Research Article

Removal of Cd(II) and Cu(II) from Aqueous Solution by Na⁺-Modified Pisha Sandstone

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Heavy metals have caused serious environmental issues, which are enriched during open-cast coal mining. It is urgent to develop sustainable remediation materials to protect and restore the contaminated soil and aquifers in mining areas. The feasibility of applying Pisha sandstone (PS) and Na⁺-modified Pisha sandstone (Na-PS) for adsorption of heavy metals was evaluated. Na-PS exhibited maximum Cd(II) and Cu(II) removal rates of 65.9% and 99.8%, respectively, exceeding the corresponding values for PS (8.2% and 1.3%, respectively) in 1×10⁻³ M solution. Efficient heavy metals adsorption occurred in the pH range 5.0–6.0. The adsorption of Cu(II) and Cd(II) on PS and Na-PS was characterized by kinetic models and adsorption isotherms and was well represented by pseudo-second-order kinetics (R² > 0.99) and the Langmuir and Freundlich isotherm models. The values of the thermodynamic parameters indicated that the interactions were spontaneous endothermic reactions. Binary solutions adsorption isotherms indicated that the linearity of the adsorption amount and initial concentration of Cu(II) and Cd(II) was better in certain ranges and the adsorbents were selective towards Cu(II) rather than Cd(II). Therefore, PSs can be used as excellent adsorbents for Cu(II) and Cd(II) remediation from contaminated surface water.

1. Introduction

Heavy metal contamination in open-cast coal mining areas has attracted great attention due to the serious effect of heavy metal toxicity and water acidification on plants and soil. A number of studies have identified that heavy metals (e.g., Cu and Cd) can be enriched during the process of open-cast coal mining, resulting in serious consequences for the surrounding ecosystems, groundwater, agricultural productivity, and human health [1–3]. The protection and restoration of soils and aquifers contaminated by heavy metals to protect agricultural products and human safety warrant the development of environmentally sustainable technologies.

Heavy metals could be removed in several ways including biosorption, chemical precipitation, electrolysis, adsorption, ultrafiltration, reverse osmosis, and ion exchange from aqueous solutions [4–7]. Among these methods, adsorption has been considered a promising method because this technique is generally easy to operate and cost-effective for the immobilization of heavy metals even at low concentrations [8]. In recent years, many synthetic materials have been developed as adsorbents that provide satisfactory performance for heavy metal removal [9, 10]. However, the overuse of synthetic adsorbents has inevitably brought a series of potential environmental problems [11]. For example, Pádrová et al. [12] found that the industrial synthetic adsorbents (e.g., Nanofer 25 and Nanofer 25S) are toxic to the soil microorganisms. Therefore, natural adsorbents, naturally formed or derived from natural materials with insignificant risks to the environment, have attracted the attention of researchers again due to their...
noninvasive properties and low cost [13, 14]. The mineral materials (montmorillonite, kaolinite, goethite, etc.) play an important role in environment as natural scavengers of pollutants from water through both ion exchange and adsorption mechanisms. These mineral materials are great adsorbent materials due to their chemical and mechanical stability, high specific surface area, high cation exchange capacity, layered structure, etc. [15]. In addition, these natural materials can be modified to further promote their metals adsorption capacity by changing their quality and characteristics via different techniques [16–18]. Based on this, there is a distinct tendency to replace the costly activated carbons and ion exchangers with those kinds of mineral materials as adsorption materials to remediate heavy metal pollution. However, mineral resources are limited, and it is particularly important to find more minerals with low cost and environmental-friendly, which have metal binding capacities.

Pisha sandstone (PS) is a type of loose rock composed of thick layers of sandstone, sandy shale, and shale [19]. On the one hand, it has a high cation exchange capacity (45.8 cmol·kg$^{-1}$) and variable charge due to its high iron oxides (18.6%) and aluminum oxides (14.5%) [20, 21]. PS also contains carbonate minerals and aluminosilicate minerals, both of which are considered beneficial for heavy metals removal [22]. On the other hand, a large amount of PS is exposed in mining areas for decades without any further use after coal mining in Northwestern China, which has led to a series of environmental problems such as soil erosion and vegetation degradation [23]. Thus, finding the means to effectively dispose of PSs has also become urgent. Previous studies have found that PS can be mainly used as large-scale soil amendment for agricultural applications in improving soil quality by increasing moisture and nutrient-holding capacity, especially for sandy soil [20]. Besides, the special geographical location of PS and its physical and chemical properties make it possible to be a promising natural material in soil remediation of heavy metals. Furthermore, modification of natural materials is often necessary because the adsorption capacity of natural mineral materials to heavy metals (e.g., kaolinite and bentonite) is generally low [24, 25]. Mineral material modification by introducing sodium salt has been reported to be an efficient method to improve the adsorption amount [26]. However, there is little information about using Na$^+$-modified Pisha sandstone (Na-PS) to adsorb heavy metals and how environmental factors influence the adsorption process. In addition, it is necessary to study the adsorption properties of PSs about specific heavy metal ions and their adsorption properties in competing ions present in polymetallic systems. Therefore, to verify the rationality usage and effectiveness of PS and Na-PS as adsorbents of heavy metals, it is highly meaningful and feasible to utilize PS and Na-PS to remove Cd(II) and Cu(II) solutions released by open mining and to explore the adsorption mechanisms in both single and binary aqueous solutions. This study may provide a feasible treatment scheme for heavy metal pollution in mining areas.

The objective of this study was to investigate the applicability of PS and Na-PS for the removal of Cd(II) and Cu(II) ions from aqueous solutions by addressing the following specific objectives: (i) characterize PS and Na-PS; (ii) evaluate PS adsorption capacity and adsorption kinetics for Cd(II) and Cu(II) in monometal or multimetal systems and investigate the effects of environmental factors in the process of adsorption; and (iii) elucidate the mechanisms that are involved in Cd(II) and Cu(II) removal by PSs. The outcomes of the study could lead to environmentally sustainable technologies and provide a reference for the application of PSs as low-cost and noninvasive natural adsorbents for heavy metal removal.

2. Materials and Methods

2.1. Materials. PS powder with a particle size of 16-mesh was acquired from the Jungar Banner of the northern Loess Plateau (latitude 40°10′ to 39°35′ N and longitude 110°35′ to 111°23′ E), China. The cation exchange capacity, specific surface area, pH, and clay composition (<0.002 mm) of the PS were 45.8 cmol·kg$^{-1}$, 1.96 m$^{2}$·g$^{-1}$, 9.25, and 15.2%, respectively. To obtain a homotopic sodium form, the PS sample was pretreated with a 3% NaCl solution and left overnight under gentle shaking. After multiple decantation and resuspension steps in fresh electrolyte solution, the sediment was thoroughly washed with deionized water until chloride ions were no longer detected by AgNO$_3$ addition. Then, the suspended PS was centrifuged, air-dried, and screened through a 16-mesh sieve. All chemicals used in this work were of analytical reagent grade and were utilized without further purification. The chemical composition and morphology of PS and Na-PS were characterized by X-ray diffraction (XRD) using Cu Kα radiation (D8 Advance A25, Bruker, Germany) and field emission scanning electron microscopy (FESEM) (S-4800, Hitachi, Japan).

2.2. Adsorption Kinetics. The 1.0 M metal ion solution was prepared and diluted according to the different initial concentrations required. Adsorption experiments were carried out at 303 ± 1 K using the batch technique in the single-component and two-component ion systems. The 25 ml metal ion solutions with initial concentrations ranging from 1 × 10$^{-3}$ M to 10 × 10$^{-3}$ M were placed in 50 ml centrifuge tubes with the required dose of PS samples (0.5 g) and shaken at a constant speed (250 rpm) for a specific contact time. The initial pH of the solutions was adjusted to 5.0 ± 0.05 or the required pH value by adding either HNO$_3$ or NaOH solution to avoid precipitation of metal ions. After shaking, the PS samples were separated through 5 min centrifugation at 4000 rpm and the solutions were filtered by a 0.45 μm Millipore filter. In the thermodynamic studies, the adsorption experiment of the PS was carried out in the single systems of Cu(II) or Cd(II) in 1 × 10$^{-3}$ M under 293, 303, and 313 K, respectively. The Cd(II) and Cu(II) concentrations were analyzed through atomic absorption spectrometry (AAS) (Z2000, Hitachi, Japan) at 324.7 nm and 228.8 nm, respectively, in the residual solutions. The amount ($q_t$) and percentage (S%) of adsorption were calculated according to the following equations, respectively:
\[ q_t = \frac{(c_0 - c_t)V}{m}, \]
\[ S\% = \frac{c_0 - c_t}{c_t} \times 100, \]

where \( q_t \) is the adsorption amount of metal ions at time \( t \) (mg\( \cdot \)g\( ^{-1} \)), \( c_0 \) and \( c_t \) are the initial and time-dependent concentrations of M(II) ions in solution, respectively (mg\( \cdot \)L\( ^{-1} \)), \( V \) is the volume of solution (L), \( m \) is the weight of the PS sample (g), and \( S\% \) is the adsorption percentage (%). When \( t \) is equal to the equilibrium contact time, \( q_e = q_f \); \( q_e \) represents the adsorption amount of M(II) at equilibrium, which could be calculated by equation (1).

According to Lagergren [27] and Yuh-Shan [28], the adsorption kinetics and dynamics of Cd(II) and Cu(II) on the PS samples were investigated by using the following pseudo-first-order kinetic equation:

\[ \log(q_f - q_t) = \log(q_f) - \frac{k_f t}{2.303}, \]

The pseudo-second-order kinetic model is expressed as the following equation [29]:

\[ \frac{t}{q_t} = \frac{1}{k_q q_f^2} - \frac{t}{q_f}, \]

The Elovich model is as follows [30, 31]:

\[ q_t = \frac{1}{b} \ln(1 + abt), \]

where \( k_f \) and \( k_r \) are rate constants (g\( \cdot \)mg\( ^{-1} \)\( \cdot \)min\( ^{-1} \)) for the pseudo-first-order and the pseudo-second-order adsorption, respectively, and \( a \) and \( b \) are the constants. The kinetic parameters \((q_0, k_f, q_0, k_r, a, \) and \( b) \) were calculated through the plots of \log(\( q_e - q_t \)) vs. \( t \), \( qt/ct \) vs. \( t \), and \( q_t \) vs. \ln(\( t \)).

2.3. Adsorption Equilibrium. The PSs samples adsorption data for the metal ions were analyzed by applying two isotherm models. The Langmuir model is expressed as follows [32]:

\[ q_e = \frac{q_0 K_L c_e}{1 + K_L c_e}, \]

where \( q_e \) is the equilibrium adsorption capacity (mg\( \cdot \)g\( ^{-1} \)) and \( c_e \) is the concentration of metal ions at equilibrium (mg\( \cdot \)L\( ^{-1} \)). The constants \( q_0 \) (mg\( \cdot \)g\( ^{-1} \)) and \( K_L \) (mg\( \cdot \)L\( ^{-1} \)) are the characteristics which can be determined from the plot of \( c_e/q_e \) vs. \( c_e \).

The Freundlich model is as follows [33]:

\[ q_e = K_f c_e^{1/n}, \]

where \( q_e \) is the equilibrium adsorption capacity (mg\( \cdot \)g\( ^{-1} \)) and \( 1/n \) is an important Freundlich constant about the surface heterogeneity. The parameters \( K_f \) and \( n \) can be calculated from the plot of \log(\( q_e \)) vs. \log(\( c_e \)).

The Temkin model is as follows [34]:

\[ q_e = \frac{RT}{B} \ln(A \times c_e), \]

\[ b = \frac{RT}{B}, \]

where \( A \) and \( B \) are the Temkin isotherm constant (dm\( ^3 \)\( \cdot \)g\( ^{-1} \)) and heat of sorption (J\( \cdot \)mol\( ^{-1} \)), respectively. \( R \) is the gas constant (J\( \cdot \)mol\( ^{-1} \)\( \cdot \)K\( ^{-1} \)), \( K \) is the Temkin isotherm constant linked to the energy parameter, and \( T \) is the absolute temperature in Kelvin. The parameters \( A \) and \( B \) can be calculated through the plot of \( q_e \) vs. \ln(\( c_e \)).

2.4. Thermodynamic Adsorption. The thermodynamic adsorption parameters were determined from the variations in the thermodynamic equilibrium constant \( K_e \) by using the following equation:

\[ \Delta G = -RT \ln K_e, \]

\[ \ln K_e = \frac{\Delta S}{R} + \frac{\Delta H}{RT}, \]

where \( K_e \) is determined by plotting \ln(\( q_e/c_e \)) vs. \( q_e \) and extrapolating to zero \( q_e \). \( T \) is the absolute temperature (K), \( R \) is the universal gas constant (8.314 J\( \cdot \)mol\( ^{-1} \)\( \cdot \)K\( ^{-1} \)), \( \Delta G \) is the standard free energy change of ion exchange (J\( \cdot \)mol\( ^{-1} \)), \( \Delta H \) is the enthalpy (kJ\( \cdot \)mol\( ^{-1} \)), and \( \Delta S \) is the entropy (J\( \cdot \)mol\( ^{-1} \)K\(^{-1} \)). The values of \( \Delta H \) and \( \Delta S \) can be calculated from the slope and intercept by the linear plot of \( \Delta G \) vs. \( T \).

2.5. Competitive Adsorption. The adsorption data for Cd(II) and Cu(II) in binary solutions were analyzed using the following ternary equation at adsorption equilibrium:

\[ y = a + bx + cz, \]

where \( y \) is the adsorption capacity (mg\( \cdot \)g\( ^{-1} \)), \( x \) and \( z \) are the initial solution concentrations (mmol\( \cdot \)L\( ^{-1} \)), and \( a, b, \) and \( c \) are constants that were calculated through the experimental data in OriginPro 9.0. We conjecture that \( a \) is connected with noncompetitive adsorption, and \( b \) and \( c \) are competitive parameters associated with the metals' properties.

3. Results and Discussion

3.1. Characterization of PS and Na-PS. The surface morphology and elemental content of PS and Na-PS were determined as shown in Figure 1. The SEM images of the PSs clearly showed that some sheet-like substances existed on the surface of both clays. Previous studies indicated that these substances are montmorillonite [26]. The XRD patterns indicated the mineral phases, which mainly include quartz, calcite, feldspar, and montmorillonite, as shown in Figure 1(c). The high crystallinity of quartz means that the PSs have high chemical stability. Besides, Figure 1(c) shows the XRD patterns of PSs before and after sodium ion modification. With Na\(^+\)-modified PS, the intensity of most diffraction peaks decreased and the width of the diffraction peaks increased slightly, suggesting that the introduction of
Na\(^+\) made the crystallization of PS poorer \[35, 36\]. Furthermore, sodium oxide peaks were clearly detected after modification with Na\(^+\), indicating that Na\(^+\) was successfully grafted onto the PS adsorbent (Figure 1(c)) \[37\].

### 3.2. Effect of pH

pH plays an important role in the surface charge of adsorbents and speciation of heavy metal ions \[38, 39\]. The effect of the initial pH of the Cd(II) and Cu(II) ion solutions on the PS adsorption capacity was studied by adjusting the initial pH, while keeping other process parameters constant. According to the speciation distribution of the metal ions determined by Medusa software (Hydrochemical Equilibrium-Constant Database, Royal Institute of Technology, Sweden), almost all the copper exists in the Cu(II) form with pH from 1.0 to 5.0 at an initial concentration of \(1 \times 10^{-3} \) M, and for Cd(II) the relevant range is 1.0–8.0. Therefore, the pH dependence of Cd(II) and Cu(II) adsorption was studied at pH values lower than 8 to avoid the uncertainty arising caused by heavy metal precipitation. As shown in Figure 2(a), the adsorption capacity \(q_e\) rapidly increased and gradually reached a plateau as the pH further increased. The effect of pH on adsorption was attributed to facilitation or hinderance of electrostatic interactions on the ability of the electric charge density of the surface in aqueous solution. Furthermore, negatively charged active sites can promote Cd(II) and Cu(II) adsorption through the electrostatic attraction between PSs and heavy metal ions \[14, 40\].

### 3.3. Effect of Agitation Time and Kinetics of Adsorption

The adsorption kinetics curve is shown in Figure 3. The increase in the metal adsorption amount was initially rapid reaching above 80% of the equilibrium amount within 5 min but slowed down as the sorption approached equilibrium. The equilibrium times for Cd(II) and Cu(II) were between 60 and 120 min and between 30 and 60 min, respectively, and the reaction time increased with increasing initial

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**Figure 1:** Scanning electron microscope images of PS (a) and Na-PS (b) and XRD patterns (c). Note: PS means Pisha sandstone; Na-PS means Pisha sandstone modified with Na\(^+\).

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concentration ($P < 0.05$). Similar observations for Cd(II) adsorption on kaolinite and montmorillonite [33] and Cu(II) adsorption on biochar [41] have been reported. Furthermore, the trend of the kinetic curve was also different between Cd(II) and Cu(II) (Figure 3). The adsorption amount of Cd(II) had a supersaturation point in the first ten minutes for both PS and Na-PS, which could, because of Cd(II), have large hydrated ion radius and weak affinity. During the process, Cd(II) may lose some adsorption sites due to competition with cationic ions (Mg$^{2+}$, Ca$^{2+}$, H$^+$, etc.), leading to a decreased adsorption amount until stabilized equilibrium. A similar phenomenon was observed for cadmium removal using brown soil [42]. Therefore, the equilibrium time and the trend of the kinetic curve were influenced by different metals and initial concentration, while Na$^+$-modified PS did not influence these properties.

The pseudo-first-order model [27], the pseudo-second-order model [29], and the Elovich model [30, 31] were used to establish the adsorption kinetic parameters and reflect the kinetic characteristics. The mentioned parameters ($q_f$, $k_f$, $q_s$, $k_s$, $a$, and $b$) were obtained by the linear fitting procedure (Table S1). The Elovich model had no adequate description of the adsorption results about Cd(II) and Cu(II) onto PS and Na-PS due to the low correlation coefficients ($R^2$), especially for Cd(II). The pseudo-first-order and pseudo-second-order kinetics models both had good $R^2$ value. Taking into account the $R^2$ values, $q_f$ and $q_{f,exp}$, the pseudo-second-order model achieved a better fit ($R^2 > 0.999$). The appropriate plots of the pseudo-second-order kinetic model showed that the $q_f$ values increase with increasing initial concentration (Figure 4) because of the stronger driving force (caused by the higher concentration gradient), which means that the process was controlled by diffusion. The results were consistent with previously reported results for Cd(II) and Cu(II) adsorption by kaolinite and montmorillonite [36, 43].

3.4. Effect of Initial Cd(II) and Cu(II) Concentration. The effect of the initial concentration of Cd(II) and Cu(II) on the removal of PS (the adsorption rate ($S\%$) and the amount adsorbed ($q_f$) at different time intervals) was studied. At initial concentrations of M(II) ions ranging from $1 \times 10^{-3}$ to $3 \times 10^{-3}$ M, the $S\%$ of Cu(II) was 98.5%, 89.1%, and 78.4%, and that of Cd(II) was 57.7%, 49.2%, and 43.8%, respectively. Moreover, Na-PS had higher adsorption rates of Cu(II) (99.8%, 91.6%, and 81.8%, respectively) and Cd(II) (65.9%, 55.4%, and 48.3%, respectively). PSs had excellent adsorption ability and almost completely removed Cu(II) from aqueous solutions at lower initial concentrations. In addition, the adsorption amount of Cu(II) was similar between PS and Na-PS (Figure 2(a) and Figures 3(c) and 3(d)) for $c_e$ below 120 mg·L$^{-1}$ ($P > 0.05$) because Cu(II) does not need to acquire extra adsorption sites from Na$^+$ at low concentrations [44]. As the ion concentration increased, the adsorption amount of Na-PS was obviously enhanced over that of PS. Therefore, in the adsorption process of Na-PS, Cu(II) may be firstly occupied by original binding sites on PS and then the additional binding sites supplied by Na$^+$-modified PS.

3.5. Adsorption Isotherm. The equation parameters of the Langmuir, Freundlich, and Temkin models can provide vital information, such as insight into the sorption mechanism and the surface properties and affinity of the sorbent, to optimize the use of adsorbents [45]. These models were applied to the experimental sorption data for PS and Na-PS, and the obtained parameters are exhibited in Table S2 and

![Figure 2: Effect of pH on Cd(II) and Cu(II) adsorption on PS and Na-PS. Note: PS means Pisha sandstone; Na-PS means modified Pisha sandstone by Na$^+$.](image-url)
Figure 5. Fitting the isotherm with the Langmuir model, the maximum adsorption capacities \( q_m \) of Cd(II) and Cu(II) were 12.79 and 19.49 mg g\(^{-1}\) for PS, respectively. Na\(^+\)-modified PS effectively increased the Cd(II) and Cu(II) sorption amounts (12.81 and 21.37 mg g\(^{-1}\), respectively). The selective adsorption of the PS adsorbents to Cd(II) or Cu(II) was dependent on the electronegativity and the hydrated ionic radius [46]; higher electronegativity and hydrated ionic radius exhibited better metal uptake [47, 48]. In addition, compared with other adsorbents such as kaolinite and bentonite (6.8 and 10.8 mg g\(^{-1}\) for Cu(II) and 4.4 and 11 mg g\(^{-1}\) for Cd(II), respectively) [24, 25, 41, 49], the PSs showed superior adsorption capacity to Cd(II) and Cu(II), which further confirmed their attractive potential for applications in adsorption of heavy metals.

In this study, the Langmuir and Freundlich models reproduced the sorption data closely for both PS and Na-PS, with correlation coefficients above 0.95. The exponent \(1/n\) of the Freundlich model fell into the range of 0–1 (0.40–0.50 for Cd(II) and 0.37 for Cu(II)), confirming that the adsorption of Cd(II) and Cu(II) was favored on the PSs [50]. In addition, the Freundlich isotherm model hypothesizes that multilayer adsorption occurs on heterogeneous surfaces and the adsorption amount increases infinitely with increasing concentration.
concentration [33], whereas the Langmuir model hypothesizes that monolayer adsorption occurs on the homogeneous surface of all identical sites that are energy-spatially independent of the adsorbed quantity [31], which indicates that PS and Na-PS uptake mainly occurred via complex process. The dependence of sorption on the nonlinearity of the sorption isotherms and solution pH was ascribed to a surface complex mechanism, which involved two types of surface hydroxyl groups (≡SsOH and ≡SWOH sites) on the clay mineral platelet edges [51]. Furthermore, the Fe$^{3+}$ ion in aqueous solution is subsequently hydrolyzed to form FeOOH [52]. The presence of hydroxyl groups on the surface of FeOOH was also an important chemical property during the adsorption process, which influences the complexation between Cu(II) and surface hydroxyl groups [15]. In addition, Figures 1(c) and 2(b) suggest that ion exchange was one of the main mechanisms during the removal of Cd(II) by PS [37, 39]. The high clay mineral component (15.2%) and cation exchange capacity of PS (45.8 cmol·kg$^{-1}$) suggest a high potential of ion exchange [53]. Therefore, the

Figure 4: Pseudo-second-order plot for the adsorption of Cd(II) (a and b) and Cu(II) (c and d) on PS and Na-PS depending on the initial concentration. Note: PS means Pisha sandstone; Na-PS means Pisha sandstone modified with Na$^+$. 
adsorption mechanism of PSs for adsorption of Cd(II) and Cu(II) generally involved ion exchange and complexes of hydroxyl groups on the surface of PS. Besides, the clay mineral component provided complex surface structure with high specific surface area, which also favored heavy metals adsorption.

3.6. Effect of Temperature. The adsorption of Cd(II) and Cu(II) on PS was also investigated as a function of temperature. The previous results suggested that Na-PS generally exhibits similar behaviors with those of PS because of their similar chemistry, so in this part we only studied the PS.

The adsorption amounts of Cd(II) and Cu(II) at 298 K, 303 K, and 313 K were calculated to obtain the thermodynamic parameters (ΔH, ΔS, and ΔG) and predict the nature of adsorption, which were evaluated using the Van’t Hoff equation. The free energy change (ΔG) and enthalpy (ΔH) were both negative, indicating a spontaneous exothermic process. The positive ΔS value suggested an increase in molecular disorder at higher temperatures (Table 1) [54]. These results were consistent with the adsorption of Cu(II) on goethite and montmorillonite reported by Fang et al. [55]. Additionally, the low positive values of ΔS (1.36 J·mol⁻¹·K for Cd(II) and 1.00 J·mol⁻¹·K for Cu(II)) indicated that Cu(II) has lower randomness at the solid/
solution interface than Cd(II) during the uptake process, which suggested the high affinity of the adsorbent for the two adsorbed species [56].

3.7. Competitive Adsorption. The simultaneous adsorption of Cd(II) and Cu(II) on PS or Na-PS was conducted to determine the interactive effect of varying concentrations of the given metal ions on each other. Representative adsorption data obtained for the Cu-Cd system are presented in Figures 6(a)–6(d), 7(a)–7(d), and Table 2 in two different forms: 3D and 2D. On the three-dimensional adsorption isotherm surfaces, the adsorption capacity at equilibrium of Cd(II) or Cu(II) (mg·g⁻¹) (z-axis) was plotted as a function of the initial solution concentrations of Cd(II) and Cu(II) (mmol·L⁻¹) in the liquid phase (x- and y-axis). As

| Metal | $\Delta G$ (kJ·mol⁻¹) | $\Delta H$ (kJ·mol⁻¹) | $\Delta S$ (J·mol⁻¹·K⁻¹) |
|-------|----------------------|----------------------|------------------------|
| Cd    | −429 293K            | −526 303K            | −548 313K              |
| Cu    | −391                | −492                | −617                   |

Note: PS means Pisha sandstone.

**Table 1:** Thermodynamic parameters of Cd(II) and Cu(II) adsorption on PS.
shown in the 3D graphs (Figures 6(a)–6(d)), a bivariate quadratic equation well described the relationship between the heavy metal adsorption amount of the PSs and the initial concentration of Cd(II) and Cu(II) in binary solution (the correlation coefficients were all above 0.97) (Table 2), indicating that the two ions are under a linear competitive relationship. To provide a meaningful comparison between experimental sets, the obtained competitive isotherms for the relationship between \( q_e \) and \( c_e \) were presented in 2D graphs showing the distribution of both competitive ions at equilibrium. In the 2D graphs (Figures 7(a) and 7(b)), an increase in Cu(II) concentration (fitted straight line) caused a decrease in the uptake of Cd(II) (downward slope). With increased Cu(II) concentration (from \( 1 \times 10^{-3} \)M to \( 3 \times 10^{-3} \)M), the adsorption capacity of the PS towards Cd(II) decreased by 17%, 24%, and 32% in \( 3 \times 10^{-3} \)M Cd(II) solution. 

![Graphs showing the relationship between adsorption and concentration](image)

Table 2: Parameters for the competitive solution of Cd(II) and Cu(II) on PS and Na-PS.

| Metal | Material | \( a \)  | \( b \)  | \( c \)  | \( R^2 \) |
|-------|----------|--------|--------|--------|---------|
| Cd    | PS       | 0.80   | 1.61   | -0.30  | 0.97    |
|       | Na-PS    | 0.94   | 1.75   | -0.41  | 0.98    |
| Cu    | PS       | 0.35   | -0.16  | 2.07   | 0.99    |
|       | Na-PS    | 0.30   | -0.11  | 2.16   | 0.99    |

Note: PS means Pisha sandstone; Na-PS means Pisha sandstone modified with Na⁺.

Figure 7: Influence of different concentrations of Cu(II) on the adsorption amount of Cd (II) on PS and Na-PS. Note: PS means Pisha sandstone; Na-PS means Pisha sandstone modified with Na⁺.
(Figures 7(c) and 7(d)). Therefore, the adsorption isotherms for binary solutions indicated that Cu(II) and Cd(II) have significant linear competition within a certain concentration range, and Cu(II) has a greater influence on the adsorption amount of Cd(II), while Cd(II) has very little influence on Cu(II).

4. Conclusions
PS and Na-PS demonstrated the efficient adsorption of Cd(II) and Cu(II) in their respective monometal systems and high selectivity for Cu(II) in the multimetal system. The results suggested that Na-PS generally exhibits similar behaviors with those of PS because of their similar chemistry, except for the higher adsorption amounts. The adsorption of Cd(II) and Cu(II) on the adsorbents takes place through sufficiently strong exothermic interactions accompanied by entropy and Gibbs energy changes and is dominated by a cation exchange and complexes of hydroxyl groups mechanism. In general, the PSs exhibited potential applications as great adsorbents for Cu(II) and Cd(II) removal from aqueous medium, especially in low concentration. The study proved the application potential of PS, a naturally abundant material, as a cost-effective and eco-friendly heavy metals adsorbent in remediation of heavy metal and water acidification.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare no conflicts of interest.

Authors’ Contributions
Xia Wang and Yongxing Cui contributed equally to this work.

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Supplementary Materials
The supplemental information includes additional tables showing the kinetic parameters of Cd(II) and Cu(II) adsorption on PS and Na-PS. (Supplementary Materials)

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