dryer, and dried for 24 hours. The phosphorylated SCG (PSCG) were stored in a desiccator for use in experiments.

2.2. Adsorbate

The Cu(II) selected as the heavy metal to be adsorbed from the aqueous solution was GR grade $Cu(NO_3)_2$ (Duksan Pure Chem., Co. Ltd. Korea, purity $\geq$ 99%). Cu(II) was prepared at a concentration of 1000 mg/L, diluted with distilled water, and used to prepare solutions of the required concentrations.

2.3. Experimental design

To investigate the effect of Cu(II) adsorption on SCG and PSCG, various experiments were conducted in batch tests. Solutions contain-ing various concentrations of Cu(II) were put into 1 L Erlenmeyer flasks, and adsorbents were added according to the experimental plan to observe the Cu(II) removal efficiency of SCG and PSCG. The ef-fects of various parameters on that efficiency were tested while con-trolling other parameters. To investigate the effect of the amount of SCG and PSCG, the amount of adsorbent was varied from 0.5 to 3 g/L, and pH and temperature were held at 7 and 25 °C, respectively. To examine the effect of pH on adsorption efficiency, it was adjusted from 1 to 10, and the amount of adsorbent and temperature were held at 1 g/L and 25 °C, respectively. The initial concentration of Cu(II) (5 - 200 mg/L), contact time (0 - 240 min) and temperature (15 - 45 °C) were varied to test their effects. Sampling was performed at pre-determined times (0, 10, 20, 30, 60, 120, 240 min) while stirring at 120 rpm in a shaking incubator. To examine the adsorption kinetics, the Cu(II) concentration was increased from 50 to 300 mg/L.

2.4. Analytical methods

pH was measured using a pH meter (HM-30R, DDK-TOA), and the carbon, hydrogen, and nitrogen contents of the SCG and PSCG were measured using a fully automatic Vario EL element analyzer (PerkinElmer, USA). The lignin and hemicellulose contents were measured according to the GB/T 2677.8-94 and GB/T 2677.10-1995 standards, respectively. The cellulose content of the SCG was determined using the chlorite method [20] and sulfuric acid solubilization [21]. The collected sample was centrifuged at 1500 rpm for 10 minutes and filtered using a 0.45 μm Whatman filter, and the amount of Cu(II) was measured using atomic absorption spectrometry (Perkin Elmer, AAS 3300, USA). The FT-IR spectra of the SCG and PSCG were analyzed using a Perkin Elmer FT-IR 1760X (USA), and the pH point of zero charge value (pHpzc) of SCG and PSCG was analyzed according to a previously published method [22]. All experiments were repeated five times, and the average value was used as the experimental result. When testing one parameter, other parameters were fixed. The pH was measured using a pH meter (SevenGO pro, Mettler Toledo). The adsorption kinetics were analyzed using pseudo-first-order (PFO) and pseudo-second-order (PSO) models, and the isothermal adsorption was analyzed using the Langmuir, Freundlich, and Temkin models. The thermodynamics were analyzed using the Gibb's free energy equation. The various models used in the interpretation of the experimental results are summarized in Table 1.

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

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

To select appropriate kinetic and isotherm models for the Cu(II) adsorption process, Chi-square (χ^2) was calculated using equation (3).

$$\chi^2 = \sum_{i=1}^{n} \frac{(q_{e,\exp} - q_{e,cal})^2}{q_{e,cal}} \tag{3}$$

where $q_{e,\exp}$ and $q_{e,cal}$ are the equilibrium adsorption capacity obtained from the experiments and models, respectively.

3. Results and discussion

3.1. Characterization of adsorbents

3.1.1. Physical characteristics

Table 2 summarizes the component analysis results of the SCG and PSCG. The major components of SCG and PSCG were carbon and oxygen, but they also contained small amounts of hydrogen and nitrogen. After phosphorylation, the oxygen content of the SCG increased and the carbon content decreased, perhaps due to the release of volatiles during phosphorylation. The relatively high oxygen content is thought to result from the high level of active chemicals used [15,21]. As the H/C ratio approaches 1, the aromaticity of the bio-adsorbent increases; as the O/C ratio increases, the anionic properties of the bio-adsorbent are strengthened by an increase of carboxylate groups on the adsorbent surface, which tends to increase the adsorption capacity for cationic substances [9,23]. After phosphorylation, the H/C ratio of the SCG improved from 0.11 to 0.16, and the O/C ratio increased from 0.64 to 0.81. Thus, the number of carboxyl groups in the SCG adsorbent increased after phosphorylation, particularly the contents of oxygen, hydrogen, and nitrogen, indicating that the numbers of -OH and -NH groups in the adsorbent increased.

Adsorbent ion exchange capacity describes its ability to adsorb an adsorbate in an aqueous solution. It is expressed as the equivalent or weight of the ions obtained by adsorbing a certain volume of adsorbent [24]. According to previous studies, the ion exchange capacity is not necessarily proportional to the adsorption amount of harmful sub-

Table 1. Adsorption Kinetic, Isotherm and Thermodynamic Models

Model	Equation	Parameters
PFO	$\ln(q_e - q_t) = \ln q_e - k_1 t$	q_t: amount of adsorbate adsorbed at time (mg/L) q_e: equilibrium adsorption capacity (mg/g) k_1: pesudo-first-order rate constant (1/min) t: time (min)
PSO	$\dfrac{t}{q_t} = \dfrac{1}{k_2 \cdot q_e^2} + \dfrac{t}{q_e}$	k_2: pseudo-second-order-rate constant (L/mg·min)
Langmuir	$\dfrac{1}{q_e} = \dfrac{1}{q_m K_L}\dfrac{1}{C_e} + \dfrac{t}{q_m}$ $R_L = \dfrac{1}{1 + K_L C_0}$	q_m: maximum adsorption capacity (mg/g) K_L: Langmuir constant (L/mg) C_e: equilibrium adsorbate concentration in solution (mg/L) C_0: initial adsorbate concentration in solution (mg/L) R_L: separation factor
Freundlich	$\ln q_e = \ln K_F + \left(\dfrac{1}{n}\right)\ln C_e$	K_F: Freundlich constant (mg/g(L/mg)$^{1/n}$) n: heterogeneity factor
Temkin	$q_e = B\ln K_T + B\ln C_e$	K_T: Temkin equilibrium binding constant (L/mg) B: Temkin constant (J/mol)
Gibbs Free Energy	$\triangle G° = \triangle H° - T\triangle S°$	$\triangle G°$: Gibbs free energy change (kJ/mol) $\triangle H°$: enthalpy change (kJ/mol) $\triangle S°$: entropy change (kJ/mol·K)

Table 2. Physico-chemical Characteristic of Spent Coffee Ground (SCG) and Phospholylated Spent Coffee Ground (PSCG) (unit: %)

Component (wt. %)		SCG	PSCG
C		56.42	49.26
O		36.23	40.14
H		5.02	7.74
N		1.82	2.08
Lignin (%)		30.8±1.7	5.1±0.4
Hemicellulose (%)		51.7±0.7	53.2±1.5
Cellulose (%)		17.4±0.3	41.4±1.2
Porosity (%)		33.6 ± 0.42	83.4 ± 1.14
Density (kg/m^3)		526 ± 11.2	274 ± 7.5
Pore size (nm)	<2	86.7 ± 2.9	2.6 ± 0.7
	2-50	12.9 ± 0.5	96.9 ± 2.1
	>50	0.4 ± 0.01	0.5 ± 0.02
BET surface area (m^2/g)		8.15	26.32
Ion exchange capacity (meq/g)		1.32	4.62

Figure 1. The pHpzc for SCG and PSCG in aqueous solution

stances in aqueous solutions, but it does affect the adsorption amount [2,7]. That is, in general, when comparing the capacity for a single adsorbent, a high ion exchange capacity indicates a high adsorption amount, and vice versa [8,12]. As a result of phosphorylation of SCG, the ion exchange capacity increased from 1.32 to 4.62, by approximately 3.5 times.

The pore size of the adsorbent also can affect its adsorption efficiency. According to previous studies [19,20], the adsorption efficiency for Cu(II) was highest when the pores size were micro-meso (2 - 50 nm) rather than super-micro (less than 1.0 nm) or macropore (50 nm or more). The SCG pores were 86.7% micropores and 12.9% mesopores, but the modification with phosphoric acid increased the proportion of mesopores to 96.9%, which was expected to improve the adsorption efficiency for copper.

3.1.2. Surface charge analysis

General process conditions play an important role in the bioadsorption process. Key factors affecting bioadsorption include temperature, pH, biosorbent dosage, and adsorbent pore size [25]. The optimal pH value for a particular biosorbent process depends on the pHpzc of the biosorbent and the target metal ion [20,26]. For pH < pHpzc, the surface of the biosorbent acquires a positive charge and repels positively charged metal ions [5,6]. On the other hand, for pH > pHpzc, the surface of the biosorbent acquires a negative charge and thus attracts positively charged metal ions. In other words, at a pH above the isoelectric point, the surface of the adsorbent becomes negatively charged, and the electrostatic interaction with a positively charged adsorbent material is strong, increasing the adsorption efficiency [17,20]. Proton bonding by all carbons exhibits positive (proton adsorption) and negative (proton emission) moieties [23]. When phosphoric acid was added to SCG, it formed carbon with an acidic surface, sharply decreasing the zero charge point from 6.43 in the neutral region to 3.96
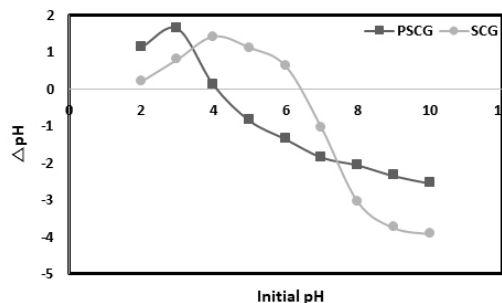
in the acidic region (Figure 1). The acidic group was attached strongly to the PSCG surface. The pH range in which Cu(II) ions can be adsorbed from an aqueous solution is widened, which could lead to an increase in adsorption capacity.

3.1.3. FT-IR spectra

The surfaces of SCG modified with phosphoric acid contained a significant number of phosphorus compounds. The IR spectrum of SCG-derived carbon shows multiple functions that can be observed in other carbons obtained through phosphoric acid activation of a lignocellulose precursor. The FT-IR spectra of the SCG and PSCG showed broadening and strengthening of certain bands according to the modification, but the basic spectrum did not change (Figure 2). A broad absorption band at 3700 - 3100 cm^{-1} (maximum 3400 - 3540 cm^{-1}) is characteristic of hydrogen-bonded hydroxyl groups (-OH) in carboxyl, phenol, or alcohol. Phosphorylation introduced a phosphate group into the SCG, forming the widest OH group (3100 - 3700 cm^{-1}) and resulting in a deeper and wider peak at 3436 cm^{-1}. The peak at 1400 cm^{-1} is a carboxyl group (-COOH) group, the one at 1059 cm^{-1} corresponds to the ether peak, and the one at 1164 - 1400 cm^{-1} corresponds to the (RO)$_3$P=O peak. The maximum value was 1220 - 1270 cm^{-1}. Absorption in that region typically occurs in oxidized carbon and corresponds to CO-stretching of acids, alcohols, phenols, ethers, and esters. The maximum value of this peak is characteristic of phosphorus and phosphorus-carbon compounds present in phosphoric acid-activated carbon. This is manifested by an increase in the content of phospho-carbon compounds such as hydrogen bonding P=O groups, P-O-C (aromatic) bonds, and P=OOH of phosphate or poly-phosphate caused by phosphorylation [2,4,27]. The small peaks at 1070 - 1090 cm^{-1} might be due to the symmetrical vibrations of the P+O- of the acidic phosphate ester and the P-O-P of the polyphosphate chain [12,23].

In the PSCG, bonded OH-groups (3000 - 3500 cm^{-1}), CH stretching (2800^{-1} - 2900 cm^{-1}), C=O carbonyl group (1740 - 1680 cm^{-1}), carboxylic group (1670 - 1640 cm^{-1}), C-O stretch (1450 - 1300 cm^{-1}), C-O-C group (1200 - 1270 cm^{-1}), PO$_3$H (1150 - 1165 cm^{-1}), and P=O group (1047 - 1120 cm^{-1}) peaks appear deep. In particular, the 1010 - 1200 cm^{-1} and 1264 - 1430 cm^{-1} peaks of the PSCG were significantly broadened compared with their counterparts in the SCG because phosphate groups were introduced there. Also, the peaks of large and small vibrations at 450 - 650 cm^{-1} indicate N-containing bioligands. In addi-
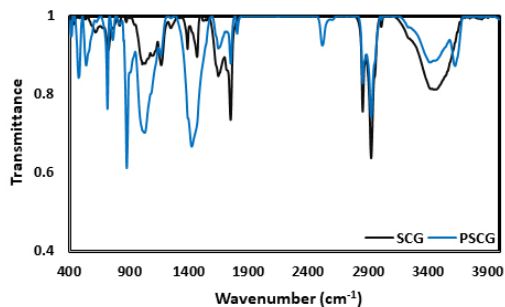
Figure 2. FT-IR spectra for SCG and PSCG

(a)

(b)

Figure 3. Effect of various dose of (a) SCG and (b) PSCG for removal of Cu(II) (pH: 7, Mixing speed: 120 rpm, T: 298 K)

tion to the surface area and porosity of the adsorbent, functional groups such as aromatic rings, -C=O, -C-O-C-, -OH, -NH$_2$, -C=S, -C=N, -P=O, -P-O-C, and P=OOH on the carbon surface play an important role in increasing the adsorption capacity for Cu(II) in an aqueous solution. In other words, as a result of reforming SCG with phosphoric acid, the number of functional groups increased, and the functional groups required for Cu(II) adsorption became wider or deeper. This indicates that phosphorylation of the SCG changed their structure into one that can easily adsorb Cu(II) in an aqueous solution. Osman *et al.* [28] reported that the adsorption capacity of metals is proportional to the number of functional groups in the adsorbent. Changes in functional groups through phosphorylation are expected to affect the adsorption efficiency for Cu(II) in an aqueous solution.

3.2. Parametric study

3.2.1. Dose of adsorbent

Figure 3 shows the adsorption capacity of the SCG and PSCG adsorbents. In both the SCG and PSCG, as the amount of adsorbent increased, the time required to reach maximum adsorption became shorter, and the total amount of Cu(II) adsorbed from the aqueous solution increased. However, the increase in the adsorption efficiency of Cu(II) was not significant when the adsorbent dose was higher than 1 g/L. In general, as the amount of biosorbent increases, the adsorption capacity for heavy metals increases [20,29]. As the amount of adsorbent increases, its adsorption capacity increases because the number of active sites available for adsorption increases [3,15]. However, several previous experiments showed that, after reaching a maximum adsorption efficiency, adsorption capacity does not increase and can even start to decrease if the biosorbent dose continues to increase [6,21] because the biosorbent particles can start to agglomerate, causing the active sites to overlap, blocking mass transfer, and reducing the efficiency of heavy metal removal [10,27]. Increasing the stirring speed of the aqueous solution can help to overcome mass transfer resistance, but it must be maintained within the optimum range of the biosorbent. If the stirring speed is too high, fragmentation of the biosorbent can occur. In general, the stirring speed is maintained at 120 - 200 rpm [15.21]. For Cu(II), maximum absorption was observed at 1 g/L of coconut shells when the stirring speed was maintained at 120 rpm at pH 5 and 30 °C [30]. For Cr(VI) ions and discharged coffee waste, the highest adsorption capacity was observed at a relatively low pH value
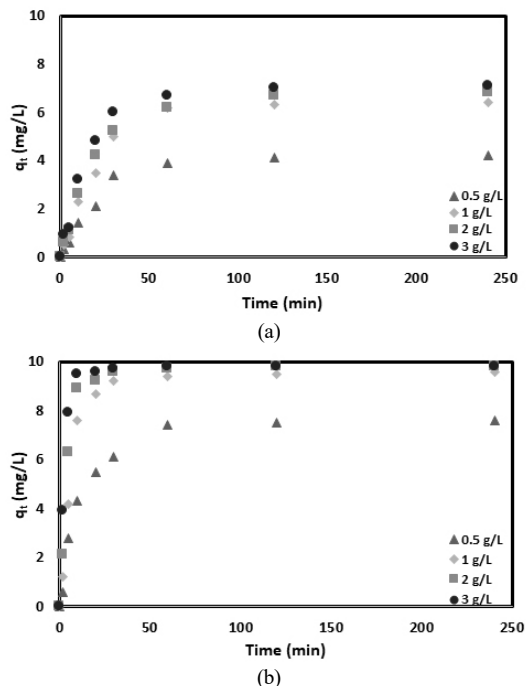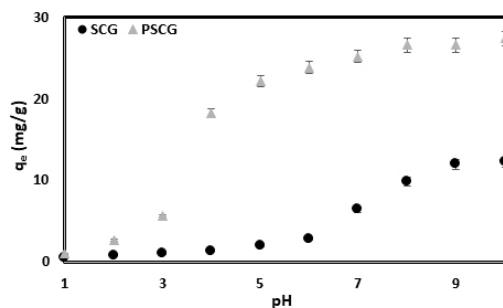

Figure 4. Effect of various pH for removal of Cu(II) on SCG snd PSCG (C: 50 mg/L, Mixing speed: 120 rpm, T: 298 K)

(pH 3); the optimal temperature, adsorbent amount, and agitation rate were 25 °C, 6.67 g/L, and 40 °C, respectively [31].

Comparing Figure 3(a) and Figure 3(b) shows that the adsorption efficiency of PSCG for Cu(II) was 1.40 - 1.81 times higher than that of SCG, and it reached the maximum adsorption value within a short time. As mentioned in the physical and surface analyses of the adsorbent, the pore size changed in favor of copper adsorption after phosphorylation introduced various functional groups and phosphate groups to the adsorbent surface. These results are consistent with the results of many other researchers who modified agricultural waste to adsorb heavy metals in aqueous solutions [5,6,10,20].

3.2.2. Effect of pH

Cu(II) removal using SCG increased at pH 7 or higher, and that with PSCG increased rapidly at pH 4 or higher (Figure 4). This phe-

nomenon is related to the pHpzc value. As mentioned above, when pH is higher than pHpzc, the surface of the adsorbent becomes negatively charged, making it easier to adsorb harmful cationic substances [12,17]. Almost all heavy metal ions, including Cd(II), Pb(II), Ni(II), Cu(II), and Zn(II), exist as cations in aqueous solutions. Therefore, a sharp increase in the adsorption efficiency was observed when pH > pHpzc. However, when the pH of the solution is lower than the pHpzc value, the H_3O^+ ions in the solution occupy active sites on the surface of the biosorbent that were expected to be occupied by metal ions, which displaces the positive charge on the surface of the biosorbent [3,17]. Therefore, when pH < pHpzc, the positively charged metal ions decrease their overall adsorption. In addition, as the pH increases, the carboxyl and phenolic hydroxyl groups of the PSCG adsorbent are de-protonated to form -P=O, -P-O-C, P=OOH, R-COO-, and R-O- groups [9,21]. That causes the surface of the PSCG adsorbent to become negatively charged, which improves the electrostatic attraction between the PSCG adsorbent and the cationic Cu(II) and increases the adsorption efficiency for Cu(II).

3.3. Adsorption kinetics and isotherms

3.3.1. Adsorption kinetics

Analyses of kinetic models in bioadsorption studies are important for understanding the reaction pathways, mechanisms, and kinetics of the bioadsorption process. In addition, understanding the adsorption kinetics makes it easier to determine the optimal conditions for physicochemical interactions, mass transport and rates, and metal adsorption processes during bioadsorption [20,22]. The bioadsorption process in this work was observed to mostly follow the PFO or PSO kinetic model. In the PFO model, the adsorption site occupancy is directly proportional to the number of free adsorption sites, but in the PSO model, heavy metal adsorption is regarded as a function of the number of free active sites and the number of heavy metal ions in the solution

Table 3. Kinetic parameters for the adsorption of Cu(II) onto SCG and PSCG (amount of adsorbent: 5g/L, pH: 7, T: 298 K)

Parameters		Concentration (mg/L)				
		50	100	150	200	300
SCG						
$q_{e,exp}$		10.69	20.37	25.26	28.63	30.56
PFO	$q_{e,cal}$	9.07	17.12	24.14	27.46	29.75
	k_1	-0.019	-0.026	-0.029	-0.037	-0.038
	R^2	0.9662	0.9658	0.9858	0.987	0.994
	χ^2	1.2849	1.3065	1.5263	1.9592	2.4654
PSO	$q_{e,cal}$	10.19	20.83	24.47	28.49	30.29
	$k_2 \times 10^{-4}$	6.59	8.40	4.82	3.53	2.97
	R^2	0.9894	0.9785	0.9987	0.9884	0.9951
	χ^2	1.1032	1.1652	1.2631	1.4286	1.6549
PSCG						
$q_{e,exp}$		40.62	72.63	95.57	126.73	148.26
PFO	$q_{e,cal}$	37.66	70.61	98.49	108.79	120.16
	k_1	-0.0245	-0.0323	-0.036	-0.0397	-0.035
	R^2	0.9519	0.9875	0.9776	0.9658	0.9649
	χ^2	1.2016	1.2653	1.3265	1.5986	1.9872
PSO	$q_{e,cal}$	39.48	71.37	95.97	125.14	148.73
	k_2	1.21e-5	2.01e-6	8.31e-7	4.05e-7	2.50e-7
	R^2	0.9908	0.9898	0.999	0.9904	0.991
	χ^2	1.0236	1.0862	1.1586	1.3265	1.5406

[15,25]. To investigate the kinetics of Cu(II) adsorption onto SCG and PSCG, the experimental results were analyzed using the PFO and PSO models, and the results are presented in Table 3 and Figure 5.

In the adsorption kinetics analysis, $q_{e,cal}$ of PSO was closer to the value of $q_{e,exp}$ than was $q_{e,cal}$ of PFO. In addition, the PSO correlation
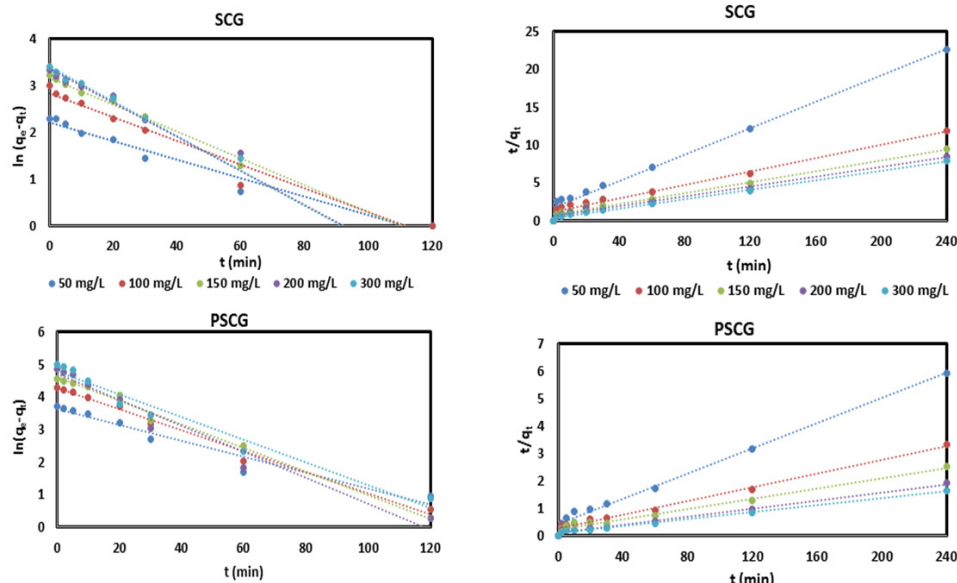

Figure 5. Linear plot of (a) PFO and (b) PSO (C: 50-300 mg/L, Mixing speed: 120 rpm, T: 298 K)

coefficient (R^2) was higher than that of the PFO model for both SCG and PSCG, and χ^2 was lower in the PSO model than the PFO model. Therefore, the process of adsorbing Cu(II) in an aqueous solution using SCG and PSCG was better described by the PSO model than the PFO model. Also, the values of k_1 in the PFO model and k_2 in the PSO model decreased as the concentration of Cu(II) increased for both the SCG and PSCG adsorbents. This indicates that the adsorption rate decreased as the concentration of Cu(II) increased. That occurred because, as the concentration of Cu(II) in the aqueous solution increased, the number of active sites available for adsorption decreased. In particular, PSCG showed higher Cu(II) adsorption efficiency than SCG, which is related to the various functional groups and ion exchange capacity on the adsorbent surface and the pore size of the adsorbent, as explained in the surface analysis above.

3.3.2. Adsorption isotherms

The interaction between the metal and the biosorbent at the equilibrium solute concentration and a constant temperature was studied with the aid of biosorbent isotherms. Adsorption isotherms help to explain the bioadsorption mechanism and determine the arrangement of bioadsorption sites and the adsorption of metal ions to the biosorbent surface [12,32]. According to the Langmuir model, adsorption of metals can only occur in a monolayer manner (only a single layer of molecules is attached to the surface of the biosorbent) [15,17]. The Freundlich isothermal equation is suitable for application when the concentration of metal ions in an aqueous solution is low [6,20]. The Freundlich model is expressed as a multilayer with heterogeneous biosorbent surfaces and intermolecular interactions with different adsorption [9,10]. The Temkin isotherm is a model used to evaluate the relationship between a biosorbent surface and the heat of adsorption of any molecule [1,23]. It shows that the heat of adsorption of all molecules

Table 4. Adsorption isotherms for Cu(II) on SCG and PSCG at 298 K.

Isotherm	Parameters	SCG	PSCG
Langmuir	q_m	42.23	162.36
	K_L	3.07	3.19
	R^2	0.9729	0.9917
	χ^2	2.0561	1.4562
Freundlich	K_F	6.48	15.38
	1/n	0.12	0.61
	R^2	0.9031	0.9428
	χ^2	3.0534	2.7542
Temkin	B	11.54	16.91
	K_T	24.59	43.25
	R^2	0.5873	0.6486
	χ^2	4.3267	3.5622

decreases linearly as the biosorbent surface coverage increases [22,26]. The results of the isothermal adsorption experiment were analyzed using the models of Langmuir, Freundlich, and Temkin, and the results are presented in Table 4 and Figure 6.

The dimensionless separation factor [R_L (=$1/(1+K_LC_o)$)] calculated by Langmuir's equation was between 0.01 and 0.02, and the Temkin isothermal adsorption constant, B, was 11.54 (J/mol) for SCG and 16.91 (J/mol) for PSCG, which corresponds to the physical adsorption region (B<20 J/mol). Therefore, adsorption of Cu(II) by SCG and PSCG was closer to physical adsorption through Van der Waals forces (dispersing and electrostatic forces) than to chemical adsorption in which the chemical form of the adsorbed material is changed by a reaction between the adsorbate and the adsorbent. K_F is a measure of the adsorption capacity calculated from Freundlich's equation, and the higher is
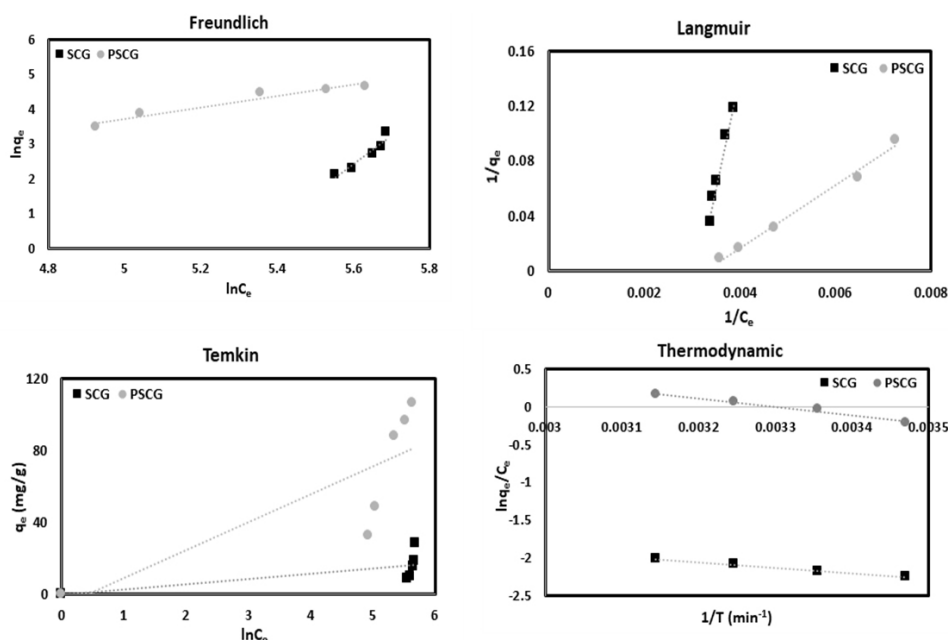

Figure 6. A plot of Langmuir, Freundlich, Temkin and Thermodynamic of Cu(II) onto SCG and PSCG

its value, the better is the adsorption capacity [1,17]. The K_F of the PSCG adsorbent was 16.38 [mg/g $(L/mg)^{1/n}$], which is higher than that of the SCG [6.48 mg/g $(L/mg)^{1/n}$], indicating that the adsorption ability of the PSCG was superior to that of the SCG. As for 1/n, which indicates adsorption strength, SCG and PSCG showed values of 0.12 and 0.61, respectively, indicating that PSCG had a higher strength than SCG in adsorbing Cu(II) in an aqueous solution. As for the correlation coefficient (R^2), which shows the applicability of each adsorption model, the Langmuir model for both SCG and PSCG was higher than that of the Freundlich or Temkin model. Thus, adsorption of Cu(II) onto SCG and PSCG was best explained by the Langmuir model. The Langmuir maximum adsorption capacity was calculated to be 42.23 mg/g for SCG and 162.36 mg/g for PSCG, indicating that PSCG adsorbed approximately 3.8 times more Cu(II) than did SCG.

3.4. Adsorption mechanism

Many functional groups can adsorb heavy metal cations in aqueous solutions. For example, O- and N-donors have yielded interesting results due to the single pair of oxygen or nitrogen atoms, and the nature of those functional groups is highly pH dependent [25,33]. Conversely, the nature of the acidic group in a polymer adsorbent changes as a function of pH, which enables efficient sorption of metal cations and easy regeneration of the material. Therefore, polymers containing carboxylic acids and phosphonic acids have been used widely to adsorb cations such as heavy metals [12]. PSCG, a strong acidic resin, have a good ion exchange capacity due to the phosphoric acid groups contained in the adsorbent. According to the literature [6,10], strong acidic resins adsorb almost all the cations contained in an aqueous solution by exchanging them with hydrogen ions. Because that ion exchange process is reversible, resins can be regenerated using strong acids when the ion exchange capacity is exhausted [12]. In addition, PSCG had a lower pHpzc than did SCG, so the range of application for cation adsorption was wider than that of SCG.

The surface functional groups of the adsorbent play an important role in binding the adsorbent surface to the adsorbate [15,20]. The FT-IR analysis showed that phosphorylation improved the number of carboxyl groups (-COOH) and increased the porosity and carbon surface area. In addition, in the process of adsorbing Cu(II), the phosphoric acid group in the PSCG expanded the pore shape and increased the exposure of anions on the surface. As a result, the adsorption efficiency of PSCG for Cu(II), a cationic ion, was improved. Peng et al. [32] reported that P-containing surface groups are important for the adsorption of Cu(II) in solution. These results are consistent with the previously discussed results showing that the adsorption capacity of Cu(II) clearly correlates with the numbers of carboxylic groups and phosphate and pyrophosphate groups. The process of adsorbing Cu(II) using an adsorbent phosphorylated in an aqueous solution can be summarized as follows.

$$R\text{-}OH + Cu(NO_3)_2 \rightarrow R\text{-}O\text{-}Cu + H(NO_3)_2 \quad (4)$$
$$R\text{-}NH_2 + Cu(NO_3)_2 \rightarrow R\text{-}N\text{-}Cu + H_2(NO_3)_2 \quad (5)$$
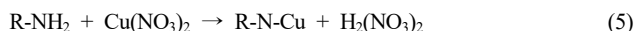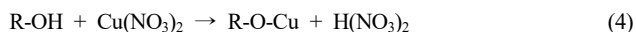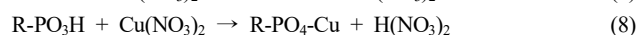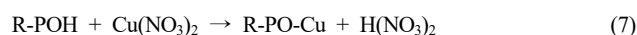$$R\text{-}COOH + Cu(NO_3)_2 \rightarrow R\text{-}COO\text{-}Cu + H(NO_3)_2 \quad (6)$$

Table 5. Thermodynamic parameters for adsorption of Cu(II) onto SCG and PSCG.

Adsorbent	Temperature (°C)	Thermodynamic		
		$\triangle G°$	$\triangle H°$	$\triangle S°$
SCG	288	-0.70		
	298	-0.72	6.11	2.45
	308	-0.75		
	318	-0.77		
PSCG	288	-8.9		
	298	-9.23	9.38	31.01
	308	-9.54		
	318	-9.85		

$$R\text{-}POH + Cu(NO_3)_2 \rightarrow R\text{-}PO\text{-}Cu + H(NO_3)_2 \quad (7)$$
$$R\text{-}PO_3H + Cu(NO_3)_2 \rightarrow R\text{-}PO_4\text{-}Cu + H(NO_3)_2 \quad (8)$$

The number of oxygen-containing functional groups in the modified PSCG was greater than that in the SCG, and the surface area was larger, allowing the PSCG to adsorb Cu(II) much more strongly than did the SCG. In addition, the surface area of the PSCG was modified by phosphoric acid, which had a significant effect on the sorption of Cu(II). The PSCG adsorbed about 4.6 times more Cu(II) than did the SCG, which is consistent with the FT-IR analysis showing that the PSCG had more carboxyl (-COOH) and hydroxyl (-OH) functional groups than the SCG, because groups such as P=O and P=OOH attached to the surface interacted with Cu(II) ions in the aqueous solution and formed a complex. Therefore, the adsorption of Cu(II) ions by the modified PSCG used the surface complexation mechanism between oxygen-containing functional groups and the Cu(II) metal.

3.5. Thermodynamic interpretation

In the adsorption process, temperature affects the solubility of metal ions and potential ion exchange materials, which can determine the adsorption rate and efficiency, because the solubility of metal ions can induce ion exchange on the adsorbent surface. Thermodynamic analysis was performed using Gibb's free energy equation, and the results are presented in Table 5.

The values of $\varDelta H$ and $\varDelta S$, calculated from the slope and intercept of the van 't Hoff plot (lnk_d vs. 1/T), are shown in Figure 5. The value of $\varDelta G$ was negative in both SCG and PSCG, so the adsorption process was spontaneous and corresponded to the range of 0 to -20 kJ/mol, and the enthalpy ($\varDelta H$) was less than 80 kJ/mol, indicating that the adsorption process was spontaneous [17,32]. The adsorption of Cu(II) to the surface was closer to physical adsorption than chemical adsorption. A positive enthalpy value indicates an endothermic reaction in which the removal efficiency increases with temperature, and a negative value indicates an exothermic reaction in which the removal efficiency decreases as temperature increases [6,22]. In this experiment, $\varDelta H$ and $\varDelta S$ have positive values, so the adsorption of Cu(II) from an aqueous solution using SCG or PSCG is an endothermic reaction, and the randomness of the adsorbent surface is high. In particular, the $\varDelta S$ value

is higher for PSCG than for SCG, so the randomness of the adsorbent surface increased in the order of SCG<PSCG. It is thought that entropy increases as the kinetic energy of molecules increases with temperature, which increases molecular motion [5,33]. Opinions about exothermic and endothermic reactions in previous studies about adsorbing heavy metal from aqueous solutions using a bio-adsorbent differ depending on the type of biomass because the stability and solubility of ligands and biosorbents vary with temperature. According to some previous studies [6,11], most of the bioadsorption process is endothermic, so increasing the temperature increased the surface activity, which increased the removal efficiency by decreasing the thickness of the boundary layer surrounding the adsorbent [12,23]. However, the temperature should be optimized by type of bio-adsorbent because excessive temperature decomposes the active biomolecules in the biosorbent; and the active site, structure, and pore size of the biosorbent are altered, reducing the removal efficiency.

4. Conclusions

This study analyzed the efficiency of removing Cu(II) from an aqueous solution by phosphorylating spent coffee grounds. After phosphorylation of SCG, P=O groups, P-O-C (aromatic) bonds, P=OOH, and P-O-P appeared on the surface of the adsorbent, and the peaks of the carboxyl groups and OH-groups became large and broad. Moreover, the specific surface area, mesopore range, and ion exchange capacity were significantly increased in the PSCG. The pHpzc of PSCG was lower than that of SCG, and it was confirmed that an acidic functional group was attached to the surface after SCG were modified with phosphoric acid. The adsorption kinetics and isothermal adsorption test results for Cu(II) on SCG and PSCG were explained by the PSO and Langmuir models. The maximum Langmuir adsorption capacity was 42.23 for SCG and 162.36 mg/g for PSCG, indicating that PSCG adsorbed about 3.8 times more Cu(II) than SCG. The adsorption process for SCG and PSCG was close to physical adsorption, and it was an endothermic reaction. PSCG modified with phosphoric acid was very effective in adsorbing Cu(II) in an aqueous solution. This finding has great significance in terms of recycling waste resources that can adsorb and remove heavy metals.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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