

Original Research Report

Removal of copper and lead ions by red mud-metakaolin based geopolymer microspheres: Insights into the efficient preparation and adsorption mechanisms

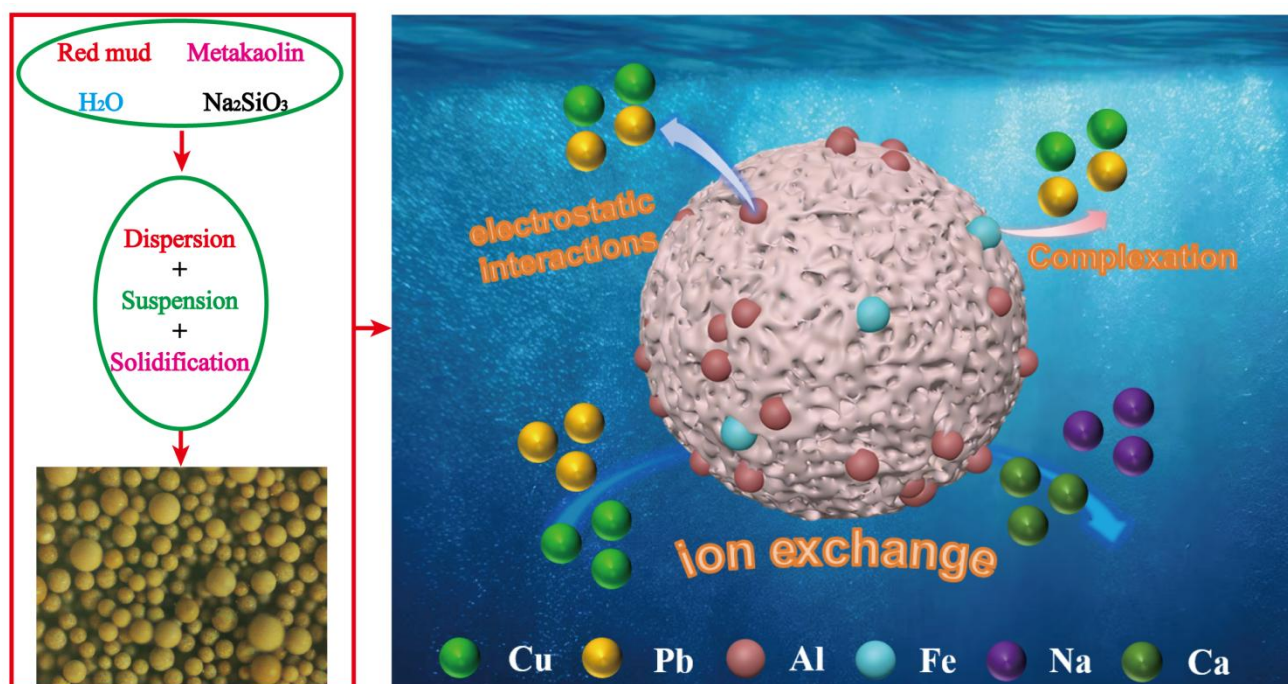
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Graphical abstract



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Abstract: This study used red mud and metakaolin as the main raw material, with sodium silicate as the alkali activator. Red mud-metakaolin based geopolymer microspheres (RM-MGMs) with good sphericity and high mechanical strength are prepared via dispersion-suspension-solidification method. By investigating the adsorption performance of RM-MGMs calcined at different temperatures for Cu^{2+} and Pb^{2+} , the uncalcined RM-MGMs exhibit excellent heavy metal cation adsorption due to their abundant surface hydroxyl groups and high ion exchange capacity. The optimal adsorption conditions for $\text{Cu}^{2+}/\text{Pb}^{2+}$ were adsorbent dosages of 1.5/0.3 g/L, pH of 5.3-5.6/5.0, respectively. Cu^{2+} adsorption reached equilibrium at 960 min. Pb^{2+} showed faster adsorption rate due to its smaller hydrated ionic radius and reached equilibrium at 60 min. Kinetic results indicated that the pseudo-second-order model better describes the adsorption process of RM-MGMs for $\text{Cu}^{2+}/\text{Pb}^{2+}$. Adsorption isotherm models showed that increasing temperature favors the adsorption of $\text{Cu}^{2+}/\text{Pb}^{2+}$ by RM-MGMs. At 318 K, the adsorption capacities of RM-MGMs for $\text{Cu}^{2+}/\text{Pb}^{2+}$ reach 0.86/1.43 mmol/g, respectively. In competitive experiments, the removal rates of $\text{Cu}^{2+}/\text{Pb}^{2+}$ by RM-MGMs both exceed 80%. RM-MGMs achieve adsorption of $\text{Cu}^{2+}/\text{Pb}^{2+}$ through synergistic mechanisms including ion exchange, electrostatic attraction and complexation.

Keywords: red mud, metakaolin, microspheres, heavy metals, adsorption

1. Introduction

Industrial wastewater discharge has become a core cause of destroying aquatic ecological balance and threatening drinking water safety due to global industrialization and urbanization. Heavy metal wastewater with high toxicity non-biodegradability and easy enrichment is a major concern for global water remediation [1]. Heavy metals (e.g. Pb^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} and Zn^{2+}) are persistent non-biodegradable pollutants. Their high toxicity and difficult degradation allow them to accumulate in organisms even at low concentrations causing long-term toxic effects. For example, excessive Cu^{2+} intake causes severe mucosal irritation and corrosion as well as capillary liver and kidney damage. It also stimulates the central nervous system leading to depression [2]. Lead is one of the most toxic heavy metals. Long-term exposure to low concentrations of lead can damage the human nervous system, while exposure to high concentrations of lead can lead to life-threatening conditions such as acute lead-induced myocarditis and kidney failure [3]. Compared with heavy metal pollution from natural activities, human-induced pollution has wider range higher toxicity concentration and faster speed. Therefore, heavy metal pollution control is a key focus for water quality restoration. The adsorption method offers the advantages of low cost, ease of operation, high efficiency, and good recyclability, and has become the preferred solution among numerous wastewater treatment methods (e.g. chemical precipitation [4] membrane separation [5] biological treatment [6]).

In recent years, the continuous growth of alumina demand has increased the environmental pressure from red mud and other solid wastes generated during production. To alleviate this

pressure, researchers have systematically studied the physicochemical properties of red mud. They find that red mud's high specific surface area and large porosity [7][8] give it excellent heavy metal adsorption performance [9][10][11]. The high alkalinity of red mud can be effectively utilized in geopolymerization [12]. The three-dimensional network structure of geopolymers can effectively immobilize alkali metals and radioactive elements in red mud, thereby solving the hazard of red mud [13][14][15]. However, most currently prepared red mud-based geopolymer adsorbents are in powder form. Powder materials suffer from difficulties in solid-liquid separation easy loss and poor filling in fixed-bed reactors in practical water treatment engineering. Therefore, preparing shaped adsorbents (e.g. granules or spheres) with high adsorption capacity high mechanical strength and ideal morphology at large scale and low cost remains a key technical challenge. Yan et al. [16] used red mud and blast furnace slag as raw materials and applied suspension solidification method combined with H_2O_2 foaming to prepare porous spherical red mud/slag-based geopolymers. Their surfaces rich in aluminosilicates hydroxyl groups and iron oxides exhibited excellent adsorption for methylene blue and Ni^{2+} . Gonçalves et al. [17] used suspension solidification to prepare porous geopolymer spheres containing red mud and fly ash and used them in fixed-bed columns to treat real acid mine drainage. These porous spheres showed synergistic effects of pH neutralization and adsorption. They released alkali to neutralize acidic wastewater inducing hydrolysis and precipitation of Fe and Al, while removing Zn, Cu, Co, Pb, Ni and other heavy metals via co-precipitation and adsorption.

This study investigates the use of red mud-metakaolin based geopolymer microspheres (RM-MGMs) calcined at different temperatures for adsorbing Cu^{2+} and Pb^{2+} from water. Factors such as pH adsorbent dosage coexisting ions and real water bodies are explored. Desorption cycling performance is also examined. Adsorption kinetics, isotherm models and multiple characterization techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS), N_2 adsorption-desorption measurements (specific surface area: BET and pore size distribution: BJH), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS) are employed to reveal the adsorption mechanism.

2. Experimental

2.1. Materials

Red mud (RM) used in this experiment came from Guangxi Branch of Aluminum Corporation of China. Metakaolin (MK) came from Chaopei Company (Inner Mongolia China). Industrial grade dimethyl silicone oil (viscosity 1000 mm^2/s) was purchased from Cuizhu Chemical Business Department (Licheng District Jinan China). Industrial grade water glass was purchased from Wuxi Yatai United Chemical Co. Ltd. (Jiangsu China), it has a water content of 58% and a modulus (molar

ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ is 2.31. Sodium hydroxide was used to adjust the modulus to 1. Sodium hydroxide (NaOH, AR, $\geq 99.5\%$) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, AR, $\geq 99.5\%$) were purchased from Guangdong Guanghua Technology Co. Ltd. Lead nitrate ($\text{Pb}(\text{NO}_3)_2$, AR, 99.0%), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AR, 99.0-102.0%), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, AR, $\geq 99.0\%$), zinc nitrate ($\text{Zn}(\text{NO}_3)_2$, AR, $\geq 99.0\%$) and nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR, $\geq 98.0\%$) were purchased from Chengdu Kelong Chemical Co. Ltd. Magnesium chloride (MgCl_2 , AR, $\geq 98.0\%$) was purchased from Tianjin Guangfu Fine Chemical Research Institute.

2.2. Preparation of RM-MGMs

The dispersion-suspension-solidification method was selected to prepare microspheres according to previous studies in our group [18][19]. A mixture of 10 g total mass of RM and MK at a 6:4 mass ratio was blended with 12 g of water glass with a modulus of 1 and 4 g water to form a uniform slurry. The slurry was dropped into silicone oil at $85\text{ }^\circ\text{C}$ to form microspheres. After curing in an oven at $85\text{ }^\circ\text{C}$ for 2 h the microspheres were filtered washed and dried to obtain uncalcined RM-MGMs. Calcination at $500\text{ }^\circ\text{C}$ and $900\text{ }^\circ\text{C}$ gave RM-MGMs-500 and RM-MGMs-900 respectively. After sieving RM-MGMs with particle size $<150\text{ }\mu\text{m}$ at different calcination temperatures were used for heavy metal adsorption studies.

2.3. Characterization

Details of the characterization and analytical methods employed in this study are provided in Supplementary Material S1.

2.4. Adsorption experiments

The adsorption conditions for Cu^{2+} and Pb^{2+} by RM-MGMs are detailed in Supplementary Material S2. The removal rate adsorption capacity desorption rate and fitting models were calculated using equations in Supplementary Materials S3-6.

3. Results and discussion

3.1. The effects of different calcination temperatures on the morphology and properties of RM-MGMs

Optical microscope (OM) and scanning electron microscope (SEM) images of RM-MGMs at different calcination temperatures are shown in Fig. 1(A/A₁-C/C₁). RM-MGMs and RM-MGMs-500 both maintained good spherical structure. As calcination temperature increased the color changed

from light brown to red-brown and then to dark brown. When the temperature reached 900 °C the microsphere surfaces showed cracks and particles shrank with adhesion among microspheres. The significant color difference between uncalcined and calcined microspheres may be related to undecomposed precursors and free/crystalline water in uncalcined microspheres. When the calcination temperature rose to 500-900 °C the microspheres presented a bright red-brown color possibly due to dehydration and oxidation of iron-bearing minerals. The adhesion and shrinkage at 900 °C indicate that this temperature approached or exceeded the melting point of some low-melting-point components causing local surface melting. The deepened color suggests changes in microsphere structure and phase composition.

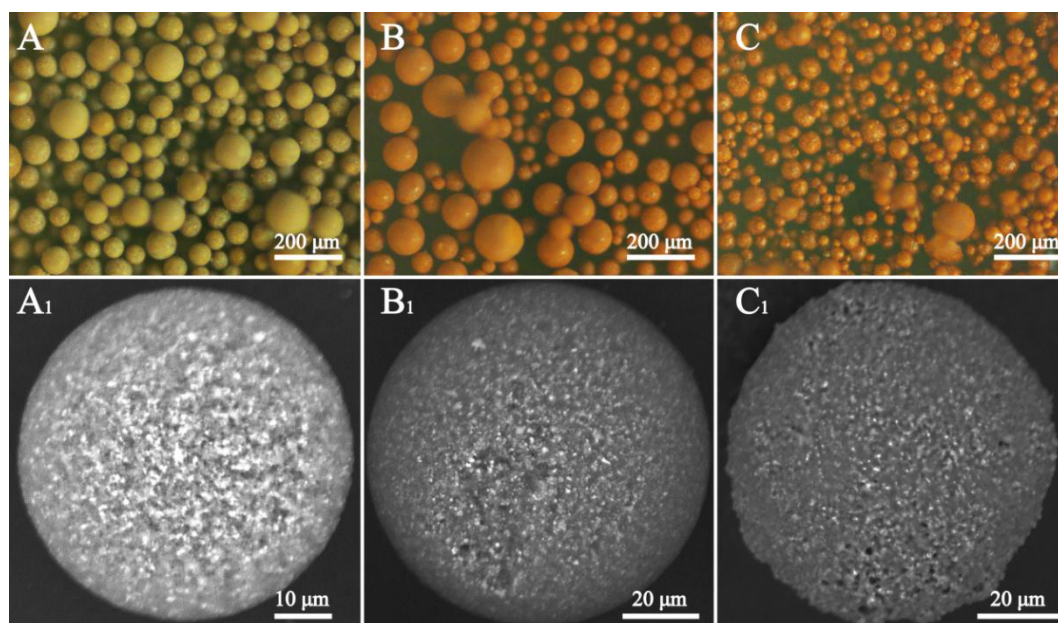


Fig. 1. OM and SEM of RM-MGMs (A/A₁), RM-MGMs-500 (B/B₁) and RM-MGMs-900,(C/C₁).

Fig. 2(A and B) shows the adsorption effects of RM-MGMs at different calcination temperatures on Cu²⁺ and Pb²⁺. RM-MGMs exhibited the best adsorption performance with removal rates of 97.60% for Cu²⁺ and 99.96% for Pb²⁺ and adsorption capacities of 0.51 and 0.16 mmol/g respectively. For calcined microspheres the removal rates decreased sharply with increasing calcination temperature. When the calcination temperature increased from 500 °C to 900 °C the Cu²⁺ removal rate fell from 19.71% to 2.04% and the Pb²⁺ removal rate fell from 48.23% to 4.34%. RM-MGMs contain abundant free water structural water and surface hydroxyl groups. These active sites effectively capture heavy metal ions via mechanisms such as ion exchange and coordination thus showing excellent adsorption performance. Compared with RM-MGMs, the RM-MGMs-500 and RM-MGMs-900 lost internal free and structural water and most -OH groups leading to decreased chemical activity [20]. However at 900 °C the adsorption performance deteriorated sharply. As shown in Fig. 1(C/C₁), localized melting at 900 °C led to pore collapse and agglomeration of microspheres, thereby limiting the diffusion of heavy metal ions and their contact with adsorption sites.

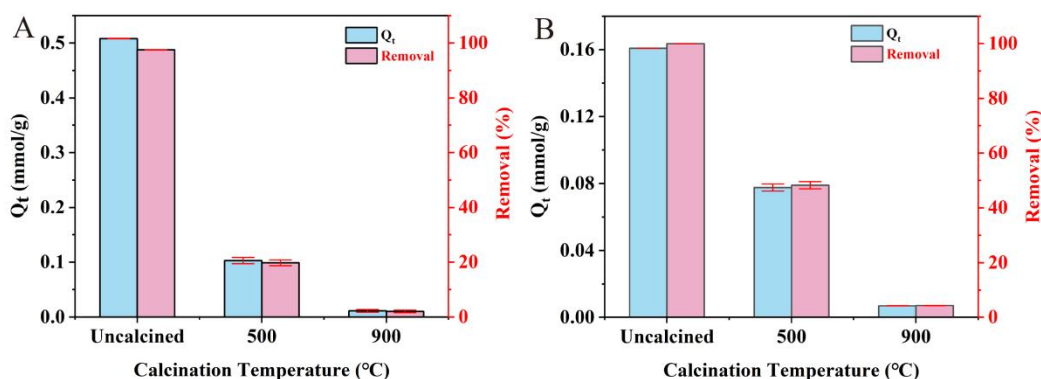


Fig. 2. Adsorption effects of Cu²⁺ (A) and Pb²⁺ (B) at RM-MGMs, RM-MGMs-500 and RM-MGMs-900.

In geopolymer structures, negatively charged alumina tetrahedra typically require association with cations such as alkali metals to achieve charge balance. These cations can exchange with external solution cations, providing ideal adsorption sites for Cu²⁺ and Pb²⁺. To further investigate the differences in adsorption performance of Cu²⁺ and Pb²⁺ under various calcination temperatures, the leaching behavior of Ca²⁺, Na⁺, K⁺, Mg²⁺, Fe³⁺, and Al³⁺ from RM-MGMs during the adsorption process at different calcination temperatures was examined. As shown in Fig. 3(A and B), RM-MGMs released higher concentrations of Ca²⁺ and Na⁺ into the solution during Cu²⁺ and Pb²⁺ adsorption. Moreover, as the calcination temperature increased from 500 to 900°C, the leaching concentrations of Ca²⁺ and Na⁺ gradually decreased.

Studies by Tian et al. [21] and Li et al. [22] demonstrated that after heat treatment, the amorphous structure in geopolymer materials transforms into crystalline phases, with cations being trapped within the crystal lattice, thereby significantly enhancing the material's leaching resistance. The leaching behavior of Ca²⁺ and Na⁺ during adsorption in RM-MGMs, RM-MGMs-500 and RM-MGMs-900 showed the same trend as their adsorption performance. By comparing the leaching concentrations of Ca²⁺, Na⁺, K⁺, Mg²⁺, Fe³⁺ and Al³⁺ from RM-MGMs in ultrapure water (leaching times of 24 h and 2 h, corresponding to the adsorption durations for Cu²⁺ and Pb²⁺ respectively). As shown in Fig. 3(C and D), it was observed that under identical leaching conditions, RM-MGMs released more Ca²⁺ and Na⁺ in Cu²⁺/Pb²⁺ solutions than in ultrapure water. Meanwhile, K⁺, Mg²⁺, Fe³⁺ and Al³⁺ exhibited low leaching levels in both Cu²⁺/Pb²⁺ solutions and ultrapure water, confirming that Ca²⁺ and Na⁺ participated in ion exchange during the adsorption process.

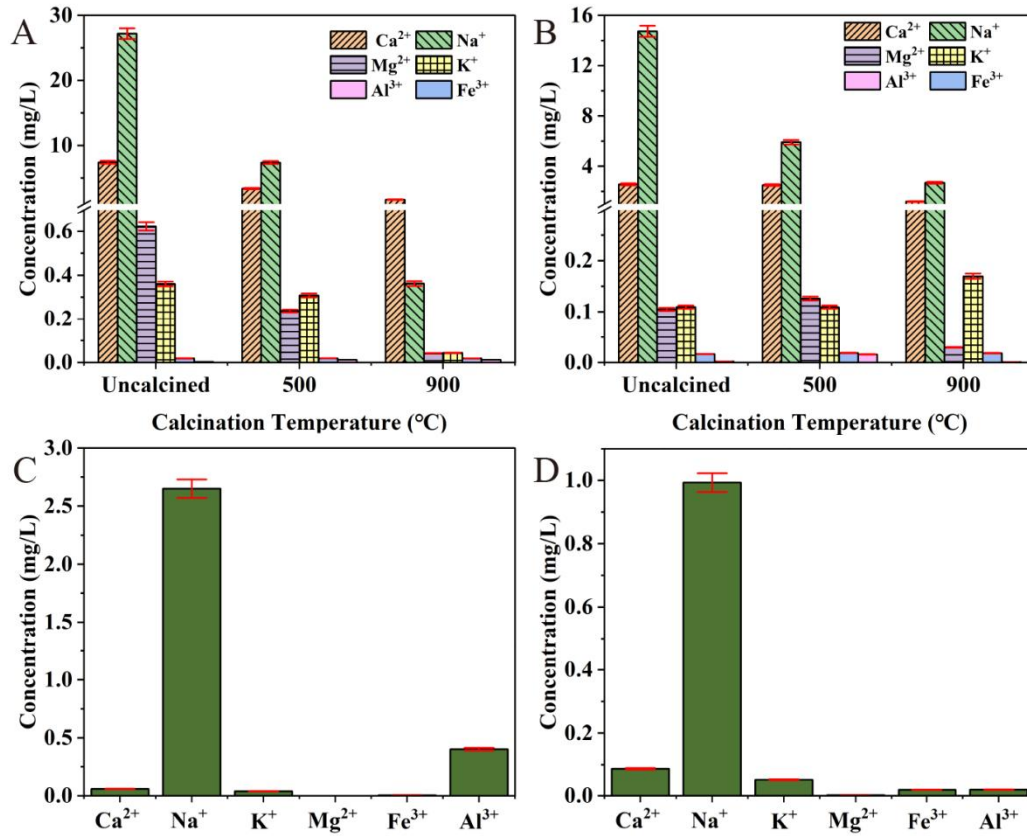


Fig. 3. The adsorption process of RM-MGMs, RM-MGMs-500 and RM-MGMs-900 for Cu²⁺ (A) and Pb²⁺ (B), as well as the leaching effect of Ca²⁺, Na⁺, K⁺, Mg²⁺, Fe³⁺ and Al³⁺ in the ultrapure water over 24 h (C) and 2 h (D).

XRD analysis was used to characterize the phase composition and crystal structure of RM-MGMs, RM-MGMs-500 and RM-MGMs-900. Fig. 4(A) shows the XRD patterns, the RM-MGMs mainly consisted of hematite (Fe₂O₃, PDF#33-0664) cancrinite (Na₆Ca_{1.5}Al₆Si₆O₂₄(CO₃)_{1.6}, PDF#34-0176) calcite (CaCO₃, PDF#86-0174) and hydroandradite (Ca₃(Fe_{0.87}Al_{0.13})₂(SiO₄)_{1.65}(OH)_{5.4}, PDF#87-1971). With increasing calcination temperature to 500 °C, the broad amorphous hump of RM-MGMs vanished. Hydroandradite underwent progressive dehydration and dehydroxylation, leading to gradual decomposition, accompanied by the disappearance of its characteristic diffraction peaks. A pronounced phase transformation was observed when the calcination temperature reached 900 °C. Cancrinite disappeared and transformed into nepheline (Na_{7.11}(Al_{7.2}Si_{8.8}O₃₂), PDF#79-0991) accompanied by the formation of albite (Na(AlSi₃O₈), PDF#89-6423). Combined with BET and BJH results (Fig. 4(B and C)), the specific surface area (S) and pore volume (V) of RM-MGMs-900 dropped sharply to 0.70 m²/g and 0.001 cm³/g due to local melting and pore structure collapse forming denser new crystals [20][22]. The pore volume of microspheres calcined at 500 °C decreased from 0.17 cm³/g to 0.13 cm³/g due to shrinkage and merging of fine mesopores and micropores caused by dehydration. Because the mean pore radius scales as $r \propto V/S$, the simultaneous rise in surface area implies that the pore-size distribution shifts to smaller diameters,

so dehydration generates micropores in addition to simply removing pore space. Although RM-MGMs-500 exhibited a higher specific surface area than RM-MGMs, the calcination decomposed active hydrated minerals (e.g. cancrinite and hydroandradite), losing hydroxyl groups and structural water thus reducing the number of chemically active sites. Calcination also made the pore structure irregular or shrunken [23], thereby decreasing the adsorption capacity for cationic pollutants. The inversion of specific surface area and adsorption capacity is decisive: adsorption capacity would follow specific surface area if physisorption dominated, whereas here the opposite is observed. This also indicates that the adsorption process is chemically dominated and the contribution of chemically active sites is much greater than that of physical adsorption associated with the specific surface area. Fig. 4(D) compares the Zeta potential of RM-MGMs and RM-MGMs-500. In the pH range of 5-7 RM-MGMs had more negative Zeta potential. More negative surface charge favors the capture of cations thus RM-MGMs showed better adsorption performance.

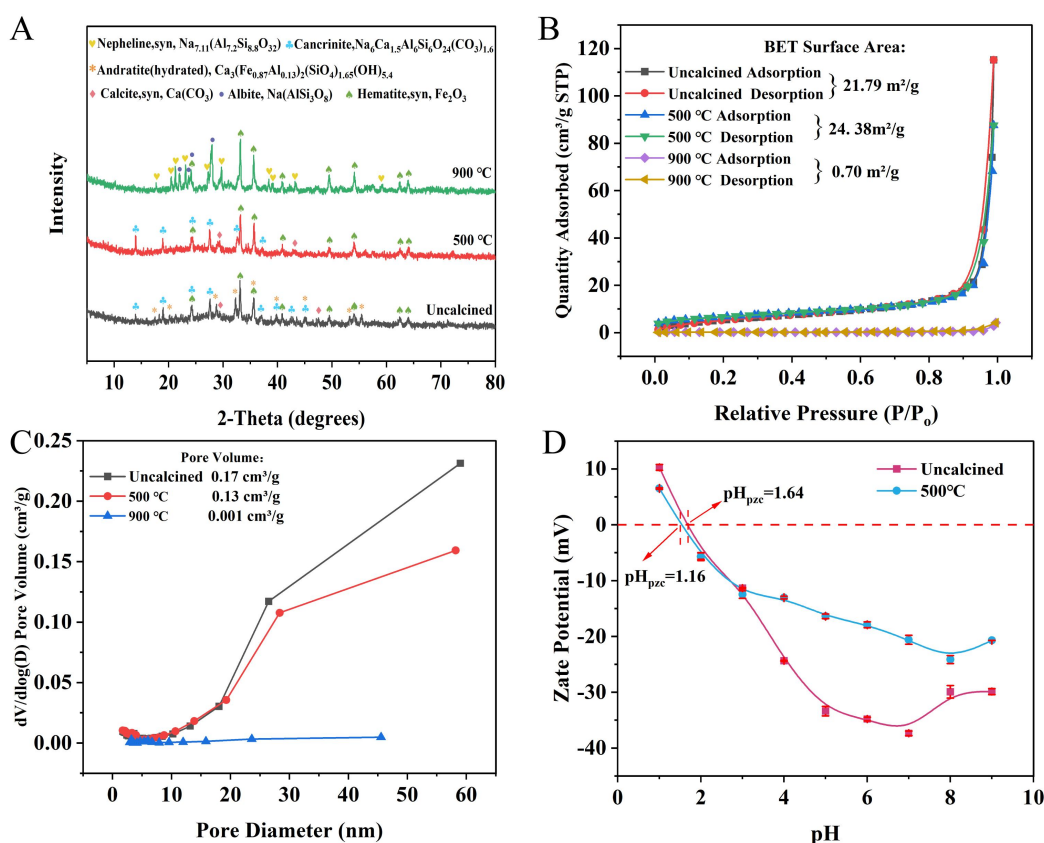


Fig. 4. XRD (A), BET (B) and BJH (C) patterns of RM-MGMs, RM-MGMs-500 and RM-MGMs-900 and Zeta potential under different solution pH conditions (D).

3.2. Effect of pH and adsorbent dosage on adsorption of Cu^{2+} and Pb^{2+}

Fig. 5(A and B) shows the adsorption effects of RM-MGMs on Cu^{2+} and Pb^{2+} at different solution pH values. The adsorption performance of RM-MGMs for Cu^{2+} and Pb^{2+} was relatively insensitive to solution pH. For Cu^{2+} RM-MGMs maintained stable adsorption performance in the pH

range of 4 to 7 with removal rates above 96%. At pH=3 (strongly acidic solution) the Cu^{2+} removal rate slightly decreased to 86.05%. In contrast RM-MGMs exhibited stable adsorption for Pb^{2+} in the same pH range with adsorption capacity always around 0.16 mmol/g and removal rate above 99%. Compared with the initial pH, the pH after adsorption equilibrium increased reflecting the alkali activation process during geopolymer synthesis. Fig. 5(C and D) show the speciation distribution of Cu and Pb in solutions at different pH values. Visual MINTEQ 3.0 software was applied to simulate the speciation of copper and lead ions and potential products as a function of pH in the aqueous solution. $\text{Cu}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$ precipitates appeared at pH=6.4 and 6 respectively. To ensure that adsorption is the main mechanism for Cu^{2+} and Pb^{2+} removal by RM-MGMs, the selected pH conditions must keep the equilibrium pH below the critical pH for metal hydroxide precipitation. Therefore, subsequent studies examined Cu^{2+} adsorption at pH= 5.3-5.6 and Pb^{2+} adsorption at pH= 5.

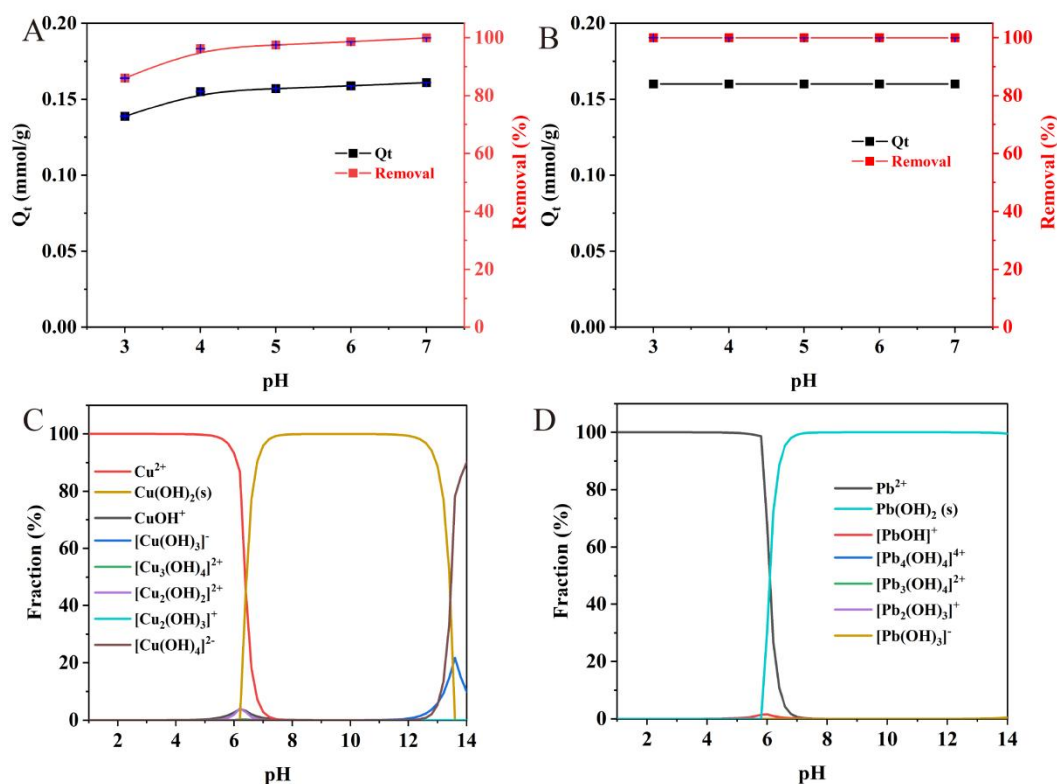


Fig. 5. The adsorption effects of RM-MGMs on Cu^{2+} (A) and Pb^{2+} (B) in different pH solutions and the distribution of the existence forms of Cu (C) and Pb (D) in different pH solutions.

The effect of adsorbent dosage on Cu^{2+} and Pb^{2+} adsorption was investigated to determine optimal conditions. Results are shown in Fig. 6(A and B), as adsorbent dosage increased the total active sites in solution increased significantly improving metal ion removal rates. However excess active sites led to a decrease in adsorption capacity. When RM-MGMs dosage increased from 0.5 to 1.5 g/L, the Cu^{2+} removal rate increased from 41.89% to 98.63%, while the adsorption capacity

dropped from 0.65 to 0.51 mmol/g. As the dose was further increased, the Cu^{2+} removal rate rose gradually to 99.98%, indicating that adsorption was nearly complete. For Pb^{2+} increasing the adsorbent dosage from 0.2 to 0.3 g/L raised the removal rate from 63.41% to 99.89%, while also achieving a high adsorption capacity of 0.72 mmol/g. This indicates that even at low dosage RM-MGMs achieve efficient and high-capacity adsorption for Pb^{2+} . Considering removal efficiency adsorption capacity and economy subsequent experiments used 1.5 g/L for Cu^{2+} and 0.3 g/L for Pb^{2+} to ensure high removal rates and excellent adsorption performance with better economic applicability.

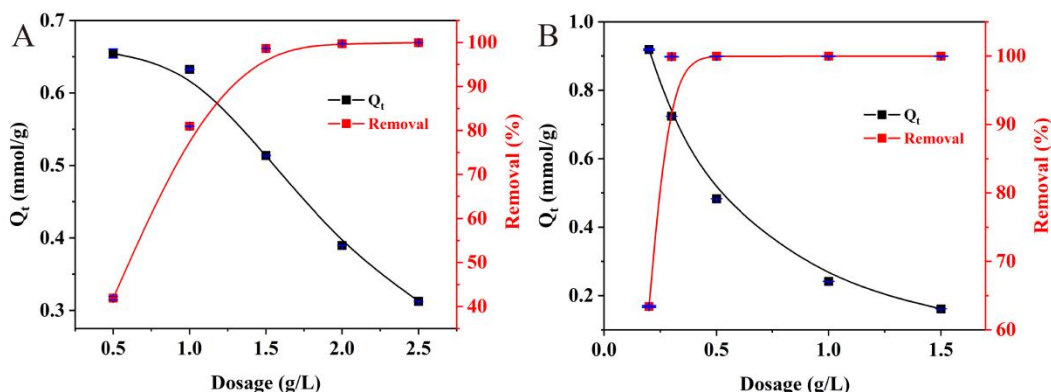


Fig. 6. The effect of dosage on the adsorption of Cu^{2+} (A) and Pb^{2+} (B).

3.3. Adsorption kinetics

Fig. 7 shows the variation of adsorption capacity of RM-MGMs for Cu^{2+} and Pb^{2+} with contact time. As shown in Fig. 7(A), as the contact time increased from 5 to 240 mins, the adsorption capacity of Cu^{2+} increased from 0.22 to 0.45 mmol/g. As time continued to elapse, the adsorption of Cu^{2+} gradually reached equilibrium after 960 min, with an adsorption capacity of 0.49 mmol/g. Rapid adsorption of Pb^{2+} occurred within 45 min, and adsorption equilibrium was gradually reached after 60 min, with an adsorption capacity of 0.72 mmol/g. The significant difference in adsorption rate and capacity between Cu^{2+} and Pb^{2+} originates from their different hydrated ionic radii. Larger ionic radius corresponds to smaller hydrated ionic radius. Smaller hydrated ionic radius means a shorter adsorption path between the ion and adsorption sites [24]. Moreover Pb^{2+} has higher electronegativity than Cu^{2+} resulting in stronger electrostatic attraction to negatively charged sites and further accelerating the surface reaction [25]. Therefore, due to its smaller hydration radius and higher electronegativity, Pb^{2+} binds more readily to adsorption sites, thereby enabling highly efficient adsorption. To further explore the adsorption mechanism of RM-MGMs for Cu^{2+} and Pb^{2+} , the pseudo-first-order (PFO), pseudo-second-order (PSO) and intra-particle diffusion (IPD) models were used to fit the adsorption capacity data at different times. The fitting coefficients for PFO and PSO models for Cu^{2+} / Pb^{2+} adsorption were 0.88/0.94 and 0.96/0.97 respectively. The PSO model better described the adsorption process of RM-MGMs for Cu^{2+} / Pb^{2+} indicating that the adsorption

process is dominated by chemisorption. The adsorption of Cu^{2+} and Pb^{2+} by RM-MGMs can be divided into three stages. First the negative charge on the RM-MGMs surface attracts the positive charge of target cations causing rapid accumulation of target cations on the surface. Then as surface active sites decrease target cations diffuse into the microsphere pores. Finally the active sites are fully occupied by target cations and adsorption equilibrium is reached [26].

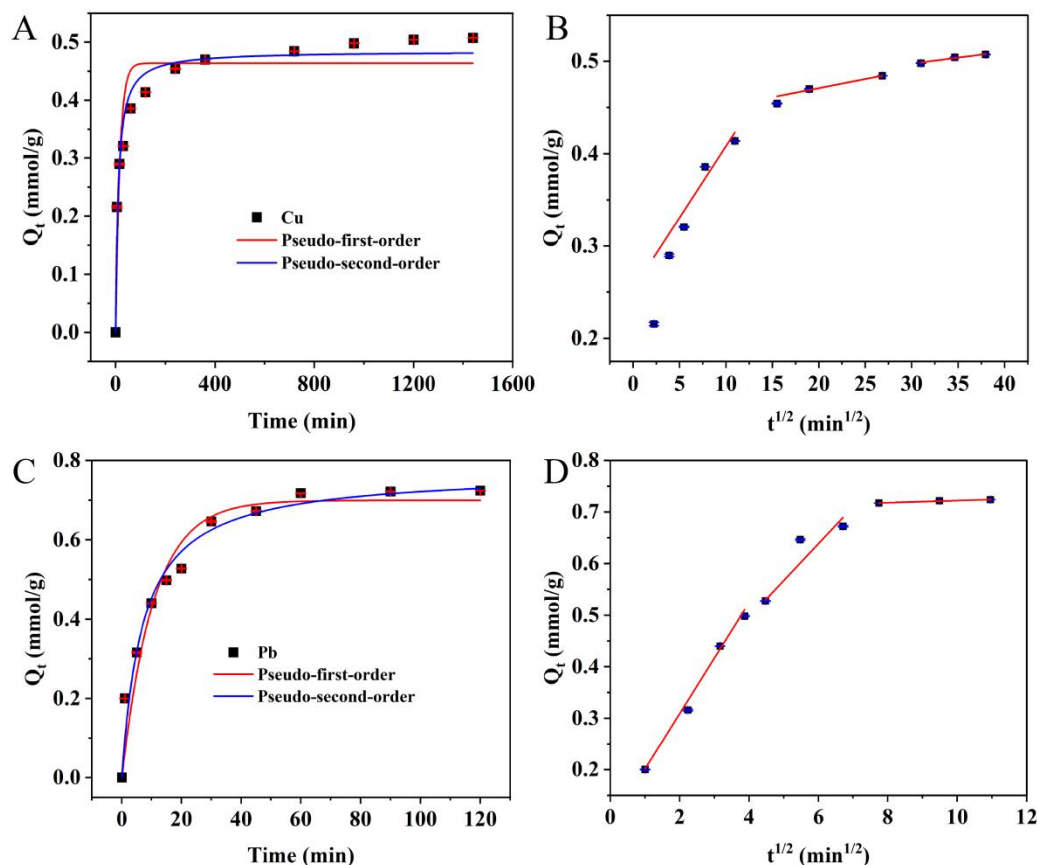


Fig. 7. The PFO and PSO kinetic model fits for Cu^{2+} and Pb^{2+} by RM-MGMs (A: Cu^{2+} , B: Pb^{2+}) and the IPD model fits (C: Cu^{2+} , D: Pb^{2+}).

Table 1. Kinetic parameters of RM-MGMs for Cu^{2+} and Pb^{2+} adsorption.

Kinetic model		Parameter	Cu	Pb
PFO		$Q_{e, \text{exp}}$ (mmol/g)	0.51	0.72
		$Q_{e, \text{cal}}$ (mmol/g)	0.46	0.69
		k_1 (1/min)	0.06	0.09
		R^2	0.89	0.94
PSO		$Q_{e, \text{cal}}$ (mmol/g)	0.48	0.77
		k_2 (g/(mmol·min))	0.19	0.18
		R^2	0.96	0.97

	k_{id} (mmol/(g·min ^{1/2}))	0.002	0.071
IPD	C	0.43	0.21
	R ²	0.94	0.93

3.4. Adsorption isotherm models

Fig. 8 shows that the adsorption capacities of RM-MGMs for Cu²⁺ and Pb²⁺ increased with increasing solution concentration. Moreover increasing temperature enhanced the adsorption capacities indicating that higher temperature favors Cu²⁺ and Pb²⁺ adsorption by RM-MGMs. Fig. 8 and Table 2 present the fitting results of Langmuir, Freundlich and Temkin isotherm models. As shown in Fig. 8(A), for Cu²⁺ at different adsorption temperatures, the R² values for Langmuir and Freundlich models were 0.98/0.83 (298 K), 0.87/0.82 (308 K) and 0.90/0.81 (318 K), respectively. The maximum Cu²⁺ adsorption capacities of RM-MGMs were 0.63 mmol/g (298 K), 0.72 mmol/g (308 K) and 0.86 mmol/g (318 K), which were basically consistent with the theoretical values of 0.60 mmol/g (298 K), 0.68 mmol/g (308 K) and 0.83 mmol/g (318 K). This indicates that Cu²⁺ adsorption by RM-MGMs follows the Langmuir model and the process is monolayer adsorption on the microsphere surface. As shown in Fig. 8(C), for Pb²⁺ as temperature increased the adsorption capacity increased from 1.20 mmol/g (298 K) to 1.43 mmol/g (318 K). The R² values for Langmuir and Freundlich models were 0.77/0.95 (298 K), 0.79/0.95 (308 K) and 0.84/0.93 (318 K), respectively. Pb²⁺ adsorption follows the Freundlich model indicating multilayer adsorption on the microsphere surface. Pb²⁺ can form complexes with various functional groups on the microsphere surface. Additionally RM-MGMs have certain alkalinity, as adsorption solution pH increases the adsorbed Pb²⁺ aggregates and forms precipitates on the microsphere surface. Multilayer adsorption and surface precipitation contribute to Pb²⁺ adsorption. According to the Freundlich isotherm fitting the 1/n values for both Cu²⁺ and Pb²⁺ are less than 1 indicating favorable adsorption [27]. Fig. 8(B and D) also presented an evaluation of the Temkin model. At 298 K, 308 K, and 318 K, the R² values for Cu²⁺ were 0.92, 0.89, and 0.89, respectively, while those for Pb²⁺ were 0.98, 0.99, and 0.99, respectively. This indicates that the adsorption process involves chemisorption [28][29].

Table 2. Isothermal parameters of Cu²⁺ and Pb²⁺ adsorption for RM-MGMs.

Isotherma	Parameters	Cu			Pb		
		298	308	318	298	308	318
I model	Temperature (K)						
	Q _{e,exp} (mmol/g)	0.63	0.72	0.86	1.19	1.26	1.43
Langmuir	Q _m (mmol/g)	0.60	0.68	0.83	1.05	1.14	1.28

Freundlich h model	model	K_L (L/mg)	9.25	25.43	11.76	10.31	22.42	27.44
		R^2	0.98	0.87	0.90	0.77	0.79	0.84
		K_F ((mmol/g)/(mg/L) ^{1/n})	0.54	0.46	0.39	0.71	0.81	0.89
		n	8.25	8.30	7.47	9.22	10.06	9.19
		R^2	0.83	0.82	0.81	0.95	0.95	0.93
Temkin model		K_T (L/mg)	1427.69	2797.36	1191.86	3303.94	1596.69	570.79
		b_T (J/mol)	27.82×10	29.78×10 ³	27.69×10	32.09×10	30.73×10 ³	29.66×10
			3		3	3		3
		R^2	0.92	0.89	0.89	0.98	0.99	0.99

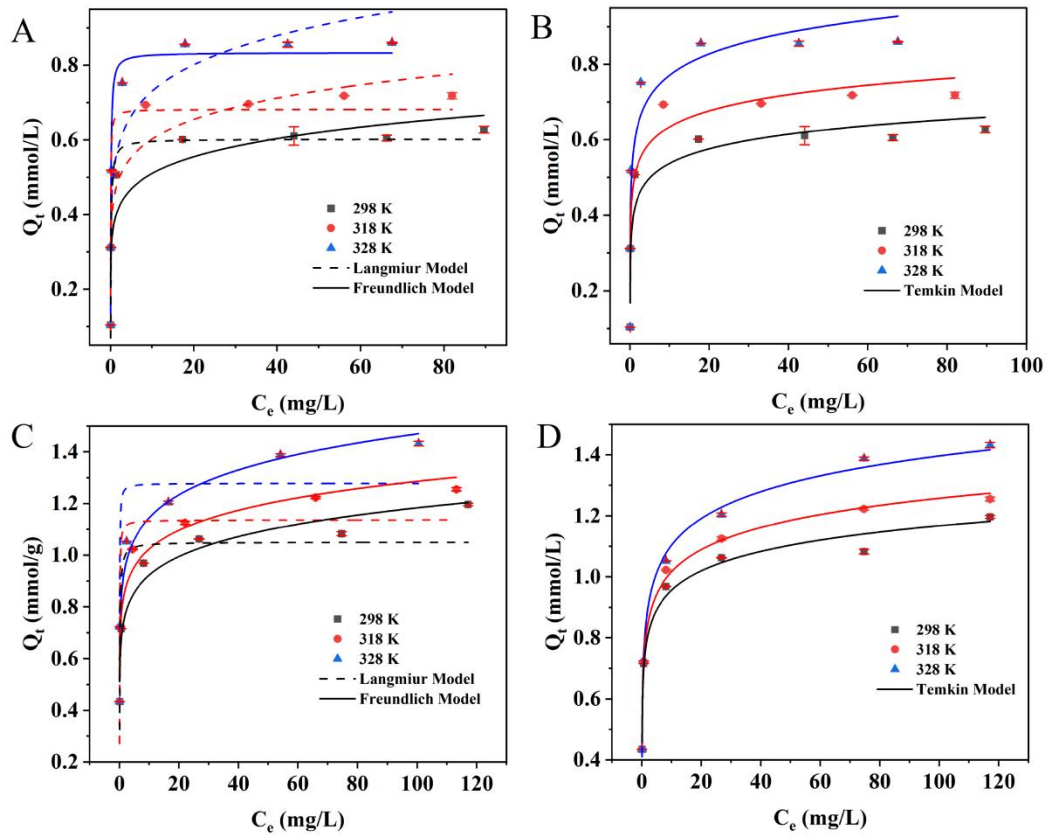


Fig. 8. Adsorption isotherm models of RM-MGMs for Cu²⁺(A: Langmuir and Freundlich, B: Temkin) and Pb²⁺(C: Langmuir and Freundlich, D: Temkin).

RM-MGMs have significant advantages in adsorption performance and preparation process compared with many reported adsorbents. As shown in Table 3, the maximum Pb²⁺ adsorption capacity of RM-MGMs reached 1.43 mmol/g, which is significantly higher than that of iron-modified peanut shell biochar (Fe@BC, 0.11 mmol/g) [30], citrate-intercalated Mg/Al layered double hydroxide

(Citrate-LDH 0.97 mmol/g) [31], KMnO₄-modified hydrochar (WSHyC-0.2KMnO₄, 0.91 mmol/g) [32], porous geopolymers (PGP, 0.41 mmol/g) [34] and geopolymer foams from mineral wastes (geo-M₂Na₁₀, 0.40 mmol/g) [35]. The Cu²⁺ adsorption capacity (0.86 mmol/g) was also superior to that of WSHyC-0.2KMnO₄ (0.51 mmol/g), Fe@BC (0.34 mmol/g) and RM (0.61 mmol/g) [27], and was close to that of geopolymer foams from mineral wastes (geo-M₂Na₁₀, 0.40 mmol/g) [35]. Although Cu²⁺-modified activated carbon (0.2-Cu-SAC) [33] showed a higher Pb²⁺ adsorption capacity (1.99 mmol/g), its equilibrium time was as long as 450 min. In contrast RM-MGMs reached Pb²⁺ equilibrium in only 60 min greatly improving treatment efficiency. In addition, the Pb²⁺ adsorption capacity (1.42 mmol/g) exhibited by raw red mud (RM) is comparable to that of RM-MGMs. However, the settling rate of micron-sized spherical RM-MGMs is much faster than that of RM powder, which facilitates solid-liquid separation and recovery. PGP, Citrate-LDH and 0.2-Cu-SAC had significantly higher Cu²⁺ adsorption capacities (1.55, 2.53 and 5.75 mmol/g, respectively) than RM-MGMs. However, in terms of preparation RM-MGMs use industrial waste red mud as the main raw material and form spheres in one step via dispersion-suspension-solidification process. They do not require high-temperature carbonization and metal impregnation like 0.2-Cu-SAC or inert atmosphere control like Citrate-LDH. The process is simple and low-cost aligning with green environmental concepts. Furthermore, RM-MGMs are micron-sized spherical particles that can be quickly separated by simple sedimentation after adsorption effectively overcoming the recovery difficulty of powder adsorbents (e.g. raw RM Fe@BC WSHyC-0.2KMnO₄).

Table 3. Comparison of Cu²⁺ and Pb²⁺ adsorption by RM-MGMs and reported adsorbents.

Adsorbent	Element	pH	T(K)	t (min)	Q _m (mmol/g)	Reference
Fe@BC	Cu ²⁺	4	298	480	0.34	[30]
	Pb ²⁺	4	298	480	0.11	
Citrate-LDH	Cu ²⁺	5	323	60	2.53	[31]
	Pb ²⁺	5	323	60	0.97	
WSHyC-0.2KMnO ₄	Cu ²⁺	\	298	300	0.51	[32]
	Pb ²⁺	\	298	300	0.96	
RM	Cu ²⁺	\	298	1440	0.61	[27]
	Pb ²⁺	\	298	540	1.42	
0.2-Cu-SAC	Cu ²⁺	5	298	450	5.75	[33]
	Pb ²⁺	5	298	450	1.99	
PGP	Cu ²⁺	6	298	300	1.55	[34]
	Pb ²⁺	6	298	300	0.41	
geo-M ₂ Na ₁₀	Cu ²⁺	5	298	120	0.87	[35]
	Pb ²⁺	5	298	120	0.40	

RM-MGMs	Cu ²⁺	5.3-5.6	308	960	0.86	This study
	Pb ²⁺	5	308	60	1.43	

3.5. Desorption and cyclic performance of RM-MGMs for Cu²⁺ and Pb²⁺

Fig. 9(A) shows the desorption effects of different desorbents on Cu²⁺. 0.1 mol/L HNO₃ exhibited the best desorption effect, but it destroyed the microsphere structure during desorption. In EDTA-2Na solutions of different concentrations, the desorption efficiency for Cu²⁺ gradually increased with increasing EDTA-2Na concentration. When desorption time increased to 24 h, the 0.005 mol/L and 0.01 mol/L EDTA-2Na showed similar desorption effects with desorption rates of 88.47% and 86.13%, respectively. When the EDTA-2Na concentration was raised to 0.05 mol/L, the RM-MGMs structure was destroyed. As an ultra-strong complexing agent, excessively high EDTA-2Na concentration can destroy metal ions in the geopolymer microsphere framework [36]. Fig. 9(B) shows the desorption effects on Pb²⁺. 0.01 mol/L HNO₃ increased the Pb²⁺ desorption rate from 75.80% to 92.27% within 2-12 h, while 0.01 mol/L EDTA-2Na increased the desorption rate from 46.86% to 88.92% within 2-12 h. Weak acidic desorbents showed better desorption efficiency for Pb²⁺ because acidic desorbents have a stronger ability to dissolve precipitates. They providing H⁺ to dissolve surface precipitates on microspheres and complexing Pb²⁺ to promote its dissolution.

Therefore, the effects of 0.005/0.01 mol/L EDTA-2Na and 0.01 mol/L HNO₃/EDTA-2Na on the cyclic adsorption performance of RM-MGMs toward Cu²⁺ and Pb²⁺ were investigated separately. As shown in Fig. 9(C), for RM-MGMs desorbed with 0.01 mol/L EDTA-2Na, the Cu²⁺ adsorption capacity decreased from 0.50 to 0.24 mmol/g with increasing cycle number. For RM-MGMs desorbed with 0.005 mol/L EDTA-2Na, the Cu²⁺ adsorption capacity dropped sharply to 0.23 mmol/g in the second cycle and further to 0.10 mmol/g in the third cycle. This is because 0.01 mol/L EDTA-2Na has sufficient concentration to fully desorb most Cu²⁺ adsorbed on the material surface and interior via complexation, thereby effectively regenerating the active sites. The lower concentration EDTA-2Na cannot completely desorb Cu²⁺. Some strongly bound Cu²⁺ remains on active sites, reducing site availability and causing a large drop in adsorption performance. As shown in Fig. 9(D), although 0.01 mol/L HNO₃ resulted in a higher initial desorption rate for Pb²⁺, in subsequent adsorption cycle tests, the adsorption capacity of RM-MGMs desorbed with 0.01 mol/L EDTA-2Na for Pb²⁺ was significantly higher than that of RM-MGMs desorbed with 0.01 mol/L HNO₃. After three desorption cycles with 0.01 mol/L EDTA-2Na, the adsorption capacity for Pb²⁺ remained at 0.25 mmol/g. In contrast, the adsorption capacity of RM-MGMs desorbed with 0.01 mol/L HNO₃ had already dropped to 0.02 mmol/g by the second cycle. HNO₃ as an acidic desorbent efficiently desorbs Pb²⁺ via protonation. However, the strongly acidic environment dissolves active components in RM-MGMs (e.g. calcite, cancrinite) [20], leading to irreversible loss of active sites.

Consequently, the adsorption capacity declines rapidly after multiple cycles. EDTA-2Na only achieves desorption through complexation with Pb^{2+} , without destroying the framework structure or active components. Therefore, the active sites are efficiently regenerated. However, the Ca^{2+} within RM-MGMs gradually decreased with the number of cycles increased, leading to a gradual reduction in the number of active sites and a consequent decline in adsorption capacity. Although its cyclic adsorption performance decreases, its cyclic stability is superior to that of 0.01 mol/L HNO_3 .

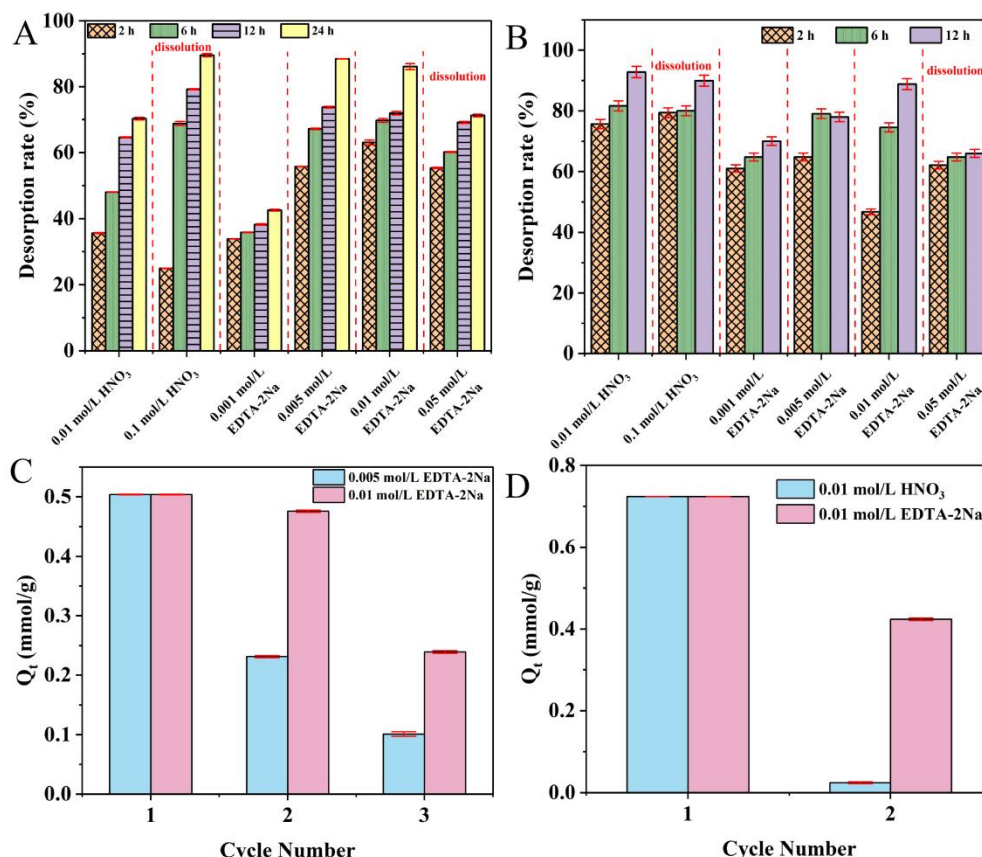


Fig. 9. Desorption performance of RM-MGMs for Cu^{2+} (A) and Pb^{2+} (B) under different desorption agents and desorption times, and their cycling performance for Cu^{2+} (C) and Pb^{2+} (D).

3.6. The effect of real water systems and coexisting ions on the Cu^{2+} and Pb^{2+} adsorption performance of RM-MGMs

Various factors in real wastewater directly affect the adsorption effect of RM-MGMs. As shown in Fig. 10(A and C), the adsorption performance of RM-MGMs for Cu^{2+} and Pb^{2+} in different water bodies followed the order tap water $\approx$ lake water $>$ seawater. For Cu^{2+} the adsorption amounts (removal rates) were 0.48 mmol/g (92.73%), 0.49 mmol/g (94.00%) and 0.42 mmol/g (80.92%), respectively. For Pb^{2+} they were 0.69 mmol/g (95.35%), 0.69 mmol/g (95.76%) and 0.49 mmol/g (68.50%), respectively. Seawater is a high-salinity complex system containing a large number of cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} , which compete with Pb^{2+} for active sites on the

microsphere surface thus reducing adsorption performance in seawater. Lake water and tap water have lower dissolved salt concentrations allowing target heavy metal ions to dominate adsorption [37]. As shown in Fig. 10(B and D), when the dosage was increased to 3 g/L, the removal rate of Cu^{2+} from seawater rose to 89.69%, while increasing the dosage to 1 g/L was sufficient to raise the removal rate of Pb^{2+} from seawater to 95.38%. This indicates that RM-MGMs are also effective at removing Cu^{2+} and Pb^{2+} from seawater.

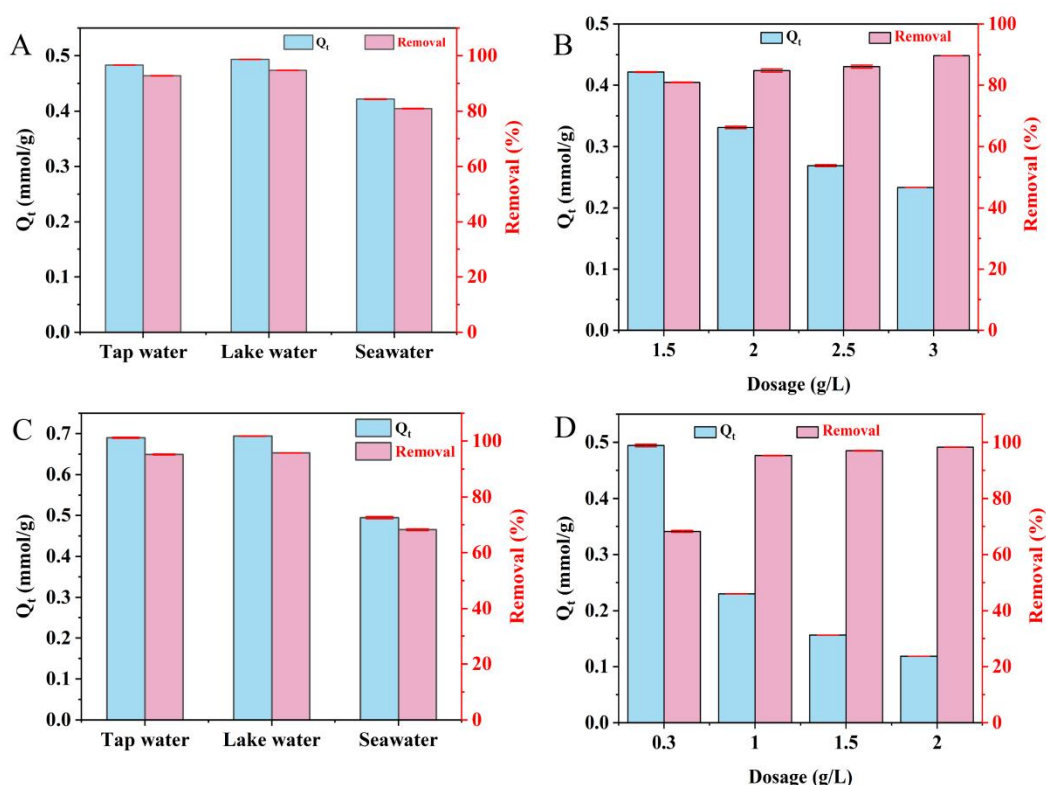


Fig. 10. The adsorption effect of RM-MGMs on Cu^{2+} (A) and Pb^{2+} (C) in real water bodies, as well as the adsorption effect of different solid-liquid ratios on Cu^{2+} (B) and Pb^{2+} (D) in seawater.

Cu^{2+} and Pb^{2+} are common heavy metal ions in industrial wastewater. They often coexist with other ions such as Ni^{2+} , Mg^{2+} , Zn^{2+} and Ca^{2+} [10]. Therefore the effect of coexisting ions on the adsorption performance of RM-MGMs for Cu^{2+} and Pb^{2+} was investigated. As shown in Fig. 11(A and B), when Cu^{2+} coexisted with Pb^{2+} , Ni^{2+} , Mg^{2+} , Zn^{2+} and Ca^{2+} the adsorption performance of RM-MGMs for Cu^{2+} was suppressed. The removal rates for Cu^{2+} decreased to 93.25%, 93.27%, 93.59%, 90.00% and 84.56%, respectively. The order of influence of competing ions on Cu^{2+} adsorption was $\text{Ca}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} \approx \text{Ni}^{2+} \approx \text{Mg}^{2+}$. When Pb^{2+} coexisted with Cu^{2+} , Ni^{2+} , Mg^{2+} , Zn^{2+} and Ca^{2+} the adsorption performance for Pb^{2+} was also suppressed. The removal rates decreased to 80.42%, 86.30%, 80.37%, 89.85% and 89.27%, respectively. The order of influence on Pb^{2+} adsorption was $\text{Mg}^{2+} \approx \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Ca}^{2+} \approx \text{Zn}^{2+}$.

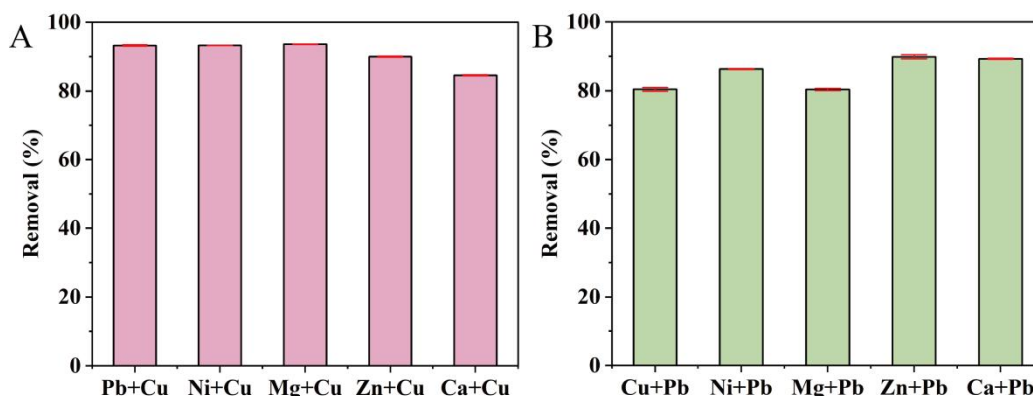


Fig. 11. The effect of coexisting ions on the adsorption performance of RM-MGMs for Cu^{2+} (A) and Pb^{2+} (B).

3.7. Adsorption Mechanism of RM-MGMs for Cu^{2+} and Pb^{2+}

The surface chemical element changes of RM-MGMs before and after Cu^{2+} and Pb^{2+} adsorption were compared by SEM/EDS as shown in Fig. 12(A-C). RM-MGMs maintained good sphericity before and after adsorption. After Cu^{2+} adsorption the RM-MGMs surface remained smooth and clean. After Pb^{2+} adsorption the surface unevenly adhered strip-like substances indicating precipitation during Pb^{2+} adsorption. The main elements of RM-MGMs before adsorption were O, Na, Al, Si, Ca and Fe. After adsorption of Cu^{2+} and Pb^{2+} , the Cu and Pb contents in the RM-MGMs increased by 6.67 wt% and 22.22 wt%, respectively, indicating that they were successfully adsorbed by the RM-MGMs. The Na and Ca contents decreased after adsorption confirming ion exchange during adsorption. XRD analysis of RM-MGMs before and after Cu^{2+} and Pb^{2+} adsorption is shown in Fig. 12(D). Before adsorption the phases included hematite cancrinite calcite and hydroandradite. After Cu^{2+} and Pb^{2+} adsorption the characteristic peaks of hydroandradite ($2\theta=53.12^\circ$) and calcite ($2\theta=29.36^\circ$, 47.52°) disappeared. After Pb^{2+} adsorption, the cancrinite peaks at $2\theta=17.53^\circ$, 18.83° , 39.67° and 42.59° also disappeared. This may be due to participation of -OH in hydroandradite in the adsorption reaction, as well as ion exchange between Ca^{2+} in calcite and heavy metal ions, leading to weakening and disappearance of characteristic peaks.

The changes in chemical bonding of RM-MGMs before and after adsorption are shown in Fig. 12(E). The peaks at 3426.52 cm^{-1} and 1643.44 cm^{-1} attributed to -OH stretching and bending vibrations shifted after Cu^{2+} / Pb^{2+} adsorption. This is because heavy metals combined with -OH formed new complexes or underwent ion exchange changing the chemical environment of -OH proving that -OH participated in chemical adsorption [38][39]. The peaks at 1007.27 cm^{-1} 686.77 cm^{-1} and 455.02 cm^{-1} correspond to Si-O-T (T=Al/Si) geopolymer framework stretching vibration, symmetric stretching vibration of Si-O-T and bending vibration of Si/Al-O tetrahedra, respectively [40][41][42]. After Cu^{2+} / Pb^{2+} adsorption, the Si-O-T and Si/Al-O peaks broadened and shifted to

varying degrees. This may be due to electrostatic attraction or ion exchange between the negatively charged $[\text{AlO}_4]/[\text{SiO}_4]$ groups and the heavy metals [42][10], leading to the enrichment of heavy metal ions around the Al-O bonds and the formation of a cation layer. The carbonate (CO_3^{2-}) characteristic peak at 1496.18 cm^{-1} shifted to $1496.22/1496.25 \text{ cm}^{-1}$ after Cu^{2+} / Pb^{2+} adsorption, this may be due to ion exchange between Cu^{2+} / Pb^{2+} and Ca^{2+} in calcium carbonate [43][44]. The Fe-O bond peak at 569.52 cm^{-1} shifted to lower wavenumber after Cu^{2+} / Pb^{2+} adsorption. This may be because Fe-OH on the RM-MGMs surface participated in the adsorption process via complexation [45][46].

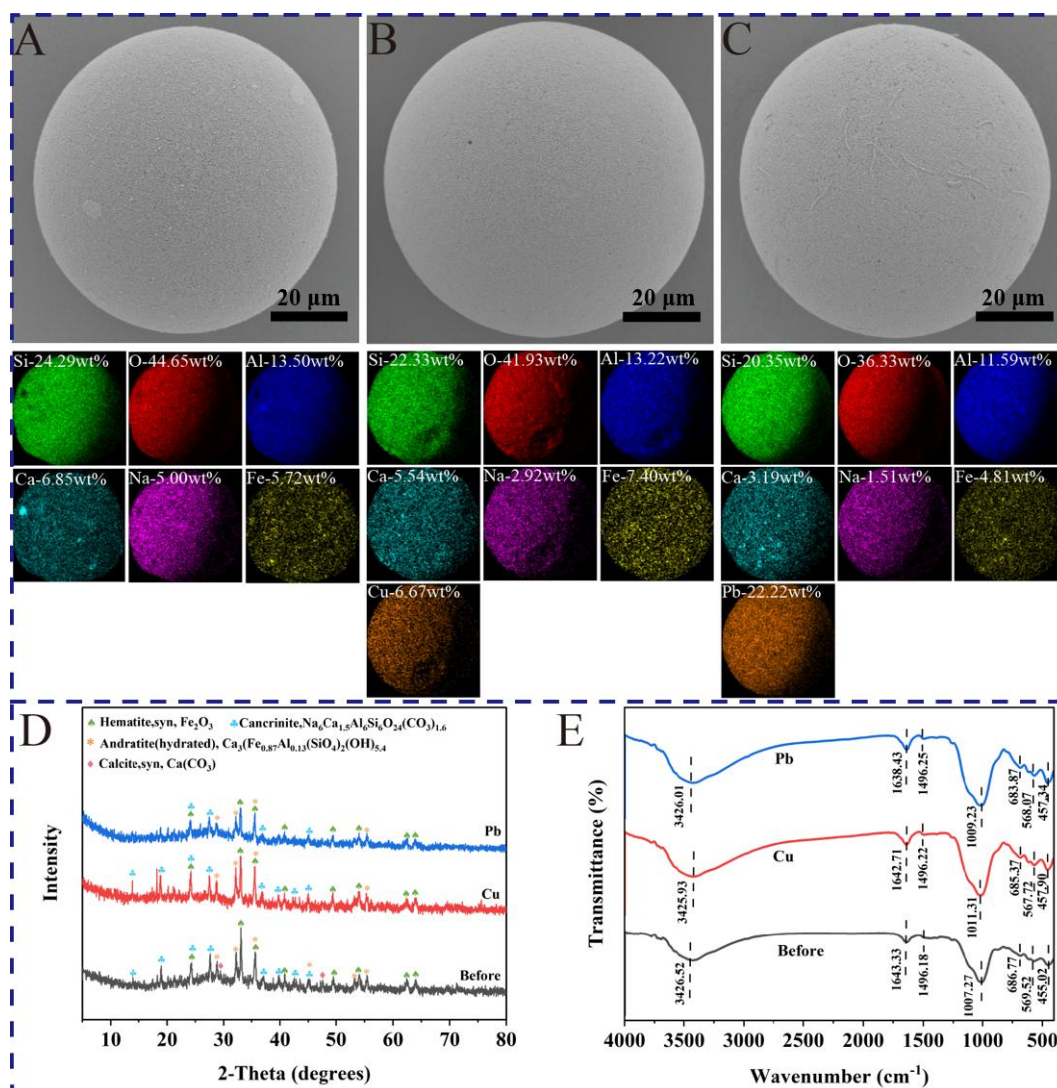


Fig. 12. SEM (A: before adsorption, B: after Cu adsorption, C: after Pb adsorption), XRD (D) and FT-IR (E) of RM-MGMs before and after adsorption of Cu^{2+} and Pb^{2+} .

Fig. 13(A) shows the XPS spectra of RM-MGMs before and after Cu^{2+} and Pb^{2+} adsorption. Before adsorption characteristic peaks of Na 1s, Fe 2p, O 1s, Ca 2p, Si 2p and Al 2p were detected at binding energies of 1071.70 706.24 531.47 347.92 101.87 and 73.96 eV, respectively. After

adsorption of Cu^{2+} and Pb^{2+} , Pb 4f and Cu 2p peaks appeared at 932.4 eV and 139.0 eV, respectively. The Ca 2p and Na 1s peaks weakened significantly indicating ion exchange participated in Cu^{2+} and Pb^{2+} adsorption. In addition, the diffraction peak for Pb appears at a lower binding energy, this indicated that the electron density around Pb is higher, resulting in a Pb–O bond with stronger covalent character. This chemical bonding explains the strong affinity of RM-MGMs for Pb^{2+} , which was consistent with the findings of higher adsorption capacity and faster adsorption rates for Pb^{2+} [46].

To further elucidate the adsorption mechanisms of RM-MGMs for Cu^{2+} and Pb^{2+} , fine-resolution scans were performed for the Cu 2p, Pb 4f, O 1s, and C 1s lines. Fig. 13(B) shows the Cu 2p spectrum after Cu^{2+} adsorption. Cu $2p_{3/2}$ and Cu $2p_{1/2}$ were located at 933.10 eV and 952.73 eV, respectively. A shake-up peak at 944.47 eV assigned to Cu(II) was observed, indicating that Cu(II) was loaded on the RM-MGMs surface. Deconvolution of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ gave Cu–O (932.84 eV, 952.59 eV) and Cu– CO_3 (935.46 eV, 955.21 eV), indicating that Cu(II) adsorbed on RM-MGMs mainly existed as Cu–O [47]. As shown in Fig. 13(C), the Pb $4f_{7/2}$ and Pb $4f_{5/2}$ peaks at 139.0 eV and 144.23 eV were split into two peaks. The peaks at 138.77 eV and 143.71 eV were assigned to Pb–O and the peaks at 139.0 eV and 144.43 eV were assigned to Pb– CO_3 [48], indicating that Pb(II) was mainly adsorbed as PbCO_3 on RM-MGMs [44][49]. Fig. 13(D/D₁/D₂) shows the O 1s spectra before and after adsorption. After Cu^{2+} and Pb^{2+} adsorption, the A–O bond energy shifted from 531.44 eV to 531.66 eV and 531.59 eV, respectively, while the A–O peak area ratios increased from 35.13% to 73.81% and 68.37%, respectively. The A–OH bond energy shifted from 532.30 eV to 533.15 eV and 532.88 eV, respectively, while the A–OH peak area ratios decreased from 64.87% to 26.19% and 31.63%, respectively. This indicates that –OH groups on the RM-MGMs surface underwent complexation with metal ions in solution, forming inner-sphere A–O–Pb/Cu complexes [27][50]. Fig. 13(E/E₁/E₂) shows the C 1s changes before and after adsorption. C 1s was deconvoluted into C–C, C–C–C and O–C=O bonds. After Cu^{2+} and Pb^{2+} adsorption the O–C=O peak shifted from 288.35 eV to 288.46 eV and 288.40 eV and its peak area ratio increased from 2.62% to 8.46% and 7.01%, respectively. The change in chemical environment of O–C=O bonds is attributed to ion exchange between calcite and metal ions in solution forming CuCO_3 and PbCO_3 [51][52].

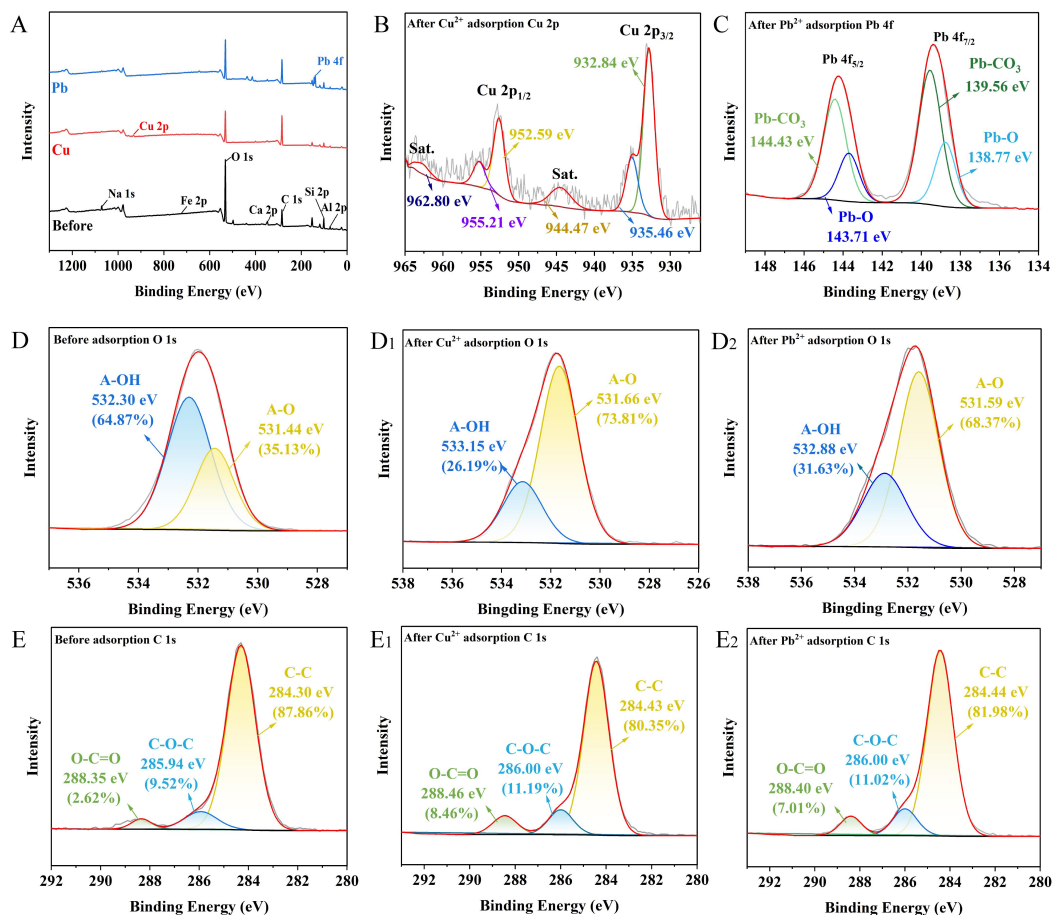


Fig. 13. XPS full spectra of RM-MGMs before and after adsorption of Cu²⁺ and Pb²⁺ (A); Cu 2p (B), Pb 4f (C), O 1s (D/D₁/D₂), and C 1s (E/E₁/E₂) fine spectra.

Combining the above experimental and characterization results the adsorption process of RM-MGMs for Cu²⁺ and Pb²⁺ mainly involves electrostatic attraction, ion exchange and complexation. As shown in Fig. 14, the negatively charged [SiO₄] and [AlO₄] tetrahedra in the RM-MGMs structure make the material surface negatively charged. Under electrostatic attraction Cu²⁺/Pb²⁺ are adsorbed on the material surface. The cations Ca²⁺ and Na⁺ that balance the negative charge in the RM-MGMs structure undergo ion exchange with Cu²⁺/Pb²⁺ during adsorption. Meanwhile abundant -OH active sites on the RM-MGMs surface undergo complexation with metal ions in solution further enhancing adsorption. RM-MGMs achieve efficient adsorption of metal cations through the synergistic action of multiple adsorption mechanisms.

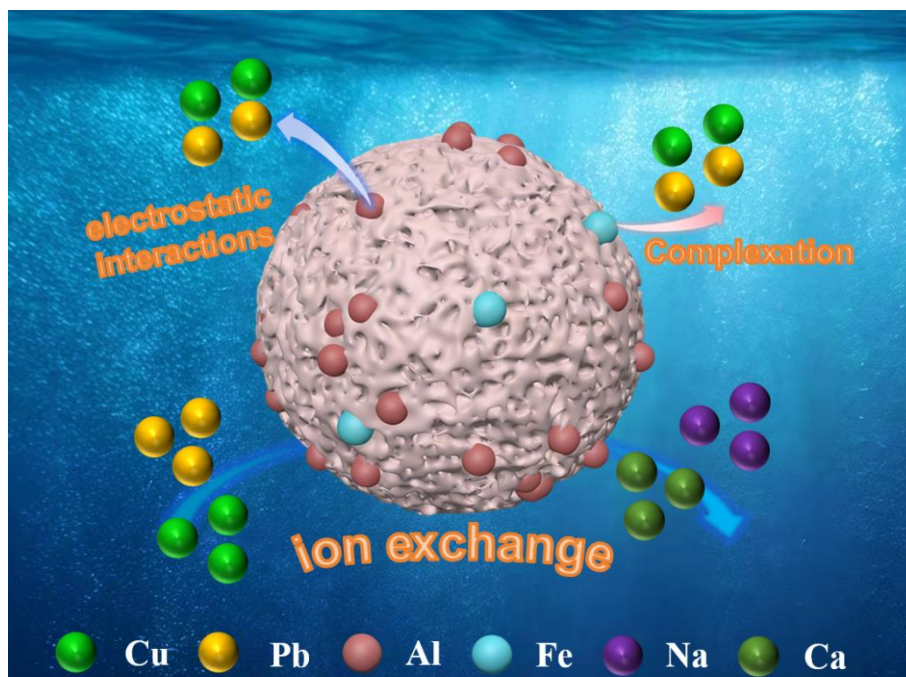


Fig. 14. Schematic illustration of the Cu^{2+} and Pb^{2+} adsorption mechanism on RM-MGMs.

4. Conclusions

This study used red mud and metakaolin to prepare geopolymer microspheres (RM-MGMs) and systematically investigated their adsorption performance and mechanism for Cu^{2+} and Pb^{2+} in water. RM-MGMs showed the best adsorption effect with removal rates of 97.60% for Cu^{2+} and 99.96% for Pb^{2+} . As calcination temperature increased, the removal of structural water and hydroxyl groups leads to a decrease in cation exchange capacity, and the pore collapse and localized melting caused by high temperatures significantly reduce the adsorption performance of RM-MGMs. The adsorption process followed the pseudo-second-order kinetic model dominated by chemisorption. The difference in adsorption rate between the two ions mainly originated from their different hydrated radii. Isotherm model fitting showed that Cu^{2+} adsorption followed the Langmuir model (monolayer adsorption), while Pb^{2+} adsorption followed the Freundlich model (multilayer adsorption). Desorption cycle experiments showed that EDTA-2Na had good regeneration and cycling performance for both Cu^{2+} and Pb^{2+} . RM-MGMs maintained good adsorption performance in real water bodies (tap water, lake water and seawater) and still exhibited high removal rates for Cu^{2+} and Pb^{2+} in coexisting cation competition systems. Multiple characterization techniques including XRD SEM-EDS FT-IR and XPS revealed a synergistic adsorption mechanism involving electrostatic attraction, ion exchange and complexation. The negatively charged $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra electrostatically attract metal cations onto the RM-MGMs surface. Ca^{2+} and Na^+ in the RM-MGMs structure undergo ion exchange with heavy metal ions. Surface $-\text{OH}$ and $\text{Fe}-\text{OH}$ functional groups further immobilize metal ions through complexation. Following the concept of “treating waste with waste”, this study achieves the

dual goals of value-added utilization of red mud and heavy metal pollution control. It systematically elucidates the effect of calcination temperature on the adsorption performance and structure of RM-MGMs and reveals the multi-mechanism synergistic adsorption mechanism.

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Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be available from the corresponding author upon request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution statement

Kaituo Wang: Conceptualization, Data curation, Formal analysis, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing. **Yuxiao Jiang:** Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft. **Haoyu Chen:** Formal analysis, Investigation, Methodology, Validation. **Min Yi:** Data curation, Formal analysis, Methodology. **Lin Shao:** Data curation, Methodology, Writing - review & editing.

Use of AI statement

None.

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