Sorption of Pb(II) and Cu(II) on the colloid of black soil, red soil and fine powder kaolinite: effects of pH, ionic strength and organic matter

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ABSTRACT

The sorption potentials of two soil colloids and fine powder kaolinite for Pb(II) and Cu(II) were analyzed, and the effects of pH, ionic strength and organic matter on the sorption were investigated. The two soil colloids and fine powder kaolinite were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analysis. Black soil had more mineral compositions and surface functional groups. The sorption was pH-dependent. In the presence of humic acid, the adsorption of Pb(II) and Cu(II) ions on soil was increased, while the increase in ionic strengths decreased the adsorption. Sorption kinetics and isotherms of Pb(II) and Cu(II) onto three soil colloids were well fitted with Pseudo-second-order model and Langmuir model/Freundlich model. Black soil had the highest sorption capacity of Pb(II) (44.287 mg g⁻¹) and Cu(II) (11.109 mg g⁻¹), followed by red soil (9.764 and 4.152 mg g⁻¹) and kaolinite (7.612 and 3.064 mg g⁻¹). The two metals competed with each other during sorption.

1. Introduction

Metals and metalloids can result in detrimental and toxicological effects to both environmental quality and human health; therefore, they are one of the hottest issues concerned all over the world. Metal(loids) in environmental media may result from a variety of anthropogenic sources such as metal dust from mining/smelting vehicular emissions, industrial dust, waste incineration, and industrial wastewater. Soil is one of the most important receptors of metal(loids) of wet and dry atmospheric deposition and discharged wastewater. When the excess metal(loids) enters into soil, soil quality decreases. Heavy metals can be bioaccumulated and transferred via the food chain to produce certain toxic effects [1,2]. They may also be transported to underground water, which may result in contamination of a broader area.

Soil colloids are the most active components of the soils and generally include different layer silicates and bi-particles with particle sizes of 10 to 1000 nm [3]. When metal(loids) enters into the soil, they will react with fine and ultrafine particles of soil colloids. So those soil colloids are regarded as potential carriers of pollutants in soils due to their small suspension particle size and large surface area [4,5]. Metal(loids) in soil colloids may undergo several complicated chemical processes [6], such as dissolution and precipitation, oxidation and reduction, adsorption and desorption. Among them, adsorption is a vital process controlling the fractionation of heavy metals in the soil system [7]. Therefore, in order to reveal the mechanism of the colloid-facilitated transport of metal(loid)s in soils to underground water, adsorption and desorption of metal(loid)s in soil colloids should be investigated carefully.

The adsorption of lead by soil is the combination of mineral component and soil organic matter working together [8,9]. The adsorption rate of copper onto soils directly reflects the migration ability of copper under certain environmental conditions. Studies of adsorption onto different kinds of soils [9,10] have discovered that the main physicochemical factors governing these processes are pH, the ion strength and the presence of organic or inorganic colloids.

In recent years, many studies illustrated the facilitated transport of contaminants by soil colloids through surface sorption [11]. Therefore, it is extremely important to study the sorption characteristics of soil colloids. In this study, three soil/solid mineral samples (Red soil colloids, Black soil colloids and Kaolinite) were used for adsorption experiments. The sorption of Pb(II) and Cu(II) onto soil colloids were performed to evaluate the sorption performance. Effect of pH, ionic strength and humic acids were investigated. Sorption isotherms and kinetics were analyzed by models. And the sorption capabilities of Pb(II) and Cu(II) in a competitive experiment were also compared.
2. Materials and methods

2.1 Preparation and characterization of soil colloids

All chemicals of analytical reagent were prepared with deionized (DI) water (18.3 MΩ cm) and purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, P.R. China. The black soil and red soil samples (0–20 cm) were collected from Nanjing and Guangzhou, respectively. And kaolinite was purchased from Sinopharm Chemical Reagent Co., Ltd. Soil/kaolinite colloids were obtained by a planetary ball mill (planetary ball mill, QM-3SP04-1, Nanjing University, CHN) at 500 rpm for 12 h. The blank soil colloid, red colloid, and kaolinite colloid were noted as BS, RS, and KL. Particle size distribution of soil colloids was determined by a dynamic light scattering particle size analyzer (90plus, BIC, USA). The pH values of samples were measured with a pH meter (pH meter, PB-10, Sartorius, GER) in deionized water (w/v = 1:2.5). Cation exchange capacity (CEC) was determined by the method of Lu [12]. The results of physical and chemical properties of the samples were presented in Table 1. As shown in Table 1, the average particle sizes of the three samples were between 400 nm and 800 nm, and BS had the largest cation exchange capacity. The crystallographic structure and functional groups of the samples were also characterized by X-ray diffraction (XRD, CAD4/PC, Enraf Noius, NED) and Fourier transform infrared spectrometer (FTIR, NEXUS870, NICOLET, USA).

2.2 Sorption experiments

The sorption of Pb(II) and Cu(II) onto BS, RS and KL were investigated by batch experiments in 50 mL centrifuge tube, 0.05 g samples with 25 mL solution, shaken at room temperature (22 ± 2°C) for 24 h. After centrifugation and filtration, the concentrations of Pb(II) and Cu(II) in the solution were detected via the ICP-OES. According to preliminary experiments, pH values of the solutions were adjusted at 3, 4, 5, and 6 by 0.1 M HCl and 0.1 M NaOH. The initial concentrations of Pb(II) and Cu(II) in the solution were detected via the ICP-OES. According to preliminary experiments, pH values of the solutions were adjusted at 3, 4, 5, and 6 by 0.1 M HCl and 0.1 M NaOH. The initial concentrations of Pb(II) and Cu(II) were 80(78.925) mg L⁻¹ for BS, 20(22.175) mg L⁻¹ for RS and 10 mg L⁻¹(10.69) for KL and the initial concentrations of Cu(II) were 40(35.335) mg L⁻¹ for BS, 10(8.961) mg L⁻¹ for RS and KL in the investigation of pH effects. The heavy metals’ concentrations were noted as designed concentrations (actual concentrations used), and the concentrations noted in the following experiments had the same format. The effect of ionic strength (IS) on the sorption was investigated at 0.05, 0.1 and 0.15 mol L⁻¹ of Ca(NO₃)₂ (pH 5.5). The initial concentrations of Pb were 80(78.260) mg L⁻¹ for BS, 20(18.310) mg L⁻¹ for RS and 10 mg L⁻¹(10.405) for KL and the initial concentrations of Cu(II) were 40(39.376) mg L⁻¹ for BS, 10(9.723) mg L⁻¹ for KL and the effects of humic acids (HA) on the sorption were studied through 10 and 20 mg L⁻¹ at pH 5.5, respectively. HA was purchased from Sinopharm Chemical Reagent Co., Ltd. The initial concentrations of Pb were 80(81.900) mg L⁻¹ for BS, 20(23.360) mg L⁻¹ for RS and 10(11.430) mg L⁻¹ for KL and the initial concentrations of Cu(II) were 40(37.405) mg L⁻¹ for BS, 10(11.230) mg L⁻¹ for KL and the initial concentrations of Cu(II) were 40(37.405) mg L⁻¹ for BS, 10(11.230) mg L⁻¹ for RS and KL. Sorption kinetics of Pb(II) and Cu(II) were determined at different contact time (5, 10, 30, 60, 120, 240, 480, 720 and 1440 min), with the initial Pb(II) concentrations of 80(78.930) mg L⁻¹ for BS, 20(20.690) mg L⁻¹ for RS and 10(11.340) mg L⁻¹ for KL, and the initial Cu(II) concentrations of 40(38.930) mg L⁻¹ for BS, 10(11.230) mg L⁻¹ for RS and KL(all in 10 mg L⁻¹ HA, pH 5.5, set according to the former experiments). The sorption isotherms were carried out with different Pb(II) concentrations (10(9.755), 45(45.015), 85(84.570), 100(105.560), 170(170.970), 180(182.560), 200(198.300) mg L⁻¹ for BS, 5(6.742), 15(14.527), 35(37.576), 50(49.215), 80(79.543), 120(120.343), 135(135.430) mg L⁻¹ for RS and 5(3.204), 10(6.742), 15(16.527), 25(23.5775), 50(48.015), 80(80.670), 140(140.020) mg L⁻¹ for KL in 10 mg L⁻¹ HA) and different Cu(II) concentrations (10(11.304), 30(32.935), 50(48.910), 60(63.635), 80(81.990), 100(101.700) mg L⁻¹ for BS, 10(9.142), 25(24.510), 40(39.105), 50(48.910), 80(80.70), 100(102.170) mg L⁻¹ for RS and 10(9.142), 15(15.315), 25(24.510), 30(32.070), 40(41.010), 50(49.810), 100(90.432) for KL, in 10 mg L⁻¹ HA) at pH 5.5. Competitive sorption was studied at 40(46.030) mg L⁻¹ Pb, 40(42.320) mg L⁻¹ Cu, 40(42.310) mg L⁻¹ Pb(II) 40(41.040) mg L⁻¹ Cu(II) for BS, and 10(15.130) mg L⁻¹ Pb, 10(11.210) mg L⁻¹ Cu, 10 mg L⁻¹ (12.78) Pb(II) + 10(10.974) mg L⁻¹ Cu(II) for RS and KL in 10 mg L⁻¹ HA, pH5.5. All samples were triplicated.

2.3 Modeling of adsorption kinetics and isotherm

The pseudo-first-order kinetic model (1) and the pseudo-second-order kinetics model (2), which were based on the adsorption capacities of solids [13], were used to test the sorption kinetic experimental data. The mathematical expressions of them are as follows:

\[
\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t
\]

\[
\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_{eq}}\right) t
\]

where \( q_e \) and \( q_t \) are the amounts of Pb(II) and Cu(II) sorbed at equilibrium and at time \( t \) (min), respectively. \( k_1 \) is the constant of pseudo-second-order adsorption.

| Soil | pH | Average particle size (nm) | CEC (cmol kg⁻¹) |
|------|----|-----------------------------|----------------|
| BS   | 6.87 | 485                        | 38.7           |
| RS   | 5.99 | 785                        | 19.2           |
| KL   | 5.65 | 403                        | 8.70           |

Table 1. Some properties of BS, RS and KL.
rate (min\(^{-1}\)) while \(k_2\) is the pseudo-second-order sorption rate constant (g mg\(^{-1}\) min\(^{-1}\)).

Langmuir adsorption isotherm model (3) and Freundlich adsorption isotherm model (4) were used to test the sorption isotherm experimental data. Langmuir adsorption model is commonly used for monolayer adsorption [14–16] while the Freundlich adsorption isotherm model is often used for multilayered molecular adsorption on inhomogeneous surfaces [17]. Equation expression is as follows:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L} C_e \quad (3)
\]

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)
\]

where \(C_e\) is the equilibrium concentrations of Pb(II) and Cu(II) in solution (mg L\(^{-1}\)), \(Q_e\) is the equilibrium adsorption amount (mg g\(^{-1}\)), \(Q_m\) is the maximum sorption capacity of adsorbent (mg g\(^{-1}\)), \(K_L\) is the Langmuir constant related to the sorption energy (L mg\(^{-1}\)), \(K_F\) is the Freundlich constant (mg g\(^{-1}\))(mg L\(^{-1}\))\(^{-1/n}\) and \(1/n\) is the intensity of adsorbent.

2.4 Statistical analysis

The results were showed as the mean of three replicates. The modeling of data was obtained using Origin 9.6 and Microsoft Excel Software (version 2010, Microsoft Corporation, USA). The level of significance was set at \(P < 0.05\).

3. Results and discussion

3.1 XRD and FTIR characterization of BS, RS and KL

The XRD patterns of three kinds of soils are shown in Figure 1. The diffraction patterns of BS samples contain different peaks corresponding to quartz (SiO\(_2\)), albite (Na\(_2\)O·Al\(_2\)O\(_3\)·6SiO\(_2\)) and illite (K\(_{1-x}\)(H\(_2\)O)\(_x\))(Al\(_{1-x}\)Si\(_{4-x}\)O\(_{10}\)(OH)\(_2\)). The spectra of BS showed typical peaks at 2\(\theta\) = 16°, 21° which represented quartz. Besides, the third peak was representative of albite at 2\(\theta\) = 28°. The spectra also showed weak peaks on BS representing illite at 2\(\theta\) = 20° and 35°. The XRD pattern of KL exhibited distinct peaks at 2\(\theta\) = 12° and 25° which were corresponded to kaolinite (Al\(_{2}\)[Si\(_2\)O\(_5\)](OH)\(_2\)). The main peak of RS was at 2\(\theta\) = 27°, with other peaks of significant strength at 2\(\theta\) = 21° and 50°. The main revealed crystalline component of RS was quartz (SiO\(_2\)). Therefore, XRD spectra revealed that BS had more mineral compositions than RS and KL. The presence of different minerals in BS colloids including quartz, albite and illite, which might contribute to the sorption process [18].

FTIR spectra have been frequently used to explore the sorption capacity of the surface functionalities of soil colloids. The FT-IR spectra of the three samples at the range of 4000–500 cm\(^{-1}\) are shown in Figure 2. BS showed a broad band at approximately 3418 and 3619 cm\(^{-1}\) which could be ascribed to the stretching vibration of O–H [19] as well as a sharp peak at 1631.7 cm\(^{-1}\) which was corresponded to C = O [19]. The bands at about 1034.6 cm\(^{-1}\), 588.4 cm\(^{-1}\) in the spectrum of BS were assigned to C-O, C-H, respectively. As expected, RS had exhibited broadband at approximately 3436 cm\(^{-1}\) for O–H, 1633.6 cm\(^{-1}\) for C = O, and 1086 and 1035 cm\(^{-1}\) for C-O, respectively [20,21]. The narrow band at approximately 695.4 cm\(^{-1}\) was assigned to C-H. In addition, FTIR spectra of KL showed a very broad absorption band at 3600–3800 cm\(^{-1}\), which was assigned to O-H [21]. Adsorption band at approximately 1031 cm\(^{-1}\) was assigned to Si-O vibration [21].

3.2. Effect of pH

pH is a major factor affecting adsorption of heavy metals on soils. Figure 3(a) reveals that the adsorption
of Pb(II) on BS increased evidently over pH range of 3.0–4.0, then increased gradually at the pH range of 4.0–6.0 and reached maximum at pH 6. The changes in pH cause a remarkable change of the sorption of Pb(II), and it is similar to the observation published earlier for the sorption of hydrolysable metal ions [22]. Besides, the increasing pH value might accelerate the hydrolysis of Pb(II), and the formed hydroxyl ion was easier to be adsorbed by soil colloids [23]. The adsorption on RS and KL have the same change tendency. They increased gently and reached maximum at pH 6.0. In accordance with this, Cozmuta et al. showed that the influence of pH on the adsorption process of lead ions on soil could be explained through the influence of H⁺ ions on the complex ion formation process [24]. Comparison to RS and KL, the Pb (II) sorption onto BS is more favorable.

As can be seen from Figure 3(b), the sorption of Cu(II) onto BS and RS both reached the maximum at pH 5.0, then began to decrease. Increasing the pH value of the solution from pH 3.0 to pH 5.0 led to a gradual decrease from pH 3.0 to pH 5.0, and the high adsorption capacity decreased from pH 5.0 to pH 6.0. For RS, the sorption increased gradually from pH 3.0 to pH 5.0 and then decreased. For KL, the sorption increased gradually in the whole pH range tested. BS showed the largest sorption capacity for Cu(II) among the three adsorbents, and RS had larger sorption capacity than KL at the pH range of 4.0 to 5.0. Under acidic conditions, decreasing the pH led to an increase in the amount of H⁺ ions in solution and the sorbents may become positively charged, thus increasing the competitive for available binding sites between Cu(II) and H⁺ [25]. Besides, at a low pH value, the hydroxyl groups on the surface of copper are protonated which was unfavorable for the sorption of Cu(II) [7]. This helps explain why the adsorption of Cu(II) at a low pH was obviously low. However, with the increasing of pH value, the surface available adsorption sites become more negatively charged, which leads to decreasing in competitive adsorption [26]. According to this, the rest sorption experiments were carried out at pH 5.5.

3.3 Effect of ionic strength

The effect of ionic strength (IS) on Pb(II) and Cu(II) sorption onto BS, RS and KL are shown in Figure 4. The results show that the two soils and KL showed the same change trends that the higher the ionic strengths were, the less Pb(II) and Cu(II) ions were adsorbed. These tendencies of adsorption onto the three colloids are in agreement with those observed with the sorption of vanadium on natural soil colloids [17]. BS seemed to have the largest decrease in the adsorption of Pb(II), reduced from 26.675 mg g⁻¹ to 14.075 mg g⁻¹, with the increase of IS.

One of the main reasons seems to be that an increase in ionic strength increased aggregation of adsorbent, and thereby decreasing the adsorption sites [27]. Nevertheless, the presence of Ca²⁺ in solution or on soils surface also competed with Pb(II) and Cu(II) for decreasing available adsorption sites [28]. Furthermore, the increasing ionic strength increased the concentrations of the accompanying anions. These accompanying anions might form a complex with Pb(II) and Cu(II), which is not easy to be adsorbed onto soil colloids. Because of this stable and soluble complex formation, free ions of Pb(II) and Cu(II) were decreased in high ionic strength solutions, resulting in a lower adsorption on soils [28,29]. At all the tested ionic strength, BS adsorbed significantly more Pb(II) and Cu(II) than RS and KL did. Nevertheless, with the increasing ionic strength, the adsorption of Pb(II) on KL becomes relatively flatter and represents that there was less change in the adsorption capacity of metal ions, suggesting that the adsorbed ions on the adsorption point are near saturation.

3.4 Effect of humic acid

The effect of initial concentrations of humic acid (HA) is illustrated in Figure 5. The initial HA concentrations were 10 and 20 mg g⁻¹ at pH 5.5. The Figure shows that the

![Figure 3](image)

Figure 3. Effect of pH on the sorption of Pb(II) and Cu(II) onto BS, RS and KL (Different lowercase letters show significant difference among treatments (P < 0.05)).
presence of HA at 10 mg g\(^{-1}\) increased the adsorption of Pb(II) and Cu(II) by the two soils and KL. When humic acid adsorbed on the surface of soil minerals, the adsorption capacity of metallic cations might improve due to its strong and active complexing sites which mainly comprised of high content of oxygen-containing functional groups. HA is a good complexing agent that can form complexes with metal ions. Ahmed et al. showed that Pb(II) formed a complex with humic acid, and thus led to a higher adsorption of metal ions [30]. The structures of the complex are S–M–HA and S–HA–M [5,31] (S represents the adsorption site and M represents the metal ions). But, in the meanwhile, the adsorption decreased with increasing humic acid concentrations. It could be ascribed to another possible role for HA in the metal adsorption system. With the increase of the HA concentrations (from 10 mg L\(^{-1}\) to 20 mg L\(^{-1}\)), Pb(II) and Cu(II) might gradually form a nonabsorbable complex with HA and HA could also compete for the available binding sites with metal ions [15].

In the rest sorption experiments, humic acid (10 mg L\(^{-1}\)) was added into the adsorption system.

### 3.5 Adsorption kinetics

The kinetic mechanism is of crucial importance to adsorption processes because it determines the adsorption-rate and controls the time of the remaining reaction. Batch experiments were conducted to discuss the rate of Pb(II) and Cu(II) adsorption by BS, RS and KL. Figure 6 shows the effect of contact time on the adsorption of Cu(II) and Pb(II) on three kinds of adsorbents which were studied within the range (5 min–24 h) at pH 5.5 (in 10 mg L\(^{-1}\) HA). The sorption of Pb(II) increased dramatically at the first 30 min and then the sorption increased gradually and came to a platform. Figure 6(a) demonstrates that the equilibria was reached in 1 h onto BS, RS and 30 min in the case of Pb(II) sorption onto KL. It is clear that the sorption of Cu(II) on BS, RS and KL increased quickly at the first 1 h of contact time and reached more than 90% of the maximum value at 1 h, and then the sorption gradually maintained a certain level (the maximum value) with increasing time (Figure 6(b)). The results show that the equilibria was reached in 2 h for Cu(II) onto BS, RS and KL. The equilibrium time of Cu(II) onto the three samples was longer than that of Pb(II), suggesting Cu(II) had slower kinetics. In general, the adsorption of the two metals onto BS, RS and KL had a sharp sorption rate in the early stage, with a following slower sorption rate, and then reached equilibrium. It is assumed that in the beginning, the adsorption progress was ion exchange and metal ions could combine easily with the accessible active sites on the bare surface; with the increase of
adsorption time, the sorption sites were covered with the adsorbate \([32]\), resulting in slower sorption rate.

Pseudo-first order equation and pseudo-second-order equation were used to describe the kinetics. Table 2 lists the computed results obtained from the pseudo-first-order equation and the pseudo-second-order equation. The comparison of correlation coefficients values \(R^2\) of the pseudo-first-order model and the pseudo-second-order model confirmed that the pseudo-second-order model exhibited a better fitting for the experimental adsorption equilibrium data, indicating that the major sorption mechanism was chemical adsorption process and chemisorption controlled the rate of reaction.

### 3.6 Adsorption isotherm

Adsorption isotherm, by definition, is the relationship between adsorption and equilibrium that helps to understand the mechanism of the adsorption \([33]\). As is shown in Figure 7, the equilibrium curves increased with increasing the initial concentrations of lead and copper ions and then the increase smoothed. At lower equilibrium concentrations, Pb(II) and Cu(II) could be adsorbed easily by BS, RS and KL. The Pb(II) adsorption capacity of the three adsorbents was probably more than twice of the sorption of Cu(II). The adsorption isotherms on RS and KL have had a slight growing tendency. In the beginning, metal ions were absorbed directly by soil colloids, and then with the increasing of initial concentrations, more metal ions were combined with the active adsorption sites, leading to an increase in the adsorption capacity. Meanwhile, higher metal concentrations increased the affinity of Cu(II) and Pb(II) to combine with the adsorbent. This may be contributing to the growing tendency on BS, RS and KL. Adsorption capacities of BS for Pb(II) and Cu(II) were notably higher than that of RS and KL. BS showed the highest adsorption capacity of Pb(II) (44.287 mg g\(^{-1}\)) and Cu(II) (11.109 mg g\(^{-1}\)), respectively (Table 3). KL displayed the minimum adsorption capacity of Pb(II) (7.612 mg g\(^{-1}\)) and Cu(II) (3.064 mg g\(^{-1}\)), respectively (Table 3). As Pb(II) equilibrium concentration was larger than 40 mg L\(^{-1}\), the equilibrium curves increased slightly with RS and KL, while still sharply with BS. Similar trends were found in Cu(II) sorption. This could be ascribed to the difference in sorption sites among the adsorbents.

Based on Langmuir and Freundlich theoretical models, adsorption isotherms can be generated.

Table 2. Fitting results of adsorption kinetics of Pb(II) and Cu(II) onto BS, RS and KL using different models.

| Metals | Treatments | \(q_e\) (mg g\(^{-1}\)) | \(k_1\) (min\(^{-1}\)) | \(R^2\) | \(q_e\) (mg g\(^{-1}\)) | \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) | \(R^2\) |
|--------|------------|--------------------------|--------------------------|--------|--------------------------|--------------------------|--------|
| Pb(II) | BS         | 33.032                   | 0.624                    | 0.806  | 33.69                    | 0.018                    | 0.992  |
|        | RS         | 9.647                    | 0.736                    | 0.815  | 9.805                    | 0.085                    | 0.985  |
|        | KL         | 4.703                    | 0.674                    | 0.925  | 4.784                    | 0.150                    | 0.976  |
| Cu(II) | BS         | 12.659                   | 0.495                    | 0.919  | 12.983                   | 0.032                    | 0.988  |
|        | RS         | 4.621                    | 0.365                    | 0.915  | 4.784                    | 0.055                    | 0.987  |
|        | KL         | 2.502                    | 0.274                    | 0.879  | 2.605                    | 0.073                    | 0.955  |

Table 3. Fitting results of adsorption isotherms of Pb(II) and Cu(II) onto BS, RS and KL using different models.

| Metals | Treatments | \(Q_m\) (mg g\(^{-1}\)) | \(K_L\) (L mg\(^{-1}\)) | \(R^2\) | \(K_L\) (mg L\(^{-1}\))^\(1/n\) | \(1/n\) | \(R^2\) |
|--------|------------|--------------------------|--------------------------|--------|--------------------------|--------|--------|
| Pb(II) | BS         | 44.287                   | 0.039                    | 0.981  | 5.683                    | 0.396  | 0.987  |
|        | RS         | 9.764                    | 0.176                    | 0.969  | 2.748                    | 0.281  | 0.991  |
|        | KL         | 7.612                    | 0.042                    | 0.991  | 1.061                    | 0.383  | 0.986  |
| Cu(II) | BS         | 11.109                   | 0.128                    | 0.838  | 2.865                    | 0.307  | 0.992  |
|        | RS         | 4.152                    | 0.139                    | 0.833  | 1.330                    | 0.250  | 0.983  |
|        | KL         | 3.064                    | 0.079                    | 0.962  | 0.693                    | 0.319  | 0.982  |

Figure 6. Effect of contact time on the sorption of Pb(II) and Cu(II) onto BS, RS and KL.
According to the correlation coefficients values ($R^2$) of Langmuir model and Freundlich model fitting, it was clear that the sorption of the two metals was well described by the two models and Freundlich model described the adsorption equilibrium data a little better. $K_F$ in Freundlich models illustrates the adsorption affinity. The higher the $K_F$ was, the stronger the degree of adsorption was. The $K_F$ value of Pb(II) and Cu(II) adsorption were both in order of BS > RS > KL, which expressed that BS had the largest adsorption affinity. These were in keeping with the results of adsorption isotherms. The maximum adsorption amount ($Q_{max}$) calculated from Langmuir equation is an important parameter to estimate the adsorption capacity of adsorbents, and BS had the largest $Q_m$ for Pb(II) and Cu(II), suggesting large adsorption capacity of BS for the two metals.

### 3.7 Competitive adsorption

Figure 8 shows the results obtained when Pb(II) and Cu(II) were added in combining in the same proportion at optional condition. The competitive adsorption followed the same trend as when the metals were added separately: the adsorption mass of Pb(II) was higher than Cu(II). However, molar amount of Pb(II) adsorbed was lower than Cu(II) due to much larger molar mass of Pb(II), which may imply priority of Cu(II) in the adsorption reaction. And it was the same in sorption kinetics experiment. However, in the isotherm experiment, the molar maximum adsorption capacity of Pb(II) by BS was higher than Cu(II), opposite to the case of RS and KL. This may be due to different sorption mechanism involved. Pb(II) has higher hydrolysis potential in hydrochemistry than Cu(II) which might make Pb(II) more favorable for specific adsorption. However, if adsorption is assumed as electrostatic interactions, the higher ionic potential ($Z^2/r$, where $Z$ is the ion charge and $r$ is the ionic radius) and the larger density of charge ($Z/r$) of Cu(II) might make it more favorable for adsorption reaction. The occurrence of these possible process was also affected by the solution chemistry, e.g. the initial concentration of the solute and so on. The adsorption of metal ions was decreased in mixture systems. The decrease can be ascribed to the competition between metal ions for a certain binding site on soil and soil components which have a negative impact on the adsorption process [34,35]. Similar trend has been observed when copper competed with cadmium for binding sites on kaolinite [36].

### 4. Conclusion

Exploring factors controlling Pb(II) and Cu(II) sorption onto three kinds of colloids are of great interest to eliminate the pollution that they produce to the ecosystem and nearby surroundings. The result achieved in this paper suggests that BS and RS have high adsorption capacity for Pb(II) and Cu(II), respectively. But the adsorption capacity of kaolinite is low. Pb(II) was more favorable for sorption onto the two soil colloids and Kaolinite.

The Pb(II) and Cu(II) sorption are high pH dependent and the increase of Ca(II) concentrations reduced the Pb(II) and Cu(II) adsorption by soils. Soil colloids have a certain available adsorption site. Positive ions such as $Ca^{2+}$ and $H^+$ are able to compete the available adsorption
sites with heavy metals, resulting in a decrease in the amount of Pb(II) and Cu(II) adsorbed. Increasing the ionic strength decreased the adsorption and ionic strength affected the adsorption onto RS most, followed by RS and KL. Comparatively, 10 mg L\(^{-1}\) HA increased the adsorption of Pb(II) and Cu(II) by the two soils and Kaolinite.

Kinetics and adsorption isotherms help to understand the adsorption mechanisms. The kinetic sorption onto two soil colloids and Kaolinite were pseudo-second-order rate processes, indicating that the sorption mechanism was chemical adsorption and the sorption was controlled by the availability of sorption sites on soil colloids surfaces. Similarly, the adsorption both onto two soil colloids and Kaolinite fitted in Freundlich isotherm and Langmuir isotherm well. According to the \(Q_{\text{max}}\) and \(K_F\), adsorption capacity followed the sequence of Blank soil > Red soil > Kaolinite.

**Disclosure statement**

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