



Article Comparative Study on the Adsorption Characteristics of Heavy Metal Ions by Activated Carbon and Selected Natural Adsorbents

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Abstract: In this study, adsorption of the heavy metal ions (Pb(II), Cu(II) and Cd(II)) from water by peanut shells (PS), sawdust (S) and commercial activated carbon (AC) were comparatively studied. Thus, the relationship between different adsorption parameters and different heavy metal ion removal rates was investigated. The adsorption capacity of the three adsorbents for heavy metal ions increased with an increase in temperature, pH value, contact time, adsorbent dosage, and heavy metal ion concentration, however, it decreased with an increase of adsorbent particle size. All the adsorption processes are better described by Langmuir isotherm or Freundlich isotherm. Thus, the results show good agreement with pseudo-second-order kinetics and the adsorption processes are spontaneous heat absorption processes. Herein, all adsorbents have higher affinity for Pb(II) ions, and hence possess higher removal rates. In addition, heavy metal ions were desorbed significantly at acidic conditions in the desorption experiments. The results demonstrate that PS can be used as a green adsorbent instead of AC for the adsorption of heavy metal ions from the water.

Keywords: adsorption; desorption; agricultural waste; natural adsorbents

1. Introduction

Industrialization is increasing along with the rapid development of human society. Generally, major industries such as the chemical industry, textiles, tanning, mining and smelting, paints and pigments, ceramics and glass, paper and pulp industries, and the alloy and storage battery industries have contributed to widespread heavy metal pollutions [1,2]. The industrial wastewater generated by these industries is typically composed of heavy metals (copper (Cu), cadmium (Cd), lead (Pb), zinc (Zn), cobalt (Co), etc.). Because heavy metals are inorganic and non-degradable, they can exist in nature for a long time and continue to accumulate, thus threatening the healthy growth of ecosystems [3]. Lead and cadmium, for instance, can cause cancer [4]. Cobalt can cause kidney and liver disease, while copper and zinc can cause brain and bone damage [5,6]. Therefore, the question of how to effectively remove heavy metals from water is an urgent problem for people to solve. Heavy metal may be effectively separated from different media using various methods based on physical, chemical and biological processes such as chemical precipitation [7], membrane separation [8], ion exchange [9], electrodialysis [10], and phytoremediation [11]. Nevertheless, these processes have inherent limitations in their application. Chemical precipitation can effectively remove heavy metal ions from water, but chemicals can cause secondary pollution to the environment and the resulting precipitation is difficult to remove [12]. Membrane separation, ion exchange, and electrodialysis are all highly effective in removing heavy metal ions, but their high cost and operating difficulties



Citation: Li, J.; Dong, X.; Liu, X.; Xu, X.; Duan, W.; Park, J.; Gao, L.; Lu, Y. Comparative Study on the Adsorption Characteristics of Heavy Metal Ions by Activated Carbon and Selected Natural Adsorbents. *Sustainability* 2022, *14*, 15579. https://doi.org/10.3390/ su142315579

Academic Editors: Yuanan Hu and Yafeng Wang

Received: 26 September 2022 Accepted: 21 November 2022 Published: 23 November 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). make them difficult to use on a large scale [13]. Although phytoremediation is a green and non-polluting method to remove heavy metal ions from the environment, the length of time required for this process restricts its further application [14]. Compared with other treatment technologies, the adsorption method has the advantages of simple operation, high adsorption rate and no secondary pollution [15,16] and is one of the most widely used methods for removing heavy metals from the water [14]. Activated carbon is prepared from raw materials containing carbon, such as wood, coal, and petroleum coke, through pyrolysis and activation processing. Moreover, it has a developed pore structure, large specific surface area, and rich surface chemical groups, hence, it is often used as a traditional adsorbent [17,18]. AC is mostly used for drinking and technological water treatment [19]. Nowadays, as coal is becoming less accessible and much more expensive than a decade before, its usage for water treatment has become more limited [20,21] and, therefore, finding one or more low-cost, high-adsorption materials is necessary.

Low-cost absorbent materials can be roughly divided into four categories: natural minerals, agricultural waste, animal and plant waste, and industrial waste [1]. Zhu et al. [22] have found that cow manure can effectively remove Pb(II) and Cd(II). Xu et al. [23] have demonstrated that oyster shell powder can efficiently remove Cu(II), Pb(II), and Cd(II) from wastewater. Veli et al. [24] have concluded that natural clay can be used as an effective adsorbent for the removal of Cu(II) and Zn(II) from aqueous solutions. Nadaroglu et al. [25] have concluded that red mud could be successfully used to remove Cu(II) from the aqueous solutions with heavy metals. However, some low-cost adsorbents, such as red mud with its strong alkalinity, have a certain degree of pollution and may produce secondary pollution in large-scale applications. Hence, the application of red mud generally requires activation treatment, which increases the cost of its use [26]. The main components of agricultural waste are cellulose, hemicellulose and lignin, which are natural substances and will not cause secondary pollution. Some studies have shown that the presence of cellulose helps adsorb heavy metal ions [27]. In addition, agricultural waste shares other advantages, such as various pores, large surface area, and stable structure. Therefore, the use of agricultural wastes as adsorbents is feasible. Most of the current research has focused on the preparation and modification of biochar, and there is less research on the comparison of natural materials with AC. In China, a large amount of agricultural waste is produced annually, and most of the agricultural waste is disposed of through incineration, which ultimately causes environmental pollution. Thus, research on agricultural waste is an urgent issue.

This study aims to compare the adsorption effects of PS, S, and AC on heavy metals from water in order to select a natural adsorbent that can replace commercial activated carbon for water treatment. Therefore, natural peanut shells and sawdust without any activation treatment were selected. The adsorption effect of the adsorbent was evaluated by batch adsorption experiments, desorption experiments, as well as SEM, FTIR, and BET. Adsorption kinetics and adsorption isotherms were also investigated.

2. Materials and Methods

2.1. Preparation of Materials

The PS and S were purchased from local farmers' markets in South Korea. Chemicals (Pb(NO₃)₂, Cu(NO₃)₂·2H₂O, Cd(NO₃)2·4H₂O, NaOH, and HNO₃) and commercial activated carbon were purchased from Merck, Germany. All the compounds used in this research were of analytical grade. All solutions were configured from distilled water. Herein, 1.60 g of Pb(NO₃)₂, 3.80 g of Cu(NO₃)₂·2H₂O, and 2.75 g of Cd(NO₃)₂·4H₂O were dissolved in distilled water in a 1000 mL volumetric flask to configure the Pb(II), Cu(II), and Cd(II) ions mother liquor at a concentration of 1000 mg/L for subsequent experiments, respectively. Meanwhile, NaOH and HNO₃ (1 M) were used to adjust pH values.

Materials were washed with distilled water (to remove residues), dried in the air, and placed in a thermostat at 110 °C for 72 h. They were then crushed in a grinder and sieved using meshes of different sizes. Adsorbents with the following different particle diameters

were obtained: 0–0.45, 0.45–0.85 mm, 0.85–1.18 mm, and 1.18–2.00 mm. The basic physical and chemical properties of the three adsorbents used in this study are shown in Table 1.

Adsorption Material	AC	PS	S
pH	7.6	6.7	5.1
Specific surface area (m ² /g)	532	3.6	1.25
Fixed carbon (%)	82.23	27.31	16.73
Volatile substances (%)	11.23	50.3	59.87
Water content (%)	3.76	8.96	9.1

Table 1. Basic physical and chemical properties of three adsorbents (particle size 0.85–1.18 mm).

A scanning electron microscope (SEM) was used to observe the surface of the adsorbent microscopically. In addition, Fourier transform infrared spectroscopy (FTIR) was used to determine the functional group and molecular structure of the adsorbent. The spectrum of the adsorbent was measured within the range of $4000-400 \text{ cm}^{-1}$ wave number.

2.2. Adsorption Experiments

Batch adsorption experiments were conducted based on the standard method recommended by the Organization of Economic Cooperation and Development (OECD,2000). In addition, a self-designed round stirrer was used for the batch adsorption experiments. The batch adsorption experiments were performed in 50 mL glass test tubes at an optimum condition with a pH of 7, reaction time of 5 h, temperature of 24 °C, adsorbent mass of 0.4 g/35 mL, particle size of 0.85–1.18 mm, and initial metal ion concentration of 60 mg/L for each of the Pb(II), Cu(II) and Cd(II) ions. Then, the batch adsorption studies were conducted for different effects, including temperature (8–24 °C, with 4 °C intervals), pH value (2–10), adsorbent particle size (0–2 mm), contact time (10–1440 min), adsorbent dosage (0.2–1 g), and initial heavy metal solution concentration (20–400 mg/L) on the adsorption efficiencies were studied. Each adsorption experiment was repeated thrice, and the average value was taken for analysis. Finally, the mass of heavy metal ions adsorbed per unit of adsorbent was calculated by Equation (1). Meanwhile, the removal ratio of heavy metal ions was calculated by Equation (2):

$$q_e = \frac{(C_0 - C_e) \times V}{M \times 1000} \tag{1}$$

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

where C_0 is the initial concentration of the heavy metal solution (mg/L), C_e is adsorbate concentrations at equilibrium (mg/L), q_e are adsorbed amount at equilibrium (mg/g), R is the removal efficiency of heavy metal (%), V is the volume of the heavy metal solution (mL), M is the mass of the adsorbent (g).

2.3. Adsorption Kinetics

Herein, kinetic models are used to investigate the batch adsorption results affected by contact time and understand the diffusion characteristics of heavy metal ions from liquid to solid [28–30]. The type of adsorption mechanism preceding heavy metal ions can be determined through kinetic studies [31]. At present, the pseudo-first-order kinetic model (Equation (3)), pseudo-second-order kinetic model (Equation (4)), and intra-particle diffusion model (Equation (5)) are widely used kinetic models and their linear expressions are as follows:

$$\log(q_e - q_t) = \log q_e - K_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

$$q_t = K_d t^{\frac{1}{2}} + D \tag{5}$$

where q_t is the adsorption capacity when the adsorbent contact time is t (mg/g), K_1 is the rate constant of the pseudo-first-order kinetic model, and K_2 is the rate constant of the pseudo-second-order kinetic model, K_d and D are diffusion kinetic parameters.

2.4. Adsorption Isotherm

Analysis of adsorption isotherms can help us to understand the process of heavy metal ions in the transfer from the solution to the surface of the adsorbent. Herein, we used Langmuir (Equation (6)) and Freundlich isotherms (Equation (7)), two commonly used isotherm models.

$$q_e = \frac{C_e K_L q_m}{1 + C_e K_L} \tag{6}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{7}$$

where K_L is the ratio of the adsorption rate and desorption rate (L/mg), b is the constant of the Langmuir model (mg/g), KF and *n* are the constants of the Freundlich model.

2.5. Adsorption Thermodynamics

Values of thermodynamic parameters are essential indicators for adsorption application. In general, the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes are calculated using Equations (8)–(10) based on the adsorption results at different temperatures.

$$K_c = \frac{q_e}{C_e} \tag{8}$$

$$\ln K_c = -\frac{\Delta H}{rT} + \frac{\Delta S}{r} \tag{9}$$

$$\Delta G = \Delta H - T \Delta S \tag{10}$$

where K_c is the thermodynamic equilibrium constant (L/g), ΔH is the enthalpy change (J/mol), ΔG is the free energy change (J/mol), ΔS is the entropy change (J/(mol·k)), *T* is the absolute temperature (K), *r* is the ideal gas constant, 8.314 J/(mol·k).

2.6. Desorption Experiment

The desorption experiment is carried out at acidic conditions (pH = 5), neutral conditions (pH = 7), and alkaline conditions (pH = 9). Acidic conditions were prepared with nitric acid and distilled water, while the neutral conditions were prepared with distilled water only, and alkaline conditions were prepared with sodium hydroxide and distilled water.

A total of 50 mL of heavy metal solution (60 mg/L) and 0.4 g of adsorbent were taken into a 70 mL glass bottle, reacted at 24 °C, and pH value of 7. After 5 h of adsorption, the glass bottle was removed from the stirrer. After standing for 2 h, 20 mL of the supernatant liquid was taken out from the bottle, then the same volume of the desorbent solution was added under different conditions into the glass bottle, and the newly obtained mixture was placed in a rotary stirrer and stirred for 24 h. The desorption process was repeated thrice. After each desorption was completed, 20 mL of the supernatant was replaced, and the same volume of desorption solution was added. All desorption experiments were carried out in three sets of parallel experiments to analyse the concentration of heavy metal ions in the supernatant replaced each time. After the desorption was completed, the mass of heavy metal ions adsorbed on the adsorbent was calculated by Equation (11) and the desorption efficiency of metal ions on the adsorbent was calculated by Equation (12).

$$Q_{di} = \frac{C_0 \times V_0 - C_{di} \times V - \sum (C_r \times V_r)}{1000 \times M}$$
(11)

Desorption efficiency =
$$\frac{Q_{d0} - Q_{d1}}{Q_{d0}}$$
 (12)

where V_0 is the volume of the solution (mL), Q_{di} is the mass of heavy metal ions adsorbed on the adsorbent after *i* analysis process (mg/g), C_{di} is the concentration of heavy metal solution after *i* desorption process (mg/L), $\sum (C_r \times V_r)$ is the total number of heavy metal ions removed from the glass bottle before the desorption process (mg), C_r is the concentration of heavy metal ions removed from the glass bottle (mg/L), and V_r is the concentration of heavy metal ions removed from the glass bottle (mL).

3. Results and Discussion

3.1. Adsorbent Characteristics

The main elemental components of the three adsorbents are composed of C and O from Table 2. The weight percentage of carbon produced by AC is above 90%. In contrast, PS and S showed a decrease in carbon for the weight percent more than the AC, which is similar with previous research results [32]. The electric field emission scanning electron (SEM) studied and analysed the microstructure of the adsorbent. The SEM images of adsorbents is shown in Figure 1. Herein, AC has various pores on the surface and has high adsorption rate for heavy metal ions (Figure 1a). Meanwhile PS has a rough texture structure with voids or pores formed on the surface and has a good adsorption structure, which can be used to adsorb heavy metal ions (Figure 1b). The surface of the S is relatively smooth, a directional structure filled in filaments with anisotropic characteristics (Figure 1c).

Table 2. Composition of EDX elements of adsorbent.

Absorbent	Element	W _t %	At%
	С	92.21	94.03
AC	0	7.91	5.97
	С	50.09	57.89
	0	47.39	41.11
PS	Mg	0.53	0.30
	K	1.05	0.37
	Ca	0.94	0.33
c	С	55.97	62.87
5	0	44.03	37.13



(**a**) AC

(**b**) PS

(c) S

Figure 1. SEM image of adsorbents showing the particle size of 1 µm at 10,000 magnification for AC, PS, and S.

The FTIR of the three adsorption materials is shown in Figure 2. Herein, the vibrational spectrum of PS and S are similar. The peak near 2900 cm⁻¹ represents the C–H and methylene CH₃ stretching vibrations on the surface of both adsorbents, thereby indicating the presence of lignin in both. Meanwhile, the peak between 1300 cm⁻¹ and 1000 cm⁻¹

can be attributed to the C–O stretching vibration of the carboxyl group. The peak between 1500 cm⁻¹ and 1300 cm⁻¹ is caused by the COO- stretch vibration of the carboxylic acid functional group, which indicates that the PS and S contains cellulose. In conclusion, PS and S contain functional groups such as carboxyl, hydroxyl, and methyl groups [33,34]. From the vibrational spectrum of AC, the broadband around 3425 cm⁻¹ indicates the existence of hydroxyl groups with O–H stretching vibration. In addition, the peak at 2900 cm⁻¹ is attributed to the C–H tensile vibration. There are five peaks between 2000 cm⁻¹ and 1000 cm⁻¹. The peak around 1800 cm⁻¹ can be attributed to the C=O stretching vibration of the carbonyl group. Meanwhile, the peak value of about 1600 cm⁻¹ belongs to C=C tensile vibration. The peak around 1000 cm⁻¹ is the C–O tensile vibration of CH₂–O–CH₂. Therefore, oxygencontaining surface functional groups play an important role in the performance of AC. The main functional groups in AC are carboxyl and hydroxyl [35].



Figure 2. FTIR spectra of AC, PS and S.

3.2. Factors Affecting Absorption

3.2.1. Effect of Contact Time

Contact time is an essential factor in studying the equilibrium state of the adsorption process, and it determines the kinetic characteristics of adsorption. The changes in the number of heavy metal ions at different times are shown in Figure 3. With the increase in contact time, the number of heavy metal ions adsorbed by different adsorbents increased rapidly and then gradually reached equilibrium. This trend is similar to other studies on heavy metal adsorption [36,37]. In the initial stage of adsorption, there are enough adsorption sites on the adsorbents' surface to adsorb a large number of heavy metal ions Consequently, the adsorption sites tend to be saturated, and the removal efficiency also decreased and reached equilibrium, thereby providing diffusion resistance [38]. In addition, the order of adsorption effect for three different heavy metal ions is as follows: Pb(II) > Cu(II) > Cd(II). This means that the affinity of the three adsorbents for Pb is higher than other metals, a result which is similar to those of Skoczko et al. [39]. The order of the adsorption performance of the three adsorbents to Cu(II) is as follows: AC > PS > S.



Figure 3. Effect of contact time on the adsorption of heavy metal ions by different adsorbents.

3.2.2. Effect of Temperature

Temperature is another important factor thar affects the adsorption process. The changes in the adsorption of heavy metal ions at different temperatures are shown in Figure 4. Herein, the amount of adsorbed heavy metal ions increases with the increase in temperature, thus indicating that the adsorption process is an endothermic reaction. The reasons for this phenomenon may be as follows: (1) a higher temperature provides more energy for the adsorption process, through which heavy metal ions can be better transferred from the solution to the adsorption site of the adsorbent [40]; (2) a higher temperature can increase the ion exchange capacity of the adsorbent [41]; and (3) a higher temperature can activate the spots on the surface of the adsorbent, thereby obtaining more effective adsorption sites, which can adsorb more of the heavy metal ions.



Figure 4. Effect of temperature on the adsorption of heavy metal ions by different adsorbents.

3.2.3. Effect of pH Value

The pH value is also an essential factor affecting the adsorption effect because it can affect the surface charge of the adsorbents and the ionization degree of the solution [42–44]. The changes in the adsorption of heavy metal ions at different pH are shown in Figure 5. It can be seen that when the pH values were between 3–7, the removal efficiency of heavy metal ions increased rapidly. Then the removal efficiency increased gradually and finally reached 100%. This may be due to low pH conditions, whereby a large number of hydrogen ions in the solution compete for binding sites on the surface of the adsorbent with heavy metal ions, thus resulting in a decrease in the number of heavy metal ions adsorbed. As the pH increases, hydrogen ions competing for binding sites decrease, and the number of heavy metal ions adsorbed increases. When the pH values were greater than 8, the precipitation rate was almost 100%. The complete removal of heavy metal ions in the solution can be attributed to precipitation because the hydroxyl ions in the solution can undergo a precipitation reaction with heavy metal ions [45].



Figure 5. Effect of solution pH values on the adsorption of heavy metal ions by different adsorbents.

3.2.4. Effect of Adsorbent Particle Size

Herein, the changes in the number of heavy metal ions adsorbed by four different adsorbent particle sizes (1.18–2 mm, 0.85–1.18 mm, 0.45–0.85 mm, and 0–0.45 mm) were studied, and the results are shown in Figure 6. The results show that the adsorption capacity of heavy metal ions decreases as the size of the adsorbent increases because of the difference in the specific surface area of the adsorbent. For the dosage of adsorbent, a smaller particle size means a higher specific surface area of the adsorbent, which can provide more binding sites for the adsorption process and a shorter internal diffusion path [46,47]. These results are consistent with those of other studies [48].



Figure 6. Effect of different adsorbent particle sizes on the adsorption of heavy metal ions.

3.2.5. Effect of Adsorbent Dosage

The effect of adsorbent dosage on adsorption is shown in Figure 7. As the adsorbent dosage increases, the number of heavy metal ions adsorbed per unit mass of adsorbent decreases. This is because the weight of the heavy metal ions in the solution was fixed. As the number of adsorbents increases, the total surface area and adsorption sites of the adsorbent in the solution also increase. Consequently, heavy metal ions assigned per unit mass adsorbent decrease, and more unsaturated adsorption sites will appear on the surface of the adsorbent.

3.2.6. Effect of Initial Concentration

The changes in heavy metal ion adsorption and removal efficiency—in different initial concentrations—are shown in Figure 8. Herein, with the increase of the initial concentration, the adsorption capacity of the adsorbent for heavy metal ions initially increased rapidly and then gradually reached a point where it remained unchanged. This phenomenon can be attributed to the driving force of the concentration gradient. In addition, as the initial solution concentration increases, the solution concentration gradient increases, and the driving force also increases. Therefore, a higher driving force can promote the diffusion of heavy metal ions from the solution to the adsorbent surface, thereby increasing the

absorption rate and leading to a saturation of adsorption points on the surface of the adsorbent. The number of adsorption sites for a certain amount of adsorbent is fixed and can only adsorb a limited amount of heavy metal ions. As the initial concentration increases, heavy metal ions also gradually increase. The surface adsorption sites will be progressively occupied by heavy metal ions and tend to be saturated. Heavy metal ions adsorbent by per unit of adsorbent increases and reaches an equilibrium state [49]. Therefore, for a certain quality of adsorbent, the greater the initial solution concentration, the lower the removal efficiency of heavy metal ions [50].



Figure 7. Effect of adsorbent dosage on the adsorption efficiency of heavy metal ions.



Figure 8. Effect of initial concentration on the adsorption efficiency of heavy metal ions by different adsorbents.

3.3. Adsorption Kinetics

In this study, the adsorption data were analysed at different times (10–1440 min). The fitting parameters and pseudo-second-order kinetics are shown in Table 3. Meanwhile, the linear fitting curves of the pseudo-first order and pseudo-second order kinetic models are shown in Figures 9 and 10. The fitting degrees (R^2) of the pseudo-second-order kinetic models were all above 0.99 and higher than the values obtained by the pseudo-first-order kinetic model. In addition, the experimental adsorption capacities are much closer to the fitting values of equation (4). In summary, the adsorption process of the studied adsorbents for heavy metals can be better represented by the pseudo-second-order model compared with the pseudo-first-order kinetic model. This suggests that the reaction processes are probably chemical adsorption processes controlled by rate limit, involving the sharing or replacing of electrons between the adsorbent and the heavy metal. Analysis of the rate controlling steps is beneficial for elaborating the adsorption mechanism. However, the intraparticle diffusion model cannot describe the whole adsorption process, but it reflects the speed limit factor before the adsorption balance is reached to a certain degree. Figure 11 illustrates the diffusion process of heavy metal ions on different adsorbents. The diffusion process of each heavy metal ion adsorption can be divided into two evident diffusion stages. In the first stage, the heavy metal ions diffuse rapidly on the adsorbent particles, then the

concentration of heavy metal in the solution decreases and the particle diffusion starts to slow down before gradually reaching an adsorption equilibrium [51].

Table 3. The fitting parameters of the pseudo-first-order and pseudo-second-order kinetic models.

Adsorbent	Metal Ions	Pseudo-First-Order Kinetic Model			Pseudo-Second-Order Kinetic Model		
1 usorbent		<i>K</i> ₁	q _e	R^2	<i>K</i> ₂	qe	R^2
	Pb	0.013	0.22	0.75	0.52	5.26	0.99
AC	Cu	0.006	2.75	0.91	0.02	5.26	0.99
	Cd	0.004	2.25	0.92	0.05	5.26	0.99
	Pb	0.028	0.11	0.98	0.26	5.26	0.99
PS	Cu	0.003	0.32	0.94	0.10	4.55	0.99
	Cd	0.014	0.93	0.77	0.15	4.00	0.99
	Pb	0.005	0.92	0.96	0.06	4.35	0.99
S	Cu	0.002	0.55	0.98	0.04	3.57	0.99
	Cd	0.023	0.99	0.79	0.03	2.63	0.99



Figure 9. Fitting curves of the pseudo-first-order kinetic model.



Figure 10. Fitting curves of the pseudo-second-order kinetic model.

Table 4 shows the fitting parameters of the intra-particle kinetic model. The slope of the straight line at each stage is called the rate parameter K_d . Herein, the K_d values of the first stage are more significant than those of the second stage. At the beginning of the adsorption process, heavy metal ions are mainly adsorbed by the external surface of the adsorbent particles, and the adsorption speed is extremely fast. Then, the external surface adsorption reaches saturation, and heavy metal ions enter through the pores in the particles and are adsorbed on the particles' inner surfaces. When heavy metal ions diffuse in the pores of the particles, the diffusion resistance increases, thereby resulting in a decrease in the diffusion rate. Simultaneously, the concentration of heavy metal ions in the solution gradually decreases, the diffusion rate also gradually decreases and finally reaches

zero. Furthermore, the diffusion driving force is significant for the adsorption process. The decrease in the concentration of heavy metals will reduce the driving force, thereby reducing the rate of diffusion.



Figure 11. Fitting curves of the intraparticle diffusion kinetic model.

	Diffusion Coeffic							
Adsorbent	Metal Ions	First Stage			Second Stage			
	_	K _d	D	R ²	K _d	D	<i>R</i> ²	
	Pb	0.05	4.83	0.73	0.01	5.19	0.87	
AC	Cu	0.35	1.47	0.98	0.11	3.48	0.99	
	Cd	0.28	1.21	0.94	0.01	5.04	0.68	
	Pb	0.43	4.76	0.99	0.01	1.97	0.86	
PS	Cu	0.06	3.84	0.92	0.03	4.01	0.89	
	Cd	0.09	3.17	0.93	0.03	3.61	0.76	
	Pb	0.08	3.34	0.9	0.01	4.19	0.84	
S	Cu	0.03	2.97	0.98	0.01	3.24	0.74	
	Cd	0.10	1.87	0.85	0.01	2.46	0.83	

Table 4. Fitting parameters of intraparticle diffusion kinetic model.

3.4. Adsorption Isotherm

Langmuir and Freundlich isotherms were used to further study the relationship between adsorption capacity and initial concentration. The Langmuir isotherm was used to express the single-layer adsorption of heavy metal ions on the adsorbent with a uniform surface and the Freundlich isotherm was used to describe the non-monolayer adsorption that occurs on the non-uniform surface of the adsorbent [52,53].

The non-linear Langmuir isotherm and Freundlich isotherm fitting results are shown in Figure 12. Meanwhile, their fitting parameters are shown in Table 5. Herein, Langmuir and Freundlich isotherms can better describe the adsorption of Pb, Cu and Cd ions by the three adsorbents. The processes of PS adsorption of Pb ions, S adsorption of Cu ions and all adsorption of Cd ions are more consistent with the Langmuir equation, thereby indicating that these adsorption processes are mainly explained by monolayer adsorption, while chemisorption occupies an important position. In contrast, other adsorption processes are dominated by multilayer adsorptions.



Figure 12. Non-linear fitting curves of Langmuir and Freundlich isotherms.

Adaanhant	Motal Iana	Fr	Freundlich Isotherm			Langmuir Isotherm		
Ausoibent	Wietal Iolis —	K _F	п	R^2	KL	Ь	<i>R</i> ²	
	Pb	4.86	5.48	0.98	3.14	11.73	0.91	
AC	Cu	1.70	2.81	0.99	0.03	13.33	0.98	
	Cd	2.33	6.66	0.87	0.96	5.11	0.96	
	Pb	2.19	3.94	0.93	0.19	8.70	0.96	
PS	Cu	0.97	2.68	0.96	0.03	8.54	0.90	
	Cd	1.30	4.17	0.92	0.07	5.23	0.98	
	Pb	1.39	4.16	0.96	0.04	5.91	0.92	
S	Cu	0.85	3.11	0.92	0.03	5.81	0.97	
	Cd	0.82	3.64	0.92	0.04	4.23	0.98	

Tał	ole	5.	Fitting	parameters	of isot	herm mod	lels.
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3.5. Adsorption Thermodynamics

The thermodynamic investigations were accomplished to verify whether adsorption occurs spontaneously in adsorption processes [54].

Table 6 presents the thermodynamic adsorption parameters of different adsorbents for different heavy metal ions. The Δ H can be calculated from the slope of ln against 1/rT (Figure 13). In addition, a positive value of Δ H indicates that the adsorption process is endothermic, which is consistent with the increasing tendency of adsorption capacity with the increase in temperature.

Table 6. Thermodynamic adsorption fitting parameters.

Adsorbent	Metal Ions	A C	A TT	ΔG					P ²
		Δ5	ΔΠ	281 K	285 K	289 K	293 K	297 K	л
	Pb	421.99	0.12	-11.86	-12.03	-12.20	-12.36	-12.53	0.99
PS	Cu	145.71	0.045	-40.94	-41.53	-42.11	-42.69	-43.28	0.96
	Cd	179.98	0.056	-50.57	-51.29	-52.01	-52.73	-53.45	0.94
	Pb	160.00	0.049	-44.96	-45.60	-46.24	-46.88	-47.52	0.94
S	Cu	93.79	0.033	-26.35	-26.73	-27.10	-27.48	-27.85	0.94
	Cd	71.24	0.028	-20.02	-20.30	-20.59	-20.87	-21.16	0.98
AC	Pb	478.43	0.13	-13.44	-13.64	-13.83	-14.02	-14.21	0.95
	Cu	405.28	0.12	-11.39	-11.55	-11.71	-11.87	-12.04	0.93
	Cd	77.41	0.025	-21.75	-22.06	-22.37	-22.68	-22.99	0.93



Figure 13. Linear fitting curves of thermodynamics.

The positive value of ΔS indicates that the degrees of freedom increased at the solidliquid interface during the adsorption process because of the redistribution of energy between the adsorbent and heavy metal ions. The distribution of rotational and kinetic energy between a small number of molecules will increase during the adsorption process, thereby resulting in a positive ΔS value. The obtained values of ΔG are negative and show an increasing trend at different temperatures, thus confirming that the adsorption of heavy metal ions is spontaneous and thermodynamically favourable. Meanwhile, the temperature is an essential factor in the heavy metal ions adsorption process. As the temperature increases, the mobility of heavy metal ions in the solution also increases, which causes a high affinity of heavy metal ions on the adsorbent [55].

3.6. Desorption Analysis

Herein, the desorption characteristics of heavy metal ions by three different solutions were also investigated. The desorption results can evaluate the secondary pollution in different environments.

Figure 14 shows the desorption effect of different adsorption solutions on Pb(II), Cu(II), and Cd(II) ions. The acidic environment (HNO₃) possesses a high desorption efficiency, while the neutral (H₂O) and alkaline environments (NaOH) are inconspicuous for the desorption of metal ions. The available studies prove that the solubility of metals increases with decreasing pH [56–59]. As the pH increases, the solubility of metals decreases and the concentration of ions in solution decreases due to the precipitation of metals with OH-in solution [60,61]. Thus, the desorption efficiency of the adsorbent is higher in the acidic environment than in other environments. The desorption efficiency of S is significantly higher than that of AC and PS in Figure 14a. This may be due to the fact that the binding of Pb ions to S is mainly by outer layer adsorption or ion exchange, whereas on AC and PS it is mainly by inner layer adsorption or complexation. Therefore, Pb is more easily desorbed from S under an acidic environment.



Figure 14. Desorption results of different desorption solutions on different adsorbents.

Figure 15 shows the adsorption capacities of AC, PS and S for heavy metals after different desorption cycles. The number of heavy metal ions adsorbed by different adsorbents remained almost unchanged during the desorption cycle by distilled water, thus indicating that there is hardly any desorption phenomenon in neutral conditions. As the number of cycles increases, the adsorption capacity in the acidic solution decreases, while, on the contrary, the adsorption capacity in an alkaline solution increases. Considering that there are precipitation reactions between OH^- and heavy metal ions in an alkaline environment, more heavy metal ions are removed by NaOH solution. However, there is a large volume of H^+ in the acidic solution, and this H^+ will compete for adsorption sites on the surface of the adsorbent with heavy metal ions, thus reducing the number of adsorption sites available to adsorb heavy metal ions, and thereby resulting in a decrease in heavy metal adsorption capacity. Meanwhile, as the number of cycles increases, the pH decreases, which makes the solubility of metal ions higher, resulting in lower adsorption of metal ions on the adsorbent. Based on desorption experiments, AC, PS and S can be used as adsorbents in alkaline and neutral environments, however, they are not suitable for acidic conditions.



Figure 15. Effect of different cycle times on desorption effect.

4. Conclusions

- (1) Peanut shell (PS), Sawdust (S), and commercial active carbon (AC) were compared for their adsorption and desorption of Pb(II), Cu(II), and Cd(II) ions from aqueous solutions. The results demonstrate that PS is a green adsorbent material that can replace the traditional adsorbent AC and has effective adsorption of Pb(II), Cu(II), and Cd(II) ions from the water.
- (2) For three adsorbents, the adsorption capacity increases with the increasing phase temperature, pH value, contact time, adsorbent dosage, and heavy metal ion concentration, but decreases with the increase of adsorbent particle size.
- (3) The adsorption kinetics were well described by the pseudo-second-order model, meanwhile, the adsorption isotherms were well described by the Langmuir or Freundlich models. The adsorption process is a spontaneous heat absorption process.
- (4) It was shown that the desorption rate of adsorbents is higher in acidic environments than in other environments.

Author Contributions: Conceptualization, X.D. and X.L.; methodology, X.X.; software, X.L. and J.L.; investigation, X.L.; data curation, X.L. and J.L.; writing—original draft preparation, X.L. and J.L.; writing—review and editing, X.L. and X.D.; visualization, X.L. and J.L.; supervision, X.X., W.D., J.P., L.G. and Y.L.; funding acquisition, X.D., X.L. and L.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (grant NO. 51978438), National Natural Science Foundation of China (grant NO. 52281340410), Natural Science Foundation of Shanxi, China (grant NO. 202103021223122), School Foundation of Taiyuan University of Technology (No.2022QN044), and Key Laboratory of Ministry of Education for Geomechanics and Embankment Engineering, Hohai University (grant No.2020001).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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