Effect of phosphorylation degree in adsorbent on lead adsorption from aqueous solutions

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ABSTRACT

An attempt was made to optimize the phosphorylation degree of the spent coffee ground (SCG) by comparatively analyzing the removal efficiency of lead, one of the toxic substances emitted in industrial processes. The SCG surface was modified using various concentrations of phosphoric acid (R1: phosphoric acid 0% (control), R2: phosphoric acid 20%, R3: phosphoric acid 40%, and R4: phosphoric acid 60%). As the concentration of phosphoric acid increased, the content of phosphocarbon compounds such as hydrogen-bonded P=O groups, P–O–C (aromatic) bonds, and P=OOH of phosphate or polyphosphate increased due to phosphorylation and slightly decreased bonded–OH groups. The maximum adsorption capacities of the Langmuir model were 33.67, 185.19, 188.68, and 192.31 mg/g for R1, R2, R3, and R4, respectively. An adsorbent optimized by phosphorylation of lignocellulose-based adsorbent that is abundant and easy to purchase anywhere, such as SCG is a promising adsorbent that can efficiently adsorb Pb(II) in aqueous solution.

Keywords: Adsorption; Kinetic; Lead removal; Phosphorylation; Spent coffee ground

1. Introduction

With the development of various industries, the amount of toxic heavy metals has also increased tremendously, which is directly related to water pollution [1]. Among various heavy metals that cause water pollution, lead accounts for the most significant proportion [2]. This is because lead is the most used heavy metal in various industries [3]. Lead is known to be a very important toxic substance that affects the human body even at low concentrations, and as the World Health Organization (WHO) recently withdrew the allowable safety standard for lead indicates that more attention should be paid to its risk [4]. Therefore, the removal of lead from industrial wastewater is essential to maintain water quality and a green environment.

In previous studies [5–7], various methods for removing lead from wastewater (electrochemical decomposition, photocatalytic decomposition, nanofiltration, adsorption, biological treatment, etc.) have been proposed. So far, adsorption has the advantages of low initial and equipment cost, ease of operation, simplicity of design, and regeneration of adsorbent [6–8]. As an adsorbent, lignocellulose-based activated carbon is inexpensive, recyclable, and has a high porosity and high specific surface area, so it is being used in various applications such as removal of harmful substances, including lead [8,9]. Lignocellulose is a polymer in which cellulose, hemicellulose, and lignin are strongly crosslinked and bound through covalent or non-covalent bonds to form a lignocellulose matrix [9,10]. The lignocellulose precursor is a highly recommended source of activated carbon because it is readily

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available, has low cost, abundant in supply, and renewable [6,8–11]. One of the promising lignocellulose-based activated carbon precursors is spent coffee grounds (SCG), which is especially loved by many people around the world. SCG is a lignocellulosic material composed of lignin (27.5%), cellulose (45.6%), and hemicellulose (21.3%) [12]. Adsorption of hazardous substances using SCG has a very useful value in terms of recycling waste. However, natural adsorbents have low adsorption efficiency and, in some cases, low mechanical strength and low selectivity for adsorbents [13,14]. To overcome these shortcomings, researchers have modified SCG through various techniques to obtain adsorbents with much improved properties. Although many studies are being conducted to adsorb harmful substances by reforming SCG, most are produced through two main processes: carbonization or thermal decomposition and activation (physical or chemical) [8,10,13,14]. Recently, many researchers have activated SCG using chemicals such as acids and bases (such as H_2SO_4, H_3PO_4, KOH, or NaOH) [5,7,14,15]. As a result, the pore structure of the adsorbents were developed and allowed the adsorbents to be activated in a short time. In addition, chemical activation increased the adsorption efficiency by attaching a functional group favorable to the adsorption of harmful substances to the surface of the adsorbents [7,9,14].

Among various activators, phosphoric acid has the advantages of lower activation temperature and higher carbon yield than sulfuric acid and mainly generates a mesoporous structure [7,14,15]. The lower the activation temperature, the more acidic functional groups, including carboxyl, phenolic hydroxyl groups, and lactones, can be retained in the lignocellulose-based activated carbon [6,14,17]. In addition, while sulfuric acid adsorbs and removes heavy metals through ion exchange, phosphoric acid has high selectivity for harmful substances compared with sulfuric acid because it adsorbs heavy metals through ion exchange and complexation [13,17–19]. Therefore, it is more efficient to use an adsorbent activated with phosphoric acid for field application rather than heavy metal removal in the laboratory. A phosphorus-containing group is an important group for adsorbing heavy metal ions in aqueous solution, and carbon activated with phosphoric acid can be considered as a potential cation exchanger for adsorbing cationic harmful substances in aqueous solution [6,13,17,18]. Phosphoric acid promotes the bond cleavage reaction on the one hand and crosslinking through cyclization and condensation on the other hand [6,13,17]. Due to this, it forms a bonding layer such as phosphate and polyphosphate that can protect the internal pore structure and serves as an excellent adsorbent in aqueous solution. According to previous studies [16,18], phosphoric acid has various advantages such as no pollution, recyclable adsorbent, and low toxicity. Moreover, phosphorylation improved the number of carboxyls (–COOH) and hydroxyl groups, porosity, and the surface area of the activated carbon [14,17]. In particular, the formation of –PO_3 groups on the surface of the adsorbent through the phosphorylation process is expected to play an important role during the adsorption of lead in aqueous solutions [14,15]. However, according to the literature [6,14,20–22], if the degree of phosphorylation is too high, the hydration shell induced by phosphoric acid groups can act as a barrier, preventing the phosphorylated adsorbent and cationic groups from approaching each other. As a result, adsorption efficiency can decrease. Therefore, it is necessary to optimize the degrees of phosphorylation of an adsorbent.

In this study, SCG was modified using various concentrations of phosphoric acid in aqueous solution. This was used to remove lead, one of the hazardous substances emitted in the industrial process, and to analyze the removal efficiency to find the optimal concentration of phosphoric acid for SCG modification. To optimize the removal of lead, various parameters (contact time, initial concentration of lead, amount of adsorbent) were evaluated, and the experimental results were analyzed by adsorption isotherms. The properties of the adsorbent and the adsorption kinetics were used to explain the adsorption mechanism.

2. Materials and methods

2.1. Materials

2.1.1. Phosphorylation of spent coffee ground

SCG was washed several times with tap water until clear water came out and then rinsed with distilled water to remove contaminants adhering to the surface. The dried SCG having a particle size of less than 60 mesh (0.4 mm) was recovered and stored in a desiccator prior to modification with phosphoric acid. The method to activate SCG into porous carbon using phosphoric acid (H_3PO_4) is as follows. First, 200 mL of phosphoric acid (85%) and 75 g of phosphorus pentoxide were mixed and completely dissolved while heating and stirring and then cooled at room temperature. To 100 g of dried SCG, various concentrations of phosphoric acid solutions were made from the prepared stock and made up with distilled water to make a total of 100 mL. This mixture was placed in a 250 mL Erlenmeyer flask and stirred at 150 rpm in a shaking incubator for 7 h to induce phosphorylation. Specific activation conditions and experimental conditions for each sample are summarized in Table 1. R1 was SCG without modification and used as a control. In the activation experiment, SCG modified using 80% concentration of the prepared phosphoric acid particles could not be identified because lignocellulose was dissolved in a strong phosphoric acid solution. Therefore, the adsorbent modified in 80% phosphoric acid solution was excluded from this study. According to the conditions in Table 1, the adsorbents of R2–R4 were activated for 7 h using various concentrations of phosphoric acid. After the reaction, the samples were left at room temperature for 4 h to allow the reaction to occur completely, and then 1 N sodium hydroxide was added to adjust the pH to be neutral. Finally, the R1–R4 adsorbents were sufficiently washed with distilled water, put in a dryer, dried for 48 h, and stored in a desiccator for further use.

2.1.2. Adsorbate

Analytical grade $Pb(NO_3)_2$ (Duksan Pure Chemicals Co., Ltd., Korea, purity ≥ 99%) was used throughout the experiment. A stock solution of 1,000 mg/L lead was prepared, while serial solutions of the required concentrations were gradually prepared from the stock solution and distilled water.

Table 1
Experimental condition for activation of spent coffee ground using various phosphoric acid concentration

Samples	R1	R2	R3	R4
Activation conditions	Spent coffee ground	SCG (100 g) + phosphoric acid (20%) + dewater (80%)	SCG (100 g) + phosphoric acid (40%) + dewater (60%)	SCG (100 g) + phosphoric acid (60%) + dewater (40%)
rpm	150			
Reaction time	7 h			

2.2. Experiment and analytical methods

2.2.1. Characterization of samples

The carbon and oxygen contents of the adsorbent were determined using a fully automatic 'Vario EL' element analyzer (PerkinElmer, USA). The surface image and the chemical composition of the adsorbent using X-rays were analyzed using SEM (scanning electron microscopy, JSM-IT500, JEOL Ltd., Japan) and EDS (energy-dispersive X-ray spectroscopy, JSM-IT500, JEOL Ltd., Japan), respectively. The functional groups attached to each adsorbent were analyzed using FTIR (Fourier-transform infrared spectroscopy, PerkinElmer (FTIR 1760X, USA)) in a scan range of 500–4,000 cm^{-1}. BET (Brunauer–Emmett–Teller) surface area was examined using a BET Surface Analyzer (Quantachrome Instruments version 11.03) through the adsorption/desorption isotherm of N_2 performed at 77 k. The amount of adsorbent was measured using an electronic balance (XP26, Mettler Toledo, Swiss), and the pH was measured using a pH meter (SevenGO pro, Mettler Toledo).

2.2.2. Parametric study

In order to find out the adsorption efficiency of lead according to the quantity of R1–R4 adsorbent in aqueous solution, an experiment was conducted with an adsorbent amount between 0.5–3 g/L, lead concentration of 50 mg/L, pH 7 at 25°C for 2 h. The adsorption performance of the adsorbent was evaluated according to various initial concentrations of lead (5–200 mg/L) in aqueous solution, with the amount of adsorbent being 1 g/L, pH 7 at 25°C for 2 h. For the experiment on the effect of competitive ions on lead removal efficiency, various heavy metal, specifically: Cr(III), Ni(II), Cd(II), Cu(II), Fe(III), and Zn(II), which are commonly discharged from industrial wastewater, were selected as competing ions. Considering that the concentration of lead ions contained in industrial wastewater on-site is generally less than 20 mg/L, the experiment was conducted using the following experimental conditions: 20 mg/L concentration of competing ions, 1 g/L of adsorbent, pH of 7 at room temperature. All experiments were repeated three times, and the average value was used as the experimental result. Samples were taken at a set time, and the amount of lead in each sample was determined using Atomic Absorption Spectroscopy (AA-6880 Shimadzu, Japan). From the measured values, the adsorption amount and adsorption efficiencies were calculated using Eqs. (1) and (2).

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

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

where R is Pb(II) removal efficiency in aqueous solution.

To select appropriate kinetic and isotherm models for Pb(II) adsorption process, chi-squre (χ^2) was calculated using Eq. (3).

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

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

2.2.3. Adsorption kinetic and isotherm

Adsorption capacity experiments using various initial concentrations were analyzed using adsorption kinetics (pseudo-first-order, pseudo-second-order, and intraparticle diffusion) and adsorption isotherms (Langmuir, Freundlich, and Temkin). The mathematical equations and linearized forms of adsorption kinetics and adsorption isothermal equations are summarized in Table S1.

2.2.4. Reusability

In order to test the reusability of the adsorbent, an adsorption experiment was performed 8 times using the same adsorbent with an initial solution of 20 mg/L lead solution and 1 g/L of R2 adsorbent. The initial solution was reacted with the adsorbent for 120 min, sampled, and the lead concentration was measured by AAS, and the removal efficiency was calculated using Eqs. (1) and (2). After the first reuse test, the adsorbents were dried in an oven at 75°C for 4 h. The second reuse experiment was performed under the same conditions as the first reuse experiment using the dried adsorbent. The adsorbent reuse experiment was repeated with the same procedure as the first up to 8 times without a desorption step using chemicals such as NaOH or HCl.

3. Results and discussion

3.1. Characteristics of adsorbents

3.1.1. Physical characteristics

The components of the adsorbents used in the study were analyzed, and the results are summarized in Table 2. BET represents the characteristics of each sample. The BET

Table 2
Physico-chemical characteristic of samples (unit: %)

Component (mass %)		R1	R2	R3	R4
C		61.62	56.72	42.67	32.28
O		38.38	39.65	42.20	45.20
P		–	3.63	15.05	22.52
Yield of adsorbent		100	93.09	71.66	52.39
	<2	86.74 ± 2.92	2.65 ± 0.72	3.62 ± 0.13	3.71 ± 0.15
Pore size (nm)	2–50	12.93 ± 0.51	96.94 ± 2.13	96.17 ± 1.92	96.25 ± 1.74
	>50	0.42 ± 0.01	0.51 ± 0.02	0.32 ± 0.05	0.24 ± 0.04
Brunauer–Emmett–Teller surface area (m^2/g)		8.27	712.38	688.12	542.43
Pore volume (cc/g)		0.02	0.38	0.35	0.24

surface area was significantly increased in the R2–R4 adsorbent compared to R1. The activation process of SCG using phosphoric acid successfully enlarged the pores of SCG, which is considered to increase the surface area of the R2–R4 adsorbents, as long-chain polymers such as aliphatic are destroyed by phosphoric acid, as observed in FTIR analysis. The large surface areas of R2–R4 adsorbents are thought to provide sufficient active sites for lead adsorption in aqueous solution. The yield of R2 was 93.09%, with a mass loss of about 7%, but a loss of about 48% was confirmed in R4 with a high phosphoric acid concentration. This is because lignocellulose contained in the adsorbent was dissolved by the action of strong phosphoric acid as the concentration of phosphoric acid increased. Therefore, considering the high yield of the adsorbent, the increase in the surface area, and the formation of mesopores, the R2 condition is recommended for the activating of the adsorbent using phosphoric acid.

The ratio of O/C gradually increased as the phosphorylation degree of the adsorbent increased from 0.62 in R1, reached 1.40 in R4. This proves that the oxygen inside the adsorbent increased after phosphorylation of SCG. According to previous studies, it is known that the higher the O/C ratio, the stronger the anionic properties of the adsorbent, and the higher the cationic material adsorption capacity [5,9,14,17,23]. The pore size of the adsorbent can also affect the adsorption efficiency. After reforming the SCG with phosphoric acid, it was confirmed that the pore size of the adsorbent increased as a whole, and the range of mesopores (2–50 nm) increased from 12.9% to 96.9–97.2%. It is thought that the pore size increased as the high molecular weight compounds contained in SCG were destroyed into small molecules during the activation step of SCG using phosphoric acid. However, due to the strong phosphoric acid, the pore sizes of R3 and R4 decreased compared to that of R2, and this phenomenon became more pronounced as the concentration of phosphoric acid increased. This occurred because the lignocellulose in R3 and R4 were dissolved due to strong acid. According to a previous study [6,14,15,19], the adsorption efficiency of lead was highest in the micromeso (2–50 nm) size than in the super-micro (less than 1.0 nm) or macropore size (50 nm or more) size. Therefore, the increase in mesopores of the adsorbent is expected to have a favorable effect on the adsorption efficiency.

3.1.2. Surface morphology

The surface morphology of each sample was obtained using SEM, and SEM images and EDS analysis are shown in Fig. 1a. It was detected that adsorbents R2–R4 were more porous compared to R1, and their surfaces were rough, with their size and shape being heterogeneous. This type of surface provides a great advantage in the adsorption of harmful substances in aqueous solution because more adsorption sites can be provided for bonding on the adsorbents. According to EDS analysis, it was confirmed that the oxygen and phosphorus contents clearly increased as the phosphoric acid concentration increased. An increase in the oxygen content of the adsorbent is expected to have a favorable effect on the adsorption of lead in aqueous solution.

3.1.3. FTIR spectra

The FTIR spectrum of the adsorbent used in the study showed band broadening and strengthening in certain areas according to the modification, but there was no significant difference in the basic spectrum (Fig. 1b). The basic spectral characteristics of R1–R4 were N-containing biologands (600–650 cm^{-1}), PO_4^{3-} stretching (950–1,300 cm^{-1}), carboxylic groups (1,640–1,670 cm^{-1}), carbonyl groups (1,680–1,750 cm^{-1}), CH-stretching of alkane groups (2,800–2,950 cm^{-1}) and 3,100–3,600 cm^{-1} of carboxyl, phenol or hydrogen-bonded hydroxyl groups (–OH).

After reforming SCG with phosphoric acid, four major changes occurred. First, the peak at 950–1,300 cm^{-1} widened and deepened as the concentration of phosphoric acid increased. This is because a phosphate group was attached here. These peaks are characteristic of phosphorus, and phosphorus-carbon compounds present in phosphoric acid activated carbon, which appear due to an increase in the content of phosphocarbon compounds (hydrogen bonding P=O groups, P–O–C (aromatic) bonds, and P=OOH of phosphate or polyphosphate etc.) due to phosphorylation [14,17,24]. In particular, the deep peak of 1,000–1,110 cm^{-1} is due to the symmetrical oscillations of the P+O– of the acid phosphate ester and the P–O–P of the polyphosphate chain [18,22]. In summary, the functional groups required for lead adsorption became wider or deeper as a result of activating
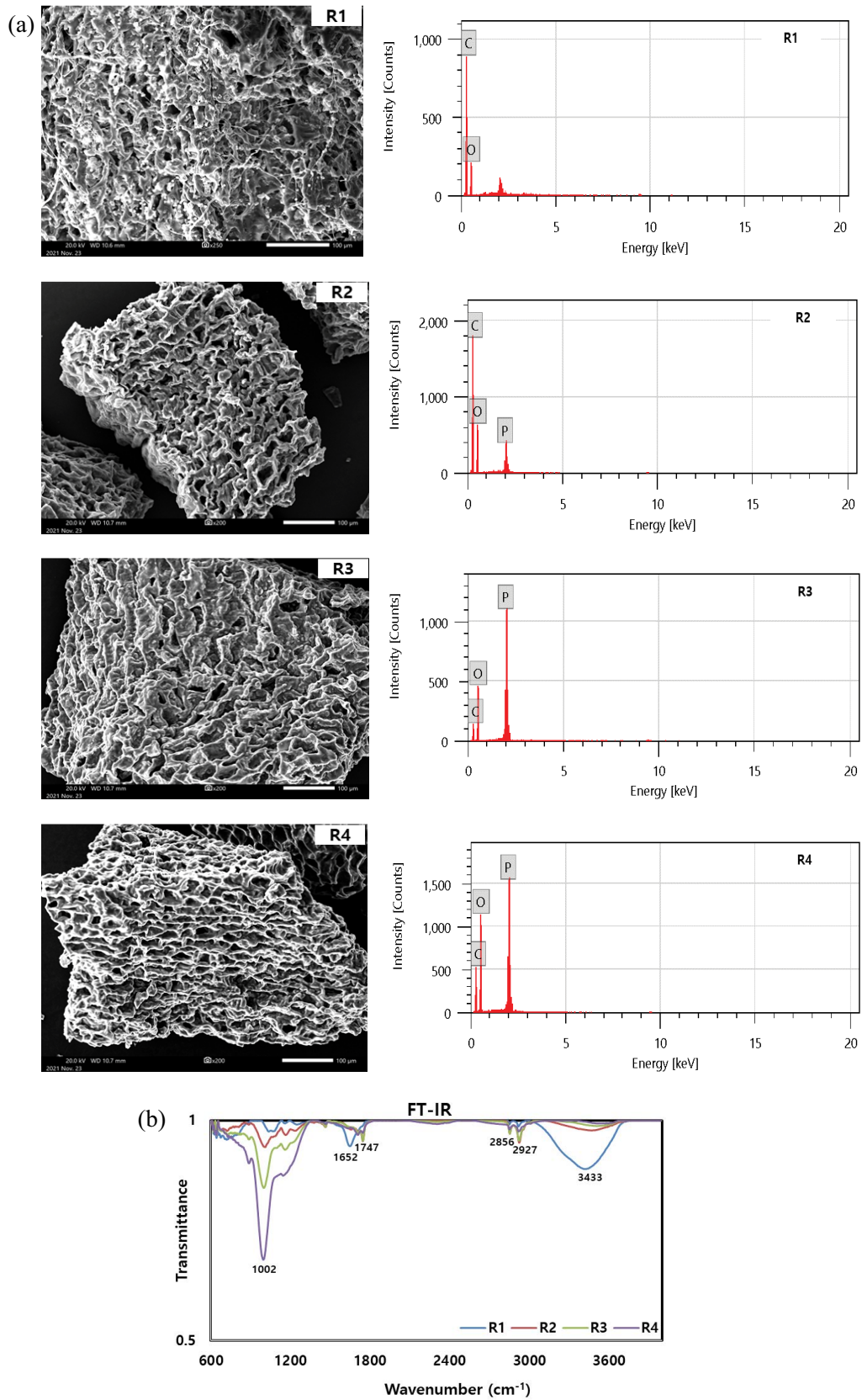
Fig. 1. Scanning electron microscopy and energy-dispersive X-ray spectroscopy (a) and Fourier-transform infrared spectra (b) for samples.

SCG with phosphoric acid. This is because the aliphatic contained in SCG was destroyed due to phosphorylation of SCG. Secondly, the bonded –OH groups (3,100–3,700 cm^{-1}) decreased with increasing phosphoric acid concentration. Thirdly, after phosphorylation of SCG, the carboxylic groups (–COOH) of 1,660 cm^{-1} slightly decreased, and the carbonyl groups (C=O) of 1,740 cm^{-1} increased. The FTIR characteristic change mentioned in the 2nd and 3rd points was that in the phosphorylation process of SCG, the hydroxyl group (–OH) shifted to the production of phospho-carbon compounds such as P=OOH, and as a result, the carboxylic group decreased and the carbonyl group increased. An increase in the carbonyl group is expected to have a favorable effect on the adsorption of lead in aqueous solution. Finally, C–H–stretching (2,800–2,950 cm^{-1}) slightly increased. The peak at 2,800–2,950 cm^{-1} is characteristic of aldehyde compounds, a group of carbonyl compounds [25]. Therefore, the increase in the C–H–stretching peak was a phenomenon that appears for the same reason as the increase in carbonyl. Carbonyls and aldehydes play an important role in the adsorption of heavy metals because they can be oxidized to carboxylic acids in aqueous solution [26,27]. The surface of the adsorbent modified with phosphoric acid contained a significant amount of phosphorus-compounds, and the surface area and porosity of the adsorbent increased due to phosphorylation of SCG. In conclusion, the presence of functional groups such as aromatic rings, –C=O, –C–O–C–, –OH, –C=N, –P=O, –P–O–C, and P=OOH on the adsorbent surface played an important role in increasing the adsorption capacity of lead in aqueous solution.

3.2. Parametric study

3.2.1. Dose of adsorbent

The adsorption efficiency according to the quantity of adsorbent plays an important role in determining whether the adsorbent can be applied to the field. This is because it is environmentally and economically advantageous if a large amount of harmful substances can be adsorbed with a small amount of adsorbent. In all of the R1–R4 adsorbents, as the amount of adsorbent increased, the time to reach the maximum adsorption was shortened, and the total concentration of lead adsorbed in aqueous solution increased. In addition, as the amount of adsorbent increased, the reaction time was very fast within the initial 10 min, and the adsorption equilibrium was quickly reached (Fig. 2a). In general, as the amount of adsorbent increases, the adsorption capacity of heavy metals increases [9,28]. This is because as the amount of the adsorbent increases, the number of active sites capable of adsorbing the adsorbent increases. However, according to the results of several previous experiments [7,13], it was observed that, after reaching the maximum adsorption efficiency, the adsorption capacity does not increase or even starts to decrease even if the amount of the adsorbent is increased. Excessive amounts of adsorbent in aqueous solution can cause the particles of the adsorbent to become entangled and clump. As a result, the active sites of the adsorbent overlap each other, and mass transfer is blocked.

In this study, lead was quantitatively removed from the aqueous solution within 30 min using 1 g/L of R2 adsorbent. In addition, it can be seen that the adsorbents R2–R4

have significantly higher lead removal efficiency compared to R1 and reached the maximum adsorption value within a short time. As already mentioned, this result is due to the change in the physical and the surface analysis of the adsorbent, from the introduction of various functional groups and phosphate groups on the surface of the adsorbent and the increase in the surface area of the adsorbent after phosphorylation. This eventually favours the adsorption of lead. This is in agreement with the research results of many researchers who reformed activated carbon to adsorb heavy metals in aqueous solution [8–10,22].

3.2.2. Initial concentration

According to the experimental results from the adsorbent dose above, the adsorption performance of the adsorbent
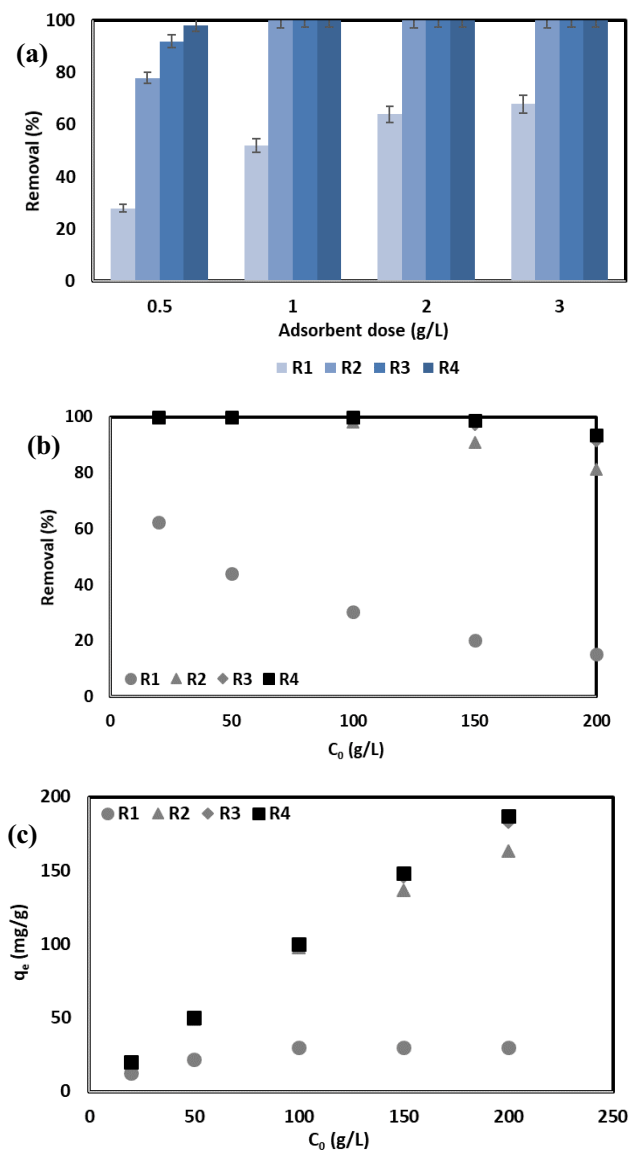

Fig. 2. Effect of (a) different adsorbent dose (adsorbent amount: 0.5–3 g/L, Pb(II) concentration: 50 mg/L, pH 7, T: 25°C), (b) initial concentration (C_o: 5–200 mg/L, adsorbent: 1 g/L, pH 7, 25°C) and (c) adsorption capacity onto various samples.

was evaluated according to various initial concentrations of lead in aqueous solution, with the amount of adsorbent being 1 g/L. As the lead concentration increased, the adsorption efficiency decreased, but the adsorption capacity increased (Fig. 2b). Adsorption of lead to R2–R4 at an initial concentration of less than 100 mg/L showed a high removal efficiency of 98% or more. Even at a concentration of 200 mg/L, R3 and R4 gave more than 90% removal efficiency and maximum adsorption capacity of 183.22 and 186.83 mg/g, respectively. The lead concentration in general industrial wastewater is less than 20 mg/L. Therefore, considering economic feasibility, an amount of 1 g/L of R2 adsorbent is recommended. The results of the adsorption capacity test according to the initial concentration of lead are shown in Fig. 2c, which is used to obtain a suitable isothermal adsorption model.

3.3. Adsorption kinetics and isotherms

3.3.1. Adsorption kinetics

Analysis of adsorption kinetic model can help understand the physical/chemical interaction of adsorbent and adsorbate, mass transport, and adsorption rate in the adsorption process, and is necessary to determine the optimal conditions for adsorption process [9,28,29]. In this study, adsorption kinetics were analyzed using three adsorption kinetic models (pseudo-first-order, pseudo-second-order and intraparticle diffusion). In order to obtain an appropriate kinetic model, the adsorption capacity of various lead concentrations was measured using various contact times and analyzed using a kinetic model. The analysis results of the adsorption kinetics are shown in Table 3 and Fig. 3a and b. The adsorption kinetics showed that the values of $q_{e,\text{cal}}$ of pseudo-second-order were closer to those of $q_{e,\text{exp}}$ than that of pseudo-first-order, the value of the correlation coefficient

(R^2) was higher, and the value of χ^2 was lower. Therefore, the process of adsorbing lead in aqueous solution using the R1–R4 adsorbent was more closely suited to the pseudo-second-order model than pseudo-first-order. Also, the values of k_1 and k_2 decreased as the concentration of lead in the aqueous solution of phosphoric acid and adsorbent increased. For each adsorbent, the adsorption rate decreased as the concentration of lead in the aqueous solution increased. This is because the higher the concentration of lead in the aqueous solution, the lower the active point that can be adsorbed to the adsorbent. In addition, it indicates that the adsorption rate increases as the phosphoric acid concentration of the adsorbent increases. This proves that the phosphoric acid functional group of the adsorbent has a very important effect on the adsorption rate and adsorption capacity.

The plot of q_t vs. t gives a straight line (Fig. 3c), and the value of k_{id} was calculated from the slope of the plot. In the internal particle diffusion model, the C value is calculated from the intercept and provides information on the thickness of the boundary layer [2,30,31]. The larger the C value, that is, the intercept, the greater the contribution of surface sorption in the speed control step. The C value showed the largest value in R4, confirming that it increased as the number of functional groups of phosphoric acid in the adsorbent increased. In addition, as the concentration of lead in the aqueous solution increased, the C value also increased.

3.3.2. Adsorption isotherm

The adsorption isotherm helps to understand the adsorption mechanism and to determine the arrangement of adsorption sites and the adsorbate on the surface of the adsorbent. The isothermal adsorption experiment data were analyzed using Langmuir, Freundlich, and Temkin models. The results are summarized in Fig. 4 and Table 4. Langmuir

Table 3
Parameters of kinetics model for adsorption of Pb(II)

| Samples	Concentration (mg/L)	Pseudo-first-order					Pseudo-second-order				Intraparticle diffusion	
		$q_{e,\text{exp}}$	$q_{e,\text{cal}}$	k_1	R^2	χ^2	$q_{e,\text{cal}}$	k_2	R^2	χ^2	k_{id}	C
R1	50	22.01	18.63	−0.0584	0.9876	1.563	22.99	8.23e-5	0.9937	1.035	0.1224	14.083
	100	30.02	21.04	−0.0579	0.9573	2.134	30.86	3.40e-5	0.9977	1.485	0.1306	22.255
	200	31.05	23.41	−0.0549	0.9535	2.895	31.65	3.15e-5	0.9987	1.896	0.1533	24.485
	300	32.18	28.47	−0.0517	0.9089	3.362	32.68	2.87e-5	0.999	2.659	0.1561	25.943
R2	50	48.32	56.72	−0.0916	0.9462	1.462	52.63	6.85e-6	0.9851	0.986	0.3385	34.437
	100	95.26	105.28	−0.0692	0.9377	1.865	102.11	8.63e-7	0.9388	1.263	0.9925	50.52
	200	163.24	211.09	−0.0656	0.9841	2.056	192.31	1.41e-7	0.9907	1.689	1.9179	69.13
	300	185.64	219.20	−0.0631	0.9834	2.526	212.77	1.04e-7	0.9925	2.068	2.1156	81.585
R3	50	49.82	55.78	−0.0923	0.9595	1.023	52.36	6.97e-6	0.9886	0.906	0.3223	35.164
	100	97.28	134.49	−0.0703	0.9094	1.285	109.89	7.54e-7	0.9562	1.175	0.9373	55.705
	200	183.46	180.07	−0.0487	0.8488	1.653	182.77	1.38e-7	0.8875	1.586	1.9889	71.682
	300	188.97	181.34	−0.0416	0.8807	1.847	187.39	1.34e-7	0.9419	1.825	2.2016	90.101
R4	50	49.95	61.73	−0.1374	0.9341	0.986	51.55	7.30e-6	0.9938	0.846	0.2523	38.545
	100	98.96	172.50	−0.1342	0.8377	1.234	107.53	8.04e-7	0.9719	1.065	0.8416	60.682
	200	186.87	204.67	−0.0681	0.9278	1.586	189.39	1.28e-7	0.9994	1.309	1.9629	78.119
	300	193.28	215.98	−0.0518	0.9418	1.764	207.13	1.07e-7	0.9404	1.618	2.1901	98.689
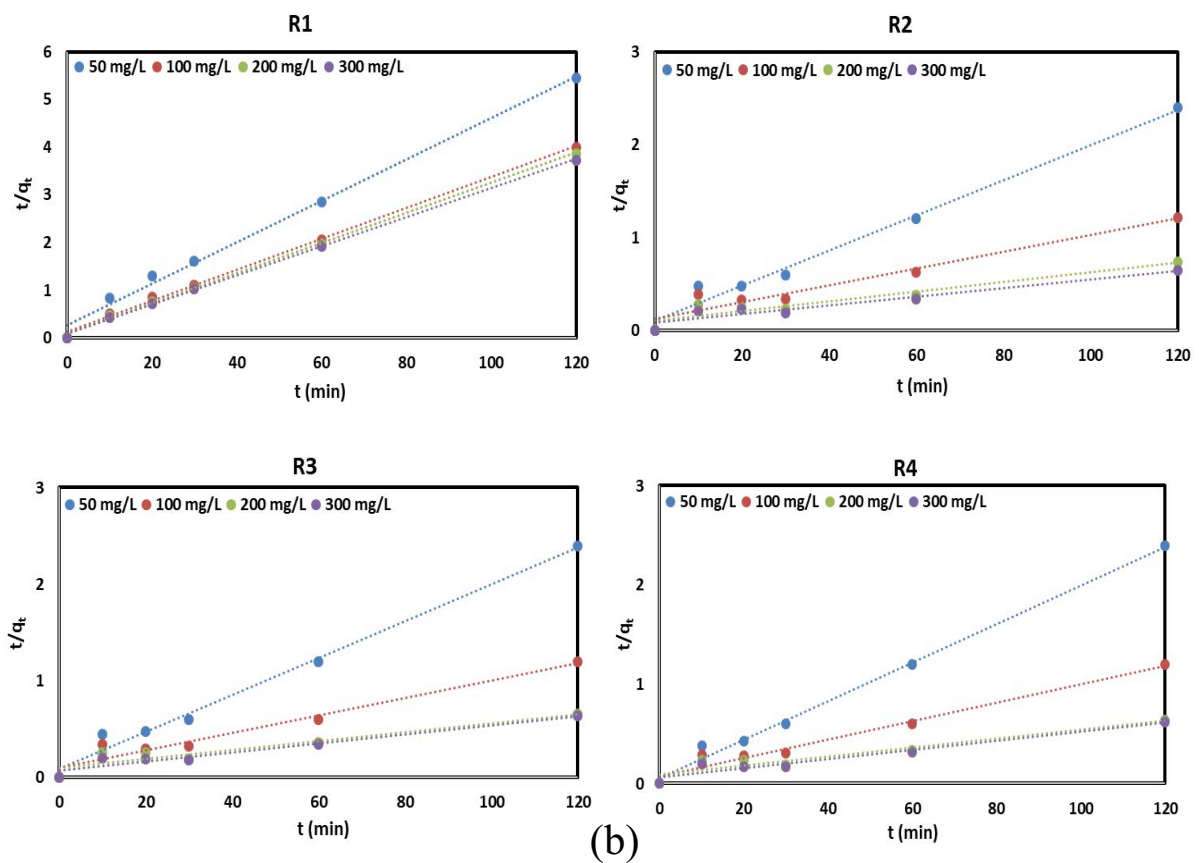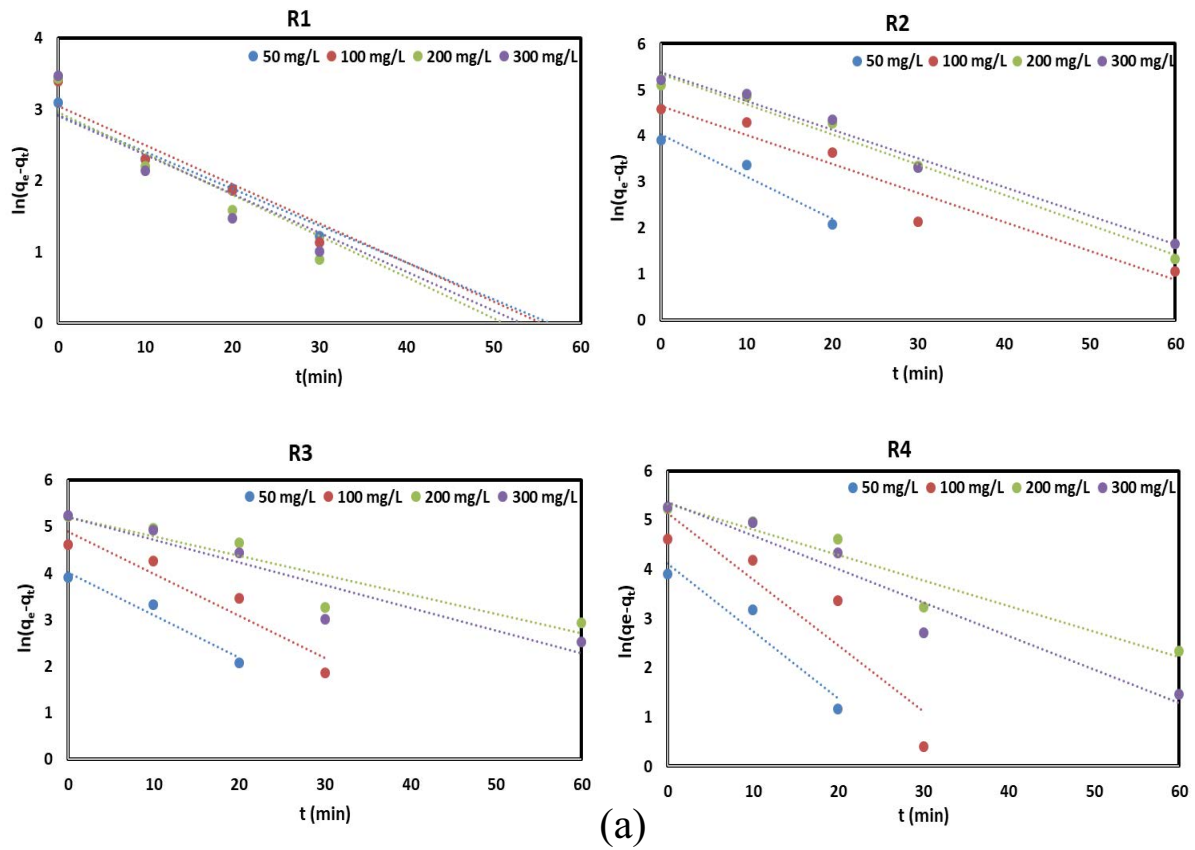
Fig. 3. (Continued)
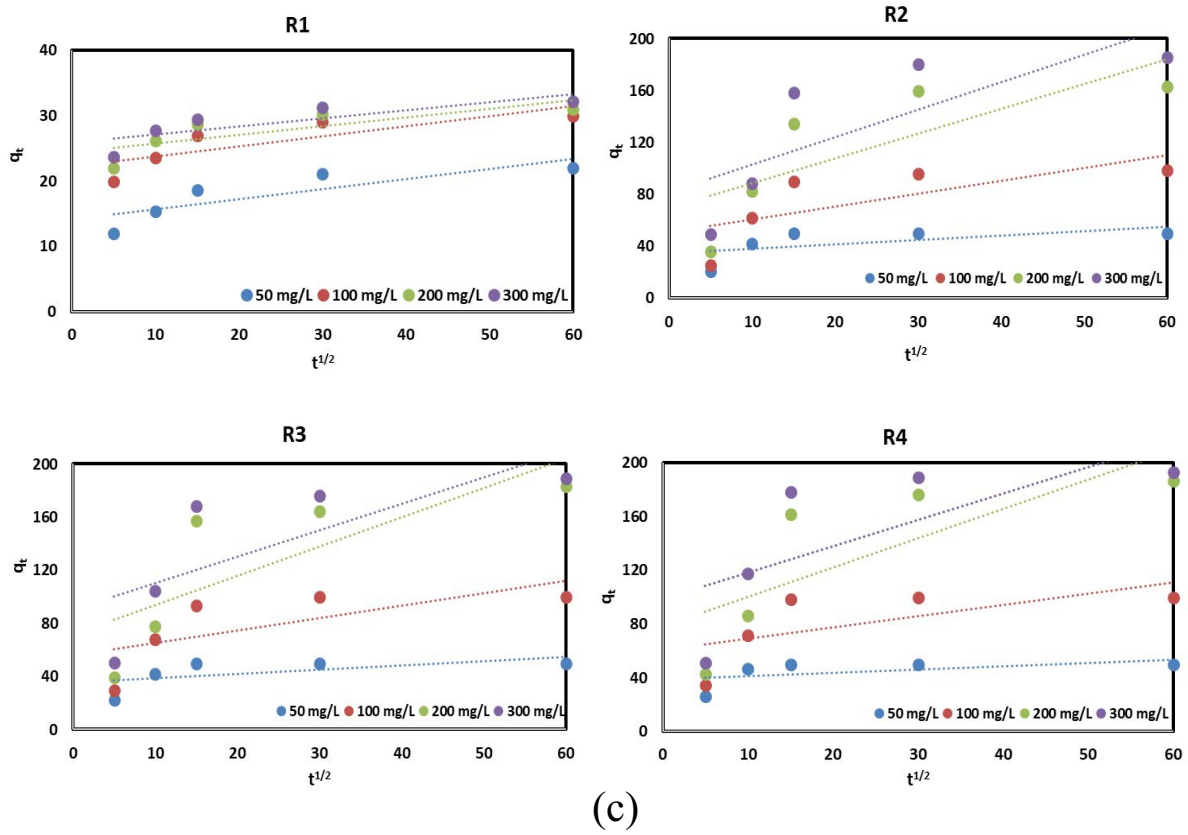
Fig. 3. A linear plot of (a) pseudo-first-order, (b) pseudo-second-order and (c) intraparticle diffusion for Pb(II) adsorption by various samples.
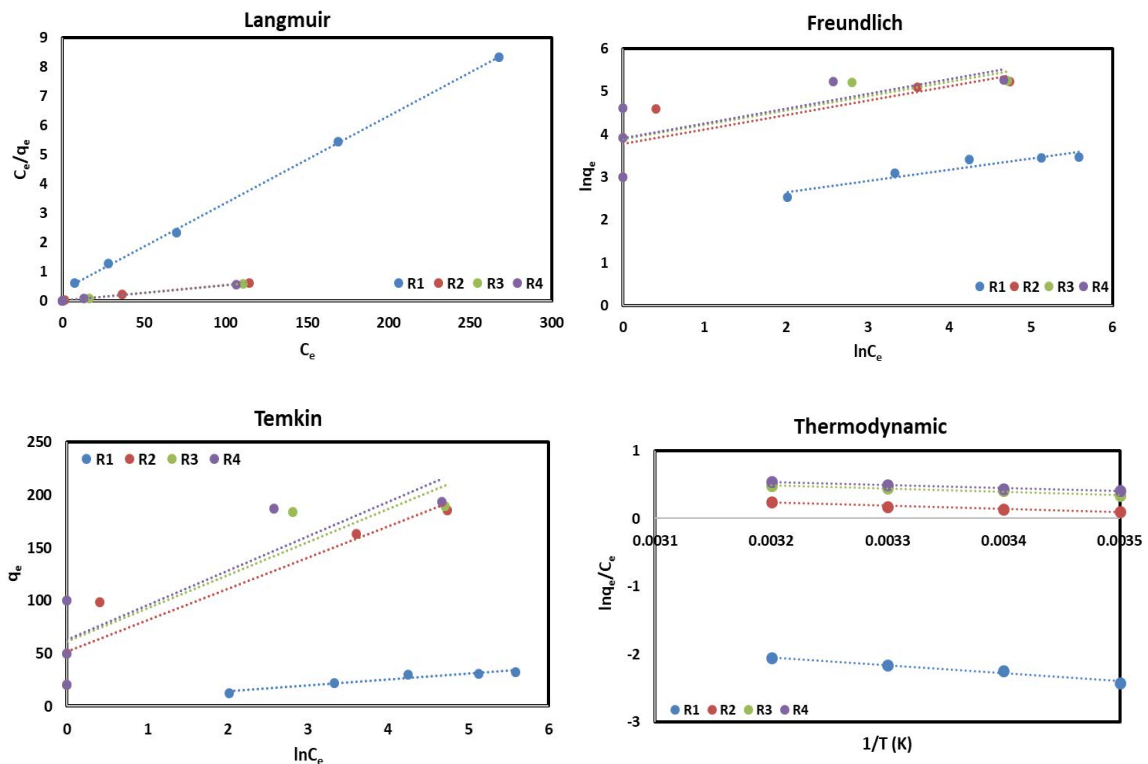

Fig. 4. A linear plot of Langmuir, Freundlich, Temkin and thermodynamic for Pb(II) removal.

Table 4
Langmuir, Freundlich, Temkin isotherm thermodynamic parameters of Pb(II) adsorption

Samples	Langmuir			Freundlich			Temkin		
	q_m	K_L	R^2	K_F	n	R^2	B	K_T	R^2
R1	33.67	0.08	0.9995	0.13	3.78	0.8938	5.62	440.89	0.9326
R2	185.19	0.77	0.998	5.98	2.98	0.6709	29.67	83.51	0.8868
R3	188.68	8.83	0.999	7.74	2.98	0.5834	31.42	78.86	0.7912
R4	192.31	10.40	0.999	8.01	2.91	0.5742	32.67	75.83	0.7787

			Thermodynamic						
Samples	Temp.	$\Delta G°$	$\Delta H°$	$\Delta S°$		Temp.	$\Delta G°$	$\Delta H°$	$\Delta S°$
R1	288	−32.31			R2	288	−38.37		
	298	−33.77	9.88	0.14		298	−39.84	3.97	0.15
	308	−35.24				308	−41.31		
	318	−36.71				318	−42.78		
R3	288	−44.55			R4	288	−42.92		
	298	−46.23	3.98	0.17		298	−44.54	3.65	0.16
	308	−47.92				308	−46.15		
	318	−49.61				318	−47.77		

hypothesized that the adsorbent forms a monolayer at a limited number of adsorption sites on a homogeneous adsorbent surface [13,28]. Freundlich assumed that the adsorbent adsorbed onto the surface of the non-uniform adsorbent as a multi-molecular layer and is particularly suitable for application when the concentration of adsorbent in aqueous solution is low [21,26]. Temkin presented an equation that considers the free adsorption energy as a function of surface coverage [9,25]. Therefore, isotherms are used to evaluate the relationship between the adsorbent surface and the heat of adsorption of all molecules, showing that the heat of adsorption of all molecules decreases linearly with increasing adsorbent surface coverage.

The correlation coefficient (R^2) was 0.998–0.999, 0.5742–0.8938, and 0.7787–0.9326 for Langmuir, Freundlich, and Temkin, respectively. Therefore, the adsorption equilibrium relationship of lead with respect to R1–R4 adsorbents could be best expressed by Langmuir's equation, which implies that lead was adsorbed in the form of a monolayer on the surface of a uniform adsorbent. Most of the adsorption processes using lignocellulose-based adsorbents reported research results that were consistent with this study (Table 5). If the adsorption process follows the Langmuir equation, the suitability of the adsorption process can be judged using the separation factor (R_L). If the separation coefficient is $0 < R_L < 1$, it means that the adsorption treatment process is suitable [11,31]. As a result of calculating the data using the experimental results, it was found that the R_L was 0.04–0.057 in all samples of R1–R4, indicating that the adsorption process was suitable.

Freundlich's K_F indicates that the higher the value, the better the adsorption ability. $1/n$ values represent 0.1–0.5 (excellent adsorption), from 0.5 to 1 (easy adsorption), and >1 (difficult adsorption) [13,28]. As a result, the K_F value increased as the concentration of phosphoric acid increased, and R2–R4 was about 6–8 times higher than that of R1, proving that SCG modified with phosphoric acid had excellent adsorption ability. The value of $1/n$ was calculated as 0.2646 for R1 and the range of 0.3356–0.3437 for R2–R4, confirming that the adsorption capacity of lead for R1–R4 adsorbent was excellent and easily adsorbed under various conditions under study.

Temkin's B value was determined to be 5.62 J/mol for R1, being $B < 20$ J/mol, it is classified as a physisorption process. However, the B value of R2–R4 adsorbents was measured in the range of 29.67–32.67, all with $B > 20$ J/mol, which belongs to chemisorption. This is because the adsorbent of R2–R4 was modified with phosphoric acid so that the adsorption of lead in aqueous solution was closer to chemisorption than to physisorption. In addition, the adsorption process is thought to be due to ion exchange and complexation caused by phosphoric acid.

The q_m of the Langmuir model is the maximum amount of adsorbent per unit mass of adsorbent, and adsorption capacity is a key parameter for evaluating the adsorption effect of an adsorbent. The maximum adsorption capacity of R1 was 33.67 mg/g, and that of R2–R4 was 185.19, 188.68, and 192.31 mg/g, respectively. SCG modified with phosphoric acid showed 5.5–5.7 times higher adsorption capacity compared to unmodified SCG. The use of phosphoric acid function played a very important role in the adsorption of lead as it provided high adsorption capacity and improved adsorption rate. However, there was no significant difference in the absorption capacity between R2, R3, and R4. Moreover, according to the physicochemical characteristic analysis of the adsorbent (Table 2), the material loss of R2 due to the reforming of SCG using phosphoric acid was very low compared to that of R3 or R4, indicating a yield of 93.09% of the adsorbent. The yield of these adsorbents is important in terms of economics when applied to the field, such as adsorption efficiency. Therefore, in the case of adsorption of lead in aqueous solution using phosphoric acid reformed SCG, comparing the various experimental results mentioned above, the experimental condition of R2 is

Table 5
Comparison of maximum adsorption capacity for Pb(II) by various adsorbents

Adsorbent		q_m (mg/g)	Adsorption model	References
	Persimmon leaves	22.3	PSO, Langmuir	[2]
	Artocarpus heterophyllus seed	4.9	Intraparticle, Temkin	[33]
	Syzygium cumini seed	3.9	Elovich, Temkin	[33]
	Coffee husk	37.0	PSO, Freundlich	[34]
	Moringa oleifera bark	34.6	PSO, Freundlich	[35]
	Coconut shell	26.1	PSO, Langmuir	[29]
	Rice straw	42.5	Langmuir	[36]
	Cassava peels	50.1	PSO, Langmuir	[15]
Unmodified	Groundnut shell	46.6	PSO, Langmuir	[15]
	Lemon	61.3	Freundlich	[37]
	Bean	88.5	Freundlich	[37]
	Artichoke shell	62.8	Freundlich	[37]
	Eggshell/coffee ground/sericite	155.7	PSO, Langmuir	[25]
	Corn straw-converted hydrochar	32.7	PSO, Langmuir	[27]
	Eggshell/sericite	33.9	PSO, Freundlich	[28]
	Tannin/chitosan/sericite	167.8	PSO, Langmuir	[26]
	R1	33.7	PSO, Langmuir	This study
	Banana peels	241.0	PSO, Langmuir	[22]
	Corn straw-converted hydrochar	353.4	PSO, Langmuir	[27]
	Bamboo sawdust	166.2	PSO, Langmuir	[38]
	Cornstalk	182.7	PSO, Langmuir	[24]
Modified with phosphoric acid	Coconut shell	49.9	PSO, Langmuir	[29]
	Waste tyre	196.0	PSO, Langmuir	[39]
	Chestnut shell	138.9	PSO, Langmuir	[32]
	R2	185.2	PSO, Langmuir	This study
	R3	188.6	PSO, Langmuir	This study
	R4	192.3	PSO, Langmuir	This study

PSO: pseudo-second-order.

recommended. These results is in agreement by Kussainova et al. [32].

Table 5 compares the maximum adsorption capacity of lead using various adsorbents and the results of this study. As can be seen from Table 5, the modified adsorbent generally exhibits higher lead removal efficiency than the unmodified adsorbent. Although the lead adsorption capacity of SCG modified with phosphoric acid did not boast a very high adsorption capacity compared to other reported modified lignocellulose adsorbents, however, it showed an adequate adsorption capacity with an appropriate amount of adsorbent. This shows that SCG modified with phosphoric acid is a promising adsorbent for adsorbing lead.

3.4. Thermodynamic interpretation

The Gibbs energy is equal to the total chemical energy of the system and shows what changes will occur in the course of a chemical reaction and whether substances interact at all [2,40]. Thermodynamic parameters such as ΔH and ΔS that are linked to Gibbs energy were calculated from the slopes and intercepts of $\ln q_e/C_e$ vs. $1/T$ (Fig. 4), respectively,

and are summarized in Table 4. A positive value of ΔH and ΔS indicates that the adsorption process is endothermic, and the randomness of the adsorbent surface increases in the adsorption process. ΔG was negative for all samples. This indicates that the adsorption process was spontaneous at all temperatures studied. In addition, the ΔG value decreased as the concentration and temperature of phosphoric acid increased, indicating that the adsorption efficiency increased as the temperature increased.

Many researchers [2,10,21,24,40] have reported that the adsorption process using lignocellulose is an endothermic reaction, and the adsorption efficiency is affected by temperature. This is because the activation of the active adsorption site of the adsorbent or the number of metal ions discharged from the adsorbent surface into the solution increases as the temperature increases. However, the lignocellulose-based adsorbent may be denatured due to physical damage to the absorbent at a high temperature of 50°C or higher. In addition, considering the economic feasibility for on-site application, it is necessary to find the optimal conditions for maximum adsorption efficiency at the temperature of the on-site wastewater.

3.5. Adsorption mechanism

Various functional groups on the adsorbent surface play an important role in bonding the adsorbate to the adsorbent [2,28]. According to the literature, there are various functional groups capable of adsorbing metal cations, but O– or N– donors present in the adsorbent can, through hydrogen bonding and electrostatic attraction, bind with harmful substances in aqueous solution due to a single pair of oxygen or nitrogen atoms [7,8,21]. Thus, polymers containing carboxylic acids and phosphonic acids have been widely used to adsorb various cations such as heavy metals [9,22,41]. The phosphoric acid-modified R2–R4 adsorbents adsorbed almost all cations in the aqueous solution by exchanging them with oxygen, nitrogen, and hydrogen ions due to the phosphoric acid group contained in the adsorbent. Since this ion exchange process is reversible, there is an advantage in that the adsorbent can be regenerated and used when the ion exchange capacity is exhausted.

According to the physicochemical properties of the adsorbent and FTIR analysis, the surface of the R2–R4 adsorbents modified with phosphoric acid contained a significant amount of phosphorus-compounds, and the surface area and porosity of the adsorbents significantly increased due to phosphorylation. Moreover, the content of phosphocarbon compounds such as hydrogen bonds, P=O groups, P–O–C (aromatic) bonds, and P=OOH of phosphate or polyphosphate increased due to phosphorylation [17,21,22,24]. This is characteristic of the phosphorus, and phosphorus-carbon compounds present in the phosphoric acid activated carbon as a result of the attachment of phosphoric acid functional groups to the adsorbent [18,19,24]. Various functional groups, such as aromatic rings, –C=O, –C–O–C–, –OH, –C=N, –P=O, –P–O–C, and P=OOH, present on the adsorbent surface played important roles in increasing the adsorption capacity of lead in aqueous solution. The increase in adsorption capacity was directly proportional to the increase in the phosphoric acid concentration when reforming SCG. Therefore, R4 adsorbent had the highest maximum adsorbent capacity. The adsorption of lead ions by the modified SCG was achieved by a surface complexation mechanism between oxygen-containing functional groups and lead ions, which can be summarized as hydrogen bonding, electrostatic attraction, and complexation (Fig. 5).
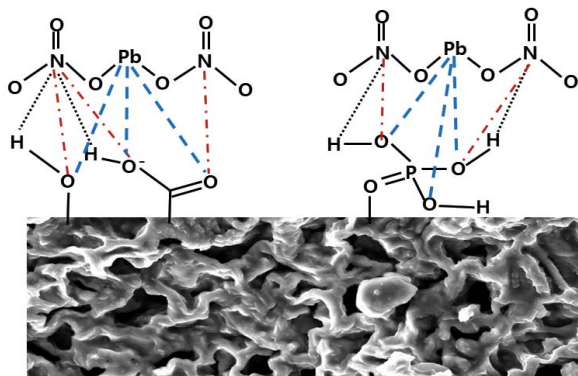
3.6. Interference of other ions

For field application of the adsorbent, it was attempted to evaluate the competitive adsorption with other heavy metals. This is because lead and various heavy metals are mixed in industrial wastewater, and these cations can interfere with the adsorption of lead to the adsorbent. Therefore, possible heavy metals (Cr, Ni, Cd, Cu, Fe, Zn) that can be mixed with lead in industrial wastewater were selected, and lead removal efficiency was analyzed using R2 adsorbent with good adsorption efficiency and yield. Considering that the concentration of general lead ions contained in industrial wastewater is less than 20 mg/L, the concentrations of competing ions were tested at 20 mg/L, 1 g/L of adsorbent, pH 7, and room temperature. As seen in Fig. 6, despite the presence of various competing ions (Cr, Ni, Cd, Cu, Fe, Zn), the lead removal efficiency was 98.4%, which was excellent for the R2 adsorbent. Of particular note, divalent cationic metals such as Cu, Zn, Cd, and Ni exhibited a removal efficiency of more than 60%. These results suggest that the metallicity of lead is lower than that of the interference ion, and the reactivity with functional groups on the surface of the adsorbent is high. Considering the above experimental results, the R2 adsorbent is very effective in adsorbing lead as well as other harmful heavy metals in aqueous solution.

3.7. Reusability

As a result of the reuse test, the removal efficiency of lead onto R2–R4 adsorbent was found to be more than 90% up to 7 consecutive times, confirming that the adsorption performance was excellent. On the other hand, the lead removal efficiency onto R1 adsorbent decreased to 83% when used twice, 71% when reused three times, and 18.6% when reused the 8th time (Fig. 7). According to previous studies, many researchers desorb using HCl or NaOH to reuse the adsorbent [RR]. However, in this study, the lead removal efficiency onto R2–R4 adsorbent was more than 90% up to 7 times without the desorption process using chemicals (Fig. 7). These results indicate that R2–R4 adsorbents have a very high affinity for lead ions. This can be understood in connection with the changed characteristics of the R2–R4 adsorbents mentioned above (Section 3.1). Summarizing the experimental results confirmed that there is no doubt that
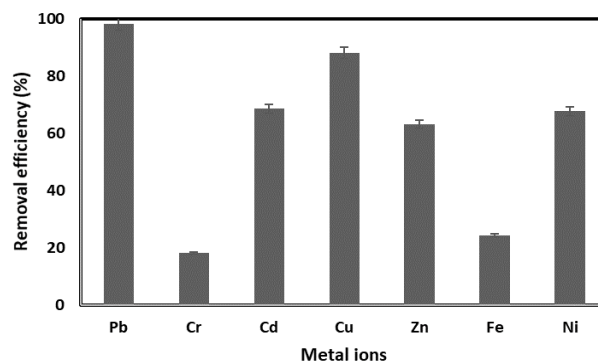

Fig. 5. A possible mechanism of Pb(II) adsorption by PSCG (hydrogen bonding, complexation and electrostatic attraction)

Fig. 6. Effect of Pb(II) removal efficiency with competing cations (Pb(II) concentration: 20 mg/L, adsorbent: 1 g/L, pH 7, *T*: 25°C).
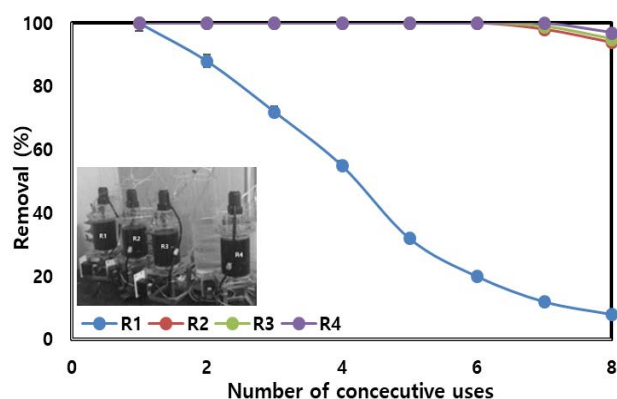
Fig. 7. Reusability of adsorbent (Pb(II) concentration: 20 mg/L, adsorbent: 1 g/L, pH 7, *T*: 25°C.

SCG modified with phosphoric acid is a promising adsorbent for lead adsorption. Adsorbent reusability is an important factor in determining commercial viability for industrial applications. In addition, the availability of coffee grounds; an abundant lignocellulose-based adsorbent that is readily available everywhere, is another key factor in ensuring the continuity of adsorbent production. Moreover, the reforming method applied to the preparation of these adsorbents has the advantage of being very simple.

4. Conclusions

In this study, coffee grounds, a mass-produced waste product, was reformed using various phosphoric acid concentrations, and the effect of the phosphorylation degree of the adsorbent on the adsorption efficiency of lead in aqueous solution was analyzed to find the optimal phosphorylation degree. After reforming the SCG with phosphoric acid, it was confirmed that the pore size of the adsorbent increased as a whole, and the range of mesopores (2–50 nm) increased from 12.9% to 96.9–97.2%. According to FTIR analysis of the adsorbents, as the concentration of phosphoric acid increased, the content of phosphocarbon compounds increased. From the adsorption kinetics and isothermal adsorption experiments, pseudo-second-order and Langmuir were most suitable, and the adsorption process was closer to chemisorption than physical adsorption. The maximum adsorption capacity by Langmuir model was found to be 33.67, 185.19, 188.68 and 192.31 mg/g for R1, R2, R3, and R4, respectively. The removal efficiency of lead was comparatively analyzed when competing ions were present using R2 adsorbent, and despite the presence of competing ions, the lead removal efficiency was as high as 98.4%, proving that the removal efficiency was excellent. As a result of the reuse test, the R2–R4 adsorbent showed excellent performance with a high lead removal efficiency of over 90% up to 7 consecutive times. Comprehensively analyzing the above experimental results: the high yield of the adsorbent, the increase in the surface area, the formation of mesopores, and the maximum adsorption amount, the R2 preparation condition is recommended for the reforming of the adsorbent using phosphoric acid. SCG modified with phosphoric acid, an abundant lignocellulose-based adsorbent that is readily available everywhere, is a promising adsorbent capable of adsorbing lead in aqueous solution. In addition, it is meaningful in terms of resource recycling because it can adsorb harmful substances using discarded waste.

Compliance with ethical standards

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

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.

Credit authorship contribution statement

Won-Jung Jang and Hee-Jeong Choi (Prof. Ph.D): Conceptualization, Methodology, Data curation, Writing - original draft, Visualization, Investigation, Software, Validation, Writing - review & editing.

Statement of informed consent, human/animal rights

No conflicts, informed consent, human or animal rights applicable.

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Supporting information

Table S1
Adsorption kinetic, isotherm and thermodynamic models

Model	Equation	Parameters
Pseudo-first-order	$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t$	q_t: Amount of adsorbate adsorbed at time (mg/L); q_e: Equilibrium adsorption capacity (mg/g); k_1: Pseudo-first-order rate constant (1/min); t: Time (min).
Pseudo-second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 \cdot q_e^2} + \dfrac{t}{q_e}$	k_2: pseudo-second-order-rate constant (L/mg·min)
Intraparticle diffusion	$q_t = k_{id} t^{1/2} + C$	k_{id}: intraparticle diffusion rate constant (mg/(g·min$^{1/2}$)); C: intercept (mg/g)
Langmuir	$\dfrac{1}{q_e} = \dfrac{1}{q_m K_L C_e} + \dfrac{1}{q_m}$ $R_L = \dfrac{1}{1 + K_L C_0}$	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	$\Delta G° = \Delta H° - \Delta G°$	$\Delta G°$: Gibbs free energy change (kJ/mol); $\Delta H°$: Enthalpy change (kJ/mol); $\Delta S°$: Entropy change (kJ/mol·K); T: Temperature (K).