

The Removal of Cd²⁺, Cu²⁺ and Pb²⁺ from Aqueous Solution with Palygorskite: The Effects of Humic Acid

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Abstract. To investigate the impact of Humic acid (HA) on Palygorskite (PAL) as the adsorbent for heavy metal ions, this study was carried out to solve the existing dispute in the effects of HA on PAL sorption capacity. The sorption properties of PAL and HA-loaded PAL (HA/PAL) for Cd²⁺, Cu²⁺, Pb²⁺ in batch experiments were evaluated. PAL and HA/PAL effects on metal ion elimination were examined under various test settings (time, dosage and starting concentration) were compared. The sorption efficiency of PAL was significantly higher than that of HA/PAL. The N₂ sorption-desorption and FTIR results showed that HA successfully adhered to the PAL surface without changing its crystal structure but reducing its specific surface area. Cd²⁺, Cu²⁺, and Pb²⁺ for PAL and Cd²⁺ and Cu²⁺ for HA/PAL were modelled by pseudo-first-order kinetics; the pseudo-second-order rate conformed to Cu²⁺ for PAL and Pb²⁺ for HA/PAL. the Langmuir linear fitting was consistent with Cd²⁺, Cu²⁺ and Pb²⁺ for PAL and HA/PAL. Pb²⁺ for PAL and Cd²⁺, Pb²⁺ for HA/PAL were consistent with the Freundlich isotherm. The results proved that HA was not conducive to improving the adsorption performance of PAL.

1 Introduction

During the production process of certain industries, all kinds of heavy metals are let out into the nature in the form of sewage. Due to their nonbiodegradability and bioaccumulation, once the quantity of heavy metal ions in the aquatic environment surpasses the permissible level, heavy metal ions inflict irreparable damage to human health and the ecological balance [1]. Palygorskite (PAL) has excellent salt tolerance and a rapid hydration rate [2]. Two aspects give PAL good sorption properties. Humic acid (HA) is important in modulating heavy metal geochemical behavior and processes [3]. HA has a large number of functional groups, leading to many different metal ion binding sites [3]. Humus soil in aged refuse provides us with a large source of HA, and the resource utilization of humus soil is of great significance for waste treatment. It is a problem worth studying whether the advantages of the both can be combined through the way of load. However, the majority of scholars have not reached a consensus on whether HA is beneficial to PAL sorption of heavy metal ions. Li et al. found that HA-PAL has good sorption of Ni²⁺ in wastewater [4]. In contrast, Rouhaninezhad et al. found that the introduction of HA into PAL could reduce the removal rate of Cr⁶⁺ in solution [5]. It provides the original intention of this paper. As a result, further research on the implications of HA on the PAL sorption of various heavy metal is required.

2 Substances and Techniques

2.1 Substances

Guangzhou Qianhui Co., LTD. in China supplied the PAL. Therefore, it has been widely used in the environmental protection field. Tianjin Guangfu Institute of Fine Chemicals in China supplied the humic acid. Shanghai Macklin Co., LTD. in China, provided the Cd(NO₃)₂·4H₂O. Cu(NO₃)₂·3H₂O was provided by Tianjing Damao Chemical Reagent Factory, China. Pb(NO₃)₂, NaOH, and HCl were supplied by Guangdong Guangshi Reagent Technology Co., Ltd., China. All the above reagents were guaranteed reagents. The water used for the whole experiment was deionized water.

2.2 Preparation

In order to improve the purity of the adsorbent, PAL was first purified with 3 mol/L HCl. After that, it was cleaned with deionized water to neutralize it before being dried for use. Next, 0.5 g HA was weighed accurately and placed in a beaker with 500 ml of water. Then, 0.1 mol/L NaOH was dribbled continuously into the solution until HA was completely dissolved. Following filtration, the filtrate was put in a beaker and the pH was adjusted to 3. Afterwards, at constant temperature of 60 °C, 5 g purified PAL and HA solution were fully stirred in a magnetic agitator for 6 h and allowed to sit for 12 h. Next, the mixture was rinsed with deionized water and filtered multiple times until the supernatant contained no HA. The HA-loaded PAL was crushed to a 200-mesh powder

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after drying at 105 °C continuous temperature for 8 hours. Finally, the HA-loaded PAL powder was stored in a dry environment. The preparation steps of the adsorbent referenced Jiang et al [6].

2.3 Experiment method

Batch sorption tests were performed with various heavy metal ions (Cd²⁺, Cu²⁺, Pb²⁺), reaction periods (10, 30, 60, 120, 180 min), PAL or HA/PAL doses (0.05, 0.1, 0.2, 0.3 g), and heavy metal starting concentrations (40, 60, 80 mg/L). The metal ions solution is kept constant at a volume of 20 ml. Measure all the Cd²⁺, Cu²⁺ and Pb²⁺ original pH values at 5.4. The temperature is kept constant at 35 °C. at a specific level of concentration, pour the heavy metals solution into 50 ml capped plastic centrifuge tubes. The solution received a particular amount of adsorbent. The mixture oscillated in an isothermal water bath shaker for a certain time at a rotation speed of 200 rpm. The supernatants were collected after centrifuging the suspensions for 2 minutes at 4000 rpm. Use an inductively coupled plasma emission spectrometer (ICP-OES) to determine. The heavy metals residual concentration. Finally, the HA/PAL heavy metal ion sorption capacity (q) and sorption efficiency (η) could be calculated.

$$q = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$$\eta = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 is the heavy metal starting concentration, and C_e is the heavy metal equilibrium concentration (mg/L); V is the solution volume (L); and m is the mass of adsorbent (g).

2.4 Characterization analyses

Using the Fourier transform infrared spectroscopy (FTIR) was to characterize the adsorbent functional groups. Using the Brunauer–Emmett–Teller (BET) was to determine the textural qualities of the samples. The aforesaid characterisation was carried out at the SCUT Analysis and Test Center and Key Laboratory of Efficient And Clean Energy Utilization of Guangdong Province.

2.5 Sorption kinetics

The sorption rate of the pseudo-first-order (PFO) kinetic equation and the quantity of adsorbent pores are relative, whereas the sorption rate and the square of the number of holes are dependent in the pseudo-second-order (PSO) kinetic equation [7]. the PFO and PSO kinetic equation are pursuing:

$$q_t = q_e (1 - e^{-K_1 t}) \quad (3)$$

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2 t} + \frac{1}{q_e} \quad (4)$$

where at equilibrium and time t (min), the heavy metal

removal amount is q_e (mg/g), and q_t (mg/g), respectively; and K_1 (min⁻¹) is the Eqs. (3) rate constants; and K_2 (g/(mg • min)) is the Eqs. (4) rate constants.

2.6 Sorption isotherms

The goal of the isotherm was to explore at the sorption patterns of adsorbents and heavy metals, as well as the distribution of heavy metal ions after the sorbent-sorbate system achieved equilibrium, sorption isotherms were employed. A heterogeneous adsorbent surface with heterogeneous energy active sites is postulated in the Freundlich [7]. The Langmuir isotherm, on the other hand, implies that the active sorption sites are equitably spread and that the surface of the adsorbent is monomolecular [7]. Eqs. (5) and (6) express the Freundlich and Langmuir isotherm equations, respectively.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (6)$$

where q_e (mg/g) is the heavy metal equilibrium removal quantity; C_e (mg/L) is the concentration in balance; K_F (mg⁽¹⁻ⁿ⁾/(L⁻ⁿ • g)) is the sorption constant of Freundlich; and n is the inhomogeneity factor of particle surface. The Langmuir theoretical maximum sorption quantity is q_m (mg/g), while the Langmuir bonding term connected with sorption strength is K_L (L/mg).

3 Discussions and analyses

3.1 Effects of time on heavy metal sorption

The sorption rates of Cd²⁺, Cu²⁺, and Pb²⁺ for PAL and HA/PAL rose over time and eventually reached equilibrium at 120 minutes (Fig. 1). The sorption of Cd²⁺, Cu²⁺ and Pb²⁺ for PAL and HA/PAL went through three stages, and the patterns were similar. In the first stage (0 - 10 minutes), The sorption rate was extraordinarily quick, and three heavy metal ions were completely absorbed. In the next stage (Cd²⁺, Cu²⁺: 10 - 120 minutes; Pb²⁺: 10 - 30 min), the sorption rate slowed down, and the sorption process gradually tended to equilibrium. In the last step (Cd²⁺, Cu²⁺: after 120 minutes; Pb²⁺: after 30 minutes), the sorption reached equilibrium. After adsorption equilibrium, Cd²⁺, Cu²⁺, and Pb²⁺ removal rates for PAL were 87 %, 91 %, and 99 %, respectively, and Cd²⁺, Cu²⁺, and Pb²⁺ removal rates for HA/PAL were 80 %, 56 %, and 98 %, respectively. Compared with PAL, HA/PAL has a slightly lower instantaneous adsorption rates. The quick response during the early stage of adsorption might be attributed to the immediate interchange of heavy metals with cations at the PAL and HA/PAL particles exterior planar and edge locations. After the rapid reaction, Cd²⁺, Cu²⁺ and Pb²⁺ may slowly diffuse into the exchange sites of PAL and HA/PAL. Therefore, 120 minutes was determined as the optimal contact time.

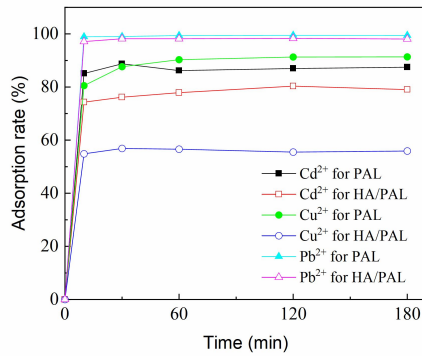


Fig. 1. Effects of time on heavy metal sorption in PAL and HA/PAL. (pH = 5.4, temperature = 35 °C, dosage = 0.2 g, volume = 20 ml, starting concentration = 80 mg/L)

3.2 Effects of dosage on heavy metal sorption

The sorption rates increased with increasing adsorbent dosage (Fig. 2 (a)). This was due to the fact that increasing the dose supplied additional sorption sites for heavy metal ions [8]. When the PAL dose exceeded 0.05 g, the sorption rate of Pb²⁺ did not increase. The sorption rate of Pb²⁺ for HA/PAL reached the highest when the dosage was 0.2 g. After adding more than 0.2 g HA/PAL, the sorption rate of Cd²⁺ and Cu²⁺ for PAL did not change much, and the sorption rate of Cd²⁺ for HA/PAL did not change much. When the HA/PAL dosage reached 0.3 g, it still increased significantly. The sorption rate of most heavy metal ions did not increase obviously after 0.2g dosage. After comprehensive consideration, 0.2 g was considered the best additive amount for PAL and HA/PAL.

The sorption capacity decreased with increasing dose, contrary to the changing trend of the sorption rate (Fig. 2 (b)). This rule was widely used as part of the heavy metal sorption investigation. The accepted explanation was that increasing the adsorbent dose caused heavy metal ions to compete with the adsorbent, the agglomeration of adsorbent particles, and the lengthening of the diffusion route [8]. This is because adsorbent particle collisions can produce particle polymerization, which reduces adsorption surface area while increasing diffusion route length. Meanwhile, the increase of the dose increased the probability of particle collision and aggregation. Therefore, when most Cd²⁺, Cu²⁺ and Pb²⁺ were adsorbed by PAL and HA/PAL, the number of heavy metal ions bound to the adsorption site did not increase with increasing dosage.

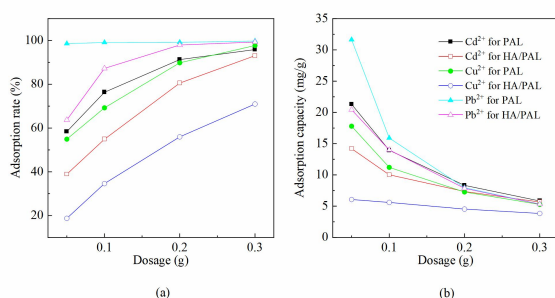


Fig. 2. Effects of dosage on heavy metal sorption in PAL and HA/PAL: (a) sorption rate; (b) sorption capacity. (time = 120 min, pH = 5.4, temperature = 35 °C, volume = 20 ml, starting concentration = 80 mg/L)

min, pH = 5.4, temperature = 35 °C, volume = 20 ml, starting concentration = 80 mg/L)

3.3 Effects of starting concentration on heavy metal sorption

The sorption rates decreased as the starting concentration increased (Fig. 3 (a)). The fundamental explanation for this is that while the dosage was fixed, the adsorbent afforded restricted sorption sites [9], leading to a result that the remaining ion quantities heightened along with the heavy metal starting concentrations grew. The starting concentration had a decreasing influence on the rise in heavy metal ion adsorption capability. Therefore, the sorption rates decreased with increasing starting concentration. However, the change in starting concentration had almost no influence on the PAL and HA/PAL sorption of Pb²⁺, indicating that these two adsorbents provided sufficient sorption sites for Pb²⁺ in the vicinity of 40-80 mg/L. In addition, the increase in starting concentration did not significantly decrease the sorption rates of PAL to Cd²⁺ and Cu²⁺, indicating that PAL had relatively sufficient sorption sites for Cd²⁺ and Cu²⁺. However, the sorption rates of HA/PAL for Cd²⁺ and Cu²⁺ decreased significantly, indicating that the addition of HA reduced the sorption sites of Cd²⁺ and Cu²⁺ in PAL.

The sorption capacity increased with increasing starting concentration (Fig. 3 (b)). Because the adsorbent effective sorption sites could meet the number of heavy metals. When the starting concentration was low, the concentration of the solution has a considerable impact on the capacity for adsorption. Furthermore, when the starting concentration grew, so did the driving power of heavy metal ion migration to sorption sites. Therefore, unit mass adsorbent could adsorb more heavy metal ion. However, when the starting concentration hit a certain threshold, the sorption site attained saturation and the sorption capacity peaked, as seen from the HA/PAL sorption capacity curve of Cu²⁺. In contrast, other sorption capacity curves in Fig. 3 (b) show an upward trend, proving that the sorption sites were not saturated, and the sorption capacity of PAL and HA/PAL did not reach the limit.

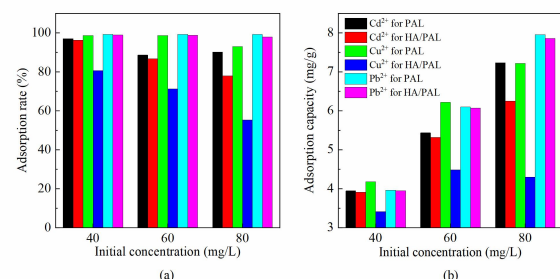


Fig. 3. Effects of starting concentration on heavy metal sorption in PAL and HA/PAL: (a) sorption rate; (b) sorption capacity. (time = 120 min, pH = 5.4, temperature = 35 °C, volume = 20 ml, dosage = 0.2 g)

3.4 BET of PAL and HA/PAL

The N₂ sorption-desorption isotherm results indicated

that PAL and HA/PAL also possessed a H3-type hysteresis loop and typical IV(a)-type isotherm (Fig. 4), in accordance with the IUPAC classification [10]. In the 0.8-1 relative pressure range, PAL and HA/PAL hysteresis loops indicated that many mesopores were evenly distributed in the material. In the whole range of relative pressures, the N₂ sorption capacity of PAL was not improved by HA loading. The BET used the static volume method for testing. when PAL was loaded with HA, the pore diameter and volume, specific surface area were all decreased. (Table 1), which was not conducive to PAL physical sorption. HA penetrated the large pores of PAL, forming smaller holes (Fig. 5), leading to a result that active sites and driving forces decrease.

Table 1. BET test results of PAL and HA/PAL

	PAL	HA/PAL
BET surface area (m ² /g)	60.1947	46.9859
Pore volume (cm ³ /g)	0.1047	0.0501
Sorption average pore diameter (Å)	69.5532	42.6476

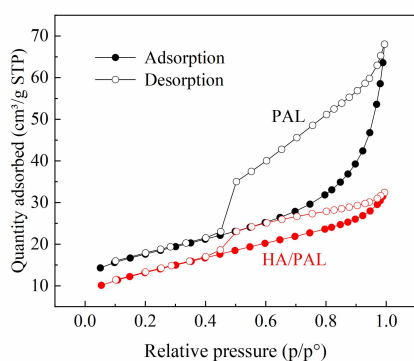


Fig. 4. PAL and HA/PAL N₂ sorption-desorption isotherms

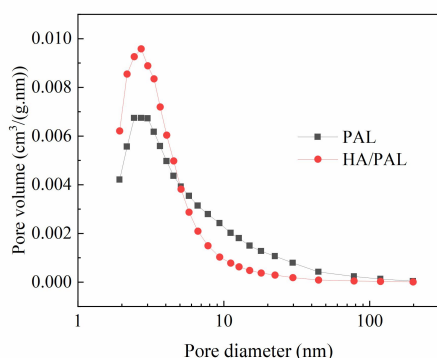


Fig. 5. Pore volume - pore diameter curve for PAL and HA/PAL

3.5 The FTIR of PAL and HA/PAL

Fig. 6 is the FTIR of PAL and HA/PAL. PAL contains distinct peaks at 3624, 3435, 913, and 836 cm⁻¹ that are linked to R-OH stretching oscillations [11]. The HA/PAL characteristic peaks are at 3625, 3443, 922, and 839 cm⁻¹, and they barely changed slightly, showing that the HA load did not modify the structure of PAL, but the decrease in characteristic peak intensity suggested that the HA load decreased the amount of PAL functional groups, consistent with the BET study results.

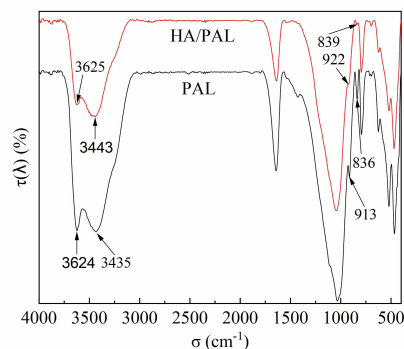


Fig. 6. FTIR of PAL and HA/PAL

3.6 Sorption kinetic results

According to Table 2, the best model for Cd²⁺, Cu²⁺, and Pb²⁺ sorption on PAL and Cd²⁺, Cu²⁺ sorption on HA/PAL was the PFO model (R² = 0.9995, 0.9987, 0.9999, 0.9982, 0.9995, respectively). In addition, Cu²⁺ sorption on PAL and Pb²⁺ sorption on HA/PAL proceeded the PSO rate expression (R² = 0.9979, 0.9259, respectively). Table 2 also shows that HA significantly reduced the sorption rate of PAL, indicating that PAL reached sorption equilibrium earlier than HA/PAL.

Table 2. Cd²⁺, Cu²⁺, and Pb²⁺ sorption kinetics model fitting parameters on PAL and HA/PAL

Adsorbent	Heavy metal ion	PFO			PSO		
		q _e (mg/g)	K ₁ (min ⁻¹)	R ²	q _e (mg/g)	K ₂ (g/(mg·min))	R ²
PAL	Cd ²⁺	7.81	0.37	0.9995	7.83	0.52	0.3772
	Cu ²⁺	7.58	0.26	0.9987	7.76	0.09	0.9979
	Pb ²⁺	8.17	2.43	0.9999	8.17	2.39	0.6328
HA/PAL	Cd ²⁺	7.00	0.30	0.9982	7.09	0.19	0.8238
	Cu ²⁺	4.70	0.05	0.9995	4.73	0.99	0.3075
	Pb ²⁺	8.06	0.05	0.5524	8.08	1.03	0.9259

3.7 Sorption isotherm results

The isothermal sorption line was studied at 35 °C, the dosage of adsorbent was 0.2 g, the solution's starting concentration was 80 mg/L, and its volume was 20 mL, and the pH value was 5.4. In accordance with Table 3, the sorption of Cd²⁺, Cu²⁺, and Pb²⁺ on PAL and HA/PAL was reported to be compatible with the the Langmuir, suggesting the monolayer nature of sorption [12]. By confining the sorption to a monolayer, Langmuir fitting revealed a substantial interaction between Cd²⁺, Cu²⁺, and Pb²⁺ and adsorbents. The sorption of Pb²⁺ on PAL and the sorption of Cd²⁺, Pb²⁺ on HA/PAL were consistent with the linear fitting of the Freundlich isotherm. 1/n was a heterogeneous factor, with n values of 1.19, 5.29 and 2.19, respectively, indicating that the sorption effect was good [13]. The sorption of Pb²⁺ on PAL and the sorption of Cd²⁺, Pb²⁺ on HA/PAL conformed to the characteristics of multilayer sorption [14].

Table 3. Sorption isotherms model fitting parameters of Cd²⁺, Cu²⁺ and Pb²⁺ on PAL and HA/PAL

Adsorbent	Heavy metal ion	Freundlich			Langmuir		
		<i>n</i>	<i>K_f</i>	<i>R</i> ²	<i>q_m</i>	<i>K_L</i>	<i>R</i> ²
PAL	Cd ²⁺	3.85	3.73	0.8265	7.35	0.83	0.9063
	Cu ²⁺	5.34	5.41	0.6673	7.65	3.05	0.9977
	Pb ²⁺	1.19	11.30	0.9953	36.45	0.42	0.9974
HA/PAL	Cd ²⁺	5.29	3.61	0.9991	6.67	0.70	0.9956
	Cu ²⁺	6.01	2.51	0.6740	4.61	0.51	0.9911
	Pb ²⁺	2.19	6.36	0.9162	11.70	1.29	0.9522

4 Conclusion

The characterisation and study of these two adsorbents revealed that the crystal structure of PAL was not altered by HA, but its sorption sites were lowered. The sorption characteristics of adsorbents are still mainly physical sorption. It is generally known, HA primarily binds heavy metal ions by complexation, which is a chemical reaction. Therefore, although the inclusion of HA increased the amount of functional groups in PAL, it also competed for heavy metal ion adsorption sites. Obviously, this competition dominated the whole adsorption process. The ability of PAL to remove heavy metals was not improved by HA loading. Overall, the findings of this investigation clearly support the contrary viewpoint. HA does not give play to the advantages of its functional groups, and Therefore, the inclusion of HA in PAL sorption of heavy metals should be avoided.

Acknowledgments

The Guangzhou Science and Technology Innovation Development Special Fund [202002030105] and the Guangdong Province Natural Science Foundation of China [2114050000829] sponsored this research..

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