Preparation and Modification of Mullite Whiskers/Cordierite Porous Ceramics for Cu²⁺ Adsorption and Removing

Yaoyao Zhang, Zhengwen Wei, Mengyao Li, Xishe Wu, and Wei Wang*

Cite This: *ACS Omega* 2020, 5, 15691–15701

Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: In this paper, mullite whiskers were prepared by a molten salt reaction method based on a porous cordierite ceramic substrate (MC), and the modified mullite whiskers/cordierite ceramic sample (MCK) was obtained via the silane coupling reaction with γ -aminopropyl triethoxysilane (KH550). The structural morphology and phase compositions of the MC were characterized by X-ray diffraction and scanning electron microscopy. The surface functional groups of MCK were characterized using Fourier transform infrared spectroscopy, and the result showed that the amino group ($-\text{NH}_2$) was successfully grafted onto the surface of cordierite ceramic. X-ray photoelectron spectroscopy analysis successfully showed inclusion of the amino and Cu²⁺ adsorption mechanism onto MCK. The adsorption properties of MCK were investigated using Cu²⁺ as the target pollutant by varying the experimental conditions such as pH, time, temperature, and initial Cu²⁺ concentration. The adsorption was found to be spontaneous, endothermic, and feasible, as indicated by the study of thermodynamic parameters. The adsorption kinetic analysis suggested that the pseudo-second-order kinetic model was best fitted for Cu²⁺ adsorption. The adsorption isotherm studies showed that the results of the Freundlich model are more suitable for experimental adsorption data than the Langmuir model. The adsorption–desorption cycle indicated that MCK had good reusability and stability. A novel porous ceramic-based adsorbent with high Cu²⁺ adsorption and removal efficiency was fabricated and has potential applications for the metal ion removing field.

1. INTRODUCTION

The problem of sustainable energy and environment is the most important challenge for our economical continuable development.¹ Heavy metal pollution is one of the serious environmental problems, because many heavy metals are easy to accumulate in living organisms and are known to be toxic.^{2–5} Heavy metals exist in various environmental media such as water, soil, and air. Some heavy metals are essential for human health at trace amounts but will become toxic when consumed at a higher concentration. For example, high health risks induced by heavy metal consumption through drinking water have been widely reported.^{6,7} Copper is an essential element in animal metabolism; excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death.⁸ Elevated copper levels have been shown to be directly linked to cancer progression.⁹ It has been characterized that neurological disorders, diabetes, cardiovascular disease, and atherosclerosis are all linked with disturbed copper homeostasis.¹⁰ High concentrations of heavy metals in the environment will affect human health via drinking water intake, inhalation, and dermal contact and reduce the ecological biodiversity.¹¹ Therefore, removal of toxic heavy metals from the environment is an important work to ensure environmental sustainability and human health.¹²

In recent years, various methods for heavy metal removal from wastewater have been extensively proposed, including but

not limited to chemical precipitation, ion exchange, adsorption, membrane filtration, and electrochemical technologies.^{13–17} Among these techniques, the adsorption method has been extensively researched because of its high removal efficiency and adsorption capacity, and simple and convenient processes.¹⁸ It has become a popular method for heavy metal removal from wastewater.¹⁹ Adsorption is an effective method to remove heavy metal ions by using the unique structure of the adsorbents, and organic functional groups on the porous materials can chelate heavy metal ions to form stable coordination compounds to remove contaminated heavy metals.^{20–22} The design and synthesis of the adsorbent with excellent adsorption performance is critical and is an important subject worthy of being further studied in adsorption research.^{23,24} Many materials have been developed to remove heavy metals in water, such as activated carbon, ion exchange resin, chelating resin, zeolite, carbon nanotubes, chitosan, and graphene.^{25–29} However, some drawbacks such as small

Received: May 6, 2020

Accepted: June 10, 2020

Published: June 18, 2020

surface area, poor adsorption performance, not easy regeneration, and so forth restrict absorbents' application in wastewater treatment. In order to improve the adsorption performance of absorbents and make them more efficient to remove heavy metal ions, it is necessary to modify the surface of the absorbents.

Porous ceramics have been used as filters, catalysts, and lightweight structural supports in industrial applications.³⁰ Porous cordierite ceramics not only have a porous structure, good thermal shock resistance, and low thermal expansion coefficient but also have the characteristics of good adsorption performance, thin pore wall, and large geometric surface area. They are considered as one of the most promising materials for use in a wide range of applications including as catalyst carrier materials,^{31–33} filtration separation materials,^{34,35} refractory materials,^{36,37} electronic equipment materials,³⁸ and infrared radiation materials.³⁹ However, the application of porous cordierite ceramic as an adsorbent in the removal of metal ions from aqueous solutions has not been reported in literature. In order to expand the application of porous cordierite ceramics, the modification of cordierite ceramics for heavy metal treatment in wastewater was studied in this paper. Mullite whisker has excellent properties such as high temperature resistance, wear resistance, oxidation resistance, small thermal expansion coefficient, high temperature strength, good thermal shock resistance, high-temperature creep reduction, and so forth. It is an excellent reinforcing agent for ceramic matrix composites.⁴⁰ Therefore, combining mullite and cordierite to prepare composite ceramics can play their respective roles and improve the properties of the materials.⁴¹ The mullite whiskers have obvious toughening and reinforcing effects on the cordierite ceramic materials and greatly increased the specific surface area of cordierite porous ceramics. The specific surface area of the mullite whiskers/cordierite composite can provide a reaction active group for the grafting of a silane coupling agent.

In this study, mullite whiskers were prepared by molten salt synthesis on a cordierite substrate, which further expanded the specific surface area of cordierite. Then, a chemical grafting method using γ -aminopropyl triethoxysilane (KH550, $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$) as a raw material was carried out on mullite whiskers/cordierite ceramic materials. A range of experiments were conducted to evaluate the adsorption ability of Cu^{2+} onto the modified mullite whiskers/cordierite ceramic sample (MCK) in aqueous solutions. The objectives of this work were as follows: (1) the physical and chemical structural studies of MCK were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), and X-ray photoelectron spectroscopy (XPS); (2) determine the effects of initial solution pH, sorbent dosage, initial Cu^{2+} concentration, and temperature on the adsorption of Cu^{2+} onto MCK; (3) adsorption kinetics, adsorption isotherm, adsorption thermodynamics, and adsorption mechanism were investigated; and (4) assess the reusability and the stability of MCK. This study could provide a theoretical basis for the application of cordierite porous ceramic for the removal of heavy metal ions.

2. RESULTS AND DISCUSSION

2.1. Characterization. **2.1.1. XRD Analysis.** The structure analysis of MC was carried through XRD analysis. It can be seen from Figure 1 that the mullite crystal diffraction peak appears in the phase of MC. The diffraction peaks at $2\theta = 16.5$,

Figure 1. XRD pattern of cordierite and MC.

31.1 , 35.2 , 37.0 , 40.9 , 43.2 , and 60.5° represented the (110), (001), (111), (130), (121), (113), and (002) lattice planes of mullite according to the Jade PDF card (15-0776), which indicated that the synthesized sample (MC) contained a mass of mullite. These results obviously confirmed the insertion of mullite whiskers in cordierite porous ceramics.

2.1.2. SEM Analysis. Figure 2 shows the morphologies of cordierite and MC. As can be seen, the surface of cordierite

Figure 2. SEM images of (a) cordierite and (b) MC.

porous ceramic was rough with a high porosity, which suggests that the cordierite porous ceramic would possess a good adsorption capacity. Mullite whiskers grew on the surface of the cordierite substrate and formed a cluster-like interface microstructure, which are well combined with cordierite. This result indicated that MC was successfully prepared through molten salt reactions.

2.1.3. Open Porosity and Pore Size Distribution. The open porosity of porous cordierite ceramic was 58.15% using the Archimedes methods. The high porosity proves that the cordierite matrix composite adsorbent is porous, which provides the possibility for the adsorption of heavy metal ions in aqueous solutions. Figure 3 shows the pore size distribution of the porous cordierite ceramics. It was obviously to find that the porous cordierite ceramics have a unimodal pore size distribution curve. The pore size distribution was between 1.63 and $3.14\ \mu\text{m}$, indicating that the pore size distribution of the porous cordierite ceramics is uniform.

2.1.4. FTIR Analysis. Figure 4 presents the FTIR spectrum of MC and MCK. The peak at $3365\ \text{cm}^{-1}$ in the MC is the stretching vibration peak of $-\text{OH}$, the peak at $1184\ \text{cm}^{-1}$ is attributed to the stretching vibration of the $[\text{SiO}_4]$ tetrahedron, the peak at $964\ \text{cm}^{-1}$ is assigned to the stretching vibration of the $[\text{AlO}_4]$ tetrahedron, the strong absorption band at the wavenumber of $772\ \text{cm}^{-1}$ corresponds to the six-membered ring structure of the cordierite. The peaks at 623 and $584\ \text{cm}^{-1}$ mainly belong to the expansion and contraction caused by the

Figure 3. Pore size distribution of the porous cordierite ceramics.

Figure 4. FTIR spectra of MC and MCK.

vibration of the Mg–O₆ octahedron. After KH550 modification, the peaks at 2934 and 2865 cm^{−1} are attributed to asymmetric stretching vibration and symmetrical stretching vibration of C–H bond in methylene (–CH₂–) groups,⁴² which illustrates the existence of organic molecular chains on the surface of MC. These results indicate that KH550 has been successfully grafted onto the surface of MC.

2.1.5. BET Analysis. Table 1 shows the specific surface area and pore volume data calculated by the BET and Barrett,

Table 1. BET Specific Surface Areas (S_{BET}), Pore Volume, and Pore Diameter of the Samples

	specific surface area/m ² ·g ^{−1}	pore volume/cm ³ ·g ^{−1}	pore diameter/nm
cordierite	5.7	0.01	50
MC	19.8	0.09	28

Joyner, and Halenda formulas. It can be seen that the specific surface area of MC is 3.5 times larger than that of cordierite, and the pore volume is also increased by 6.7 times, which confirms that mullite whiskers that grow on the cordierite matrix expand the specific surface area of cordierite. Therefore, it is expected that MC should be more suitable for Cu²⁺ adsorption than cordierite, because MC has a greater number of adsorption sites than cordierite.

2.2. Adsorption Studies. **2.2.1. Effect of Reaction Time on the Adsorption Properties.** As can be seen from the variation trends of the two curves in Figure 5, the removal efficiencies of MC and MCK were relatively high at the

Figure 5. Effect of reaction time on adsorption.

beginning of the Cu²⁺ adsorption process; with the increase of time, the removal efficiency is gradually reduced, the vacant sites are occupied, and the adsorption equilibrium is attained at 120 min. The MCK removal efficiency can reach 98.13%, which is much higher than that of the MC sample. MC has an adsorption effect on heavy metal ions because of its porous structure. The reactive group (–NH₂) of the surface of MCK can coordinate with Cu²⁺, which increases the removal efficiency and adsorption capacity of MCK. In addition, the adsorption reaction time was set at 120 min in subsequent experiments.

2.2.2. Effect of pH on the Adsorption Properties. The effect of pH on the removal efficiency of Cu²⁺ is shown in Figure 6.

Figure 6. Effect of pH on adsorption.

Initial pH values were adjusted to 2, 3, 4, 5, 6, and 7, respectively. It can be seen that the initial pH of the solution has a significant effect on the removal of Cu(II), and the removal efficiency of Cu(II) by MCK increases, while the pH increases until a certain value. When the solution pH < 3, the removal efficiency of Cu(II) by the adsorbent is very low. When the pH > 5, the adsorption of Cu(II) by the adsorbent tends to be stable. Under acidic conditions, copper ions are mainly present as Cu²⁺ in aqueous solutions, a large amount of H⁺ exist in the solutions, and H⁺ suffered competitive adsorption with Cu²⁺ on the chelate adsorption site on the surface of the adsorbent. The protonation of amine and hydroxyl groups decreases the binding sites for Cu²⁺, leading to a decrease in the adsorption. With an increase of the pH value, the number of hydrogen ions decreased and the MCK allowed more ligands to form complexes with Cu(II), which leads to

the higher adsorption capability. With the increase of pH (>5), three species of Cu(II) coexisting in this solution, Cu^{2+} , $\text{Cu}(\text{OH})^+$, and $\text{Cu}(\text{OH})_2$, compete with each other, precipitation of metal hydroxides formed, and a bigger error is caused. Thus, pH 5 was chosen for further experiments.

2.2.3. Effect of Adsorbent Dosage on the Adsorption Properties. The effect of adsorbent dosage on the adsorption of Cu^{2+} is shown in Figure 7. It can be seen that the removal

Figure 7. Effect of adsorbent dosage on adsorption.

efficiency increases with the increase of adsorbent dosage from 0.4 to 2.0 g. This can be explained that an increased amount of adsorbent results in an increase in surface area as well as the number of vacant active sites. Although increasing the dosage can increase the removal efficiency of Cu^{2+} , the optimum dosage of the inflection point of the removal efficiency curve is selected, that is, 0.8 g is the optimal dosage.

2.2.4. Effect of the Initial Concentration on the Adsorption Properties. When the pH is 5 and adsorbent dosage is 0.8 g, the effect of the initial concentration on adsorption is shown in Figure 8. It can be seen that the

Figure 8. Effect of the initial concentration on adsorption.

removal efficiency decreases with the increase of the initial concentration of Cu^{2+} . The active sites are limited on the adsorbent surface when the initial concentration reaches a certain value. At the same initial concentration condition, the removal efficiency of the sample MCK is higher than that of the sample MC because the silane coupling reaction increases the quantity of active sites on the surface of MCK.

2.2.5. Effect of Reaction Temperature on the Adsorption Properties. The relationship between the removal efficiency and reaction temperature is shown in Figure 9. The removal

Figure 9. Effect of the reaction temperature on adsorption.

efficiency of samples MCK and MC increases while the temperature increases. It is suggested that the adsorption of Cu^{2+} by MCK and MC is an endothermic reaction and the effect of temperature on the removal efficiency is not significant. Therefore, the adsorption can occur at room temperature.

2.2.6. Thermodynamic Analysis. The thermodynamic parameters of MCK for Cu^{2+} adsorption at different temperatures are calculated to determine whether the adsorption reaction is endothermic or exothermic, spontaneous or nonspontaneous.⁴³ The feasibility and the direction of the adsorption phenomena can be predicted by studying the thermodynamics of the adsorption as shown in Figure 10.

Figure 10. Van't Hoff plot for Cu^{2+} adsorption at different temperatures.

Table 2 shows the thermodynamic parameters for Cu^{2+} adsorption on MCK. The negative values of ΔG° indicate the spontaneous process of the reactions and the more negative value with an increase of the temperature shows that a high temperature was advantageous for the adsorption process. The positive value of ΔH° indicates that the adsorption process is an endothermic process. The positive value of ΔS° indicates that there is an increase in the randomness at the solid–solution interface and it is also entropically favored during the adsorption process.⁴⁴ Therefore, the adsorption of Cu^{2+} by MCK is a spontaneous endothermic process.

Table 2. Thermodynamic Parameters for Cu²⁺ Adsorption on MCK

T/K	$\Delta G^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S^\circ/(\text{J}\cdot\text{mol}^{-1}\text{K}^{-1})$
298	−8.55		
303	−9.81		
308	−10.72	43.28	177.58
313	−11.29		
318	−12.23		

2.2.7. Adsorption Kinetics. In order to understand the adsorption phenomenon, a pseudo-first-order kinetic model and a pseudo-second-order kinetic model have been used to examine experimental data.^{45–47}

Figure 11 presents the nonlinear and linear curves of the pseudo-first-order and the pseudo-second-order models fitted with the experimental data of Cu²⁺ adsorption on MCK. The corresponding fitting kinetic parameters, and computed values are listed in Table 3. It is well known that the nonlinear method can be applied to obtain kinetic model parameters that are more accurate than those obtained using the linear method. It was found that both the nonlinear ($R^2 = 0.9987$) and linear ($R^2 = 0.9994$) methods of the pseudo-second-order described the Cu²⁺ adsorption kinetic data very well. Compared to the pseudo-first-order kinetic model, the correlation coefficient of the linear pseudo-second-order kinetic model ($R^2 = 0.9994$) was higher. Moreover, its calculated equilibrium adsorption capacity ($q_{e,\text{cal}} = 19.88 \text{ mg}\cdot\text{g}^{-1}$) was closest to the experimental equilibrium adsorption capacity ($q_{e,\text{exp}} = 19.25 \text{ mg}\cdot\text{g}^{-1}$). Thus, the adsorption of Cu²⁺ onto MCK follows the pseudo-second-order kinetic model.

2.2.8. Adsorption Isotherms. In order to understand the adsorption mechanism of Cu²⁺ adsorption on MCK, the adsorption data were analyzed by adsorption isothermal models. Both Langmuir and Freundlich isotherms were applied to analyze the experimental data of Cu²⁺ adsorption onto MCK.^{48,49}

The fitting plots of the two models in their linear and nonlinear forms are shown in Figure 12. The corresponding calculated parameters obtained from the linear and nonlinear equations are listed in Table 4. It was found that the correlation coefficients of both the nonlinear ($R^2 = 0.9917$) and linear ($R^2 = 0.9895$) methods obtained from the Freundlich model were higher than those of the Langmuir model ($R^2 = 0.9628$, and $R^2 = 0.9861$, respectively) for Cu²⁺ adsorption. Thus, the experiment data of Cu²⁺ adsorption satisfactorily fitted the Freundlich isotherm model, which indicated that the adsorption of Cu²⁺ occurs on heterogeneous surfaces by multilayer adsorption. The value for the constant n was 0.342 (between 0 and 10) in the Freundlich model, which indicated that the adsorption was favorable and Cu²⁺ could be easily adsorbed onto MCK.

2.2.9. Adsorption Mechanism of MCK. XPS analysis was carried out to discuss the adsorption mechanism and interaction of functional groups of MCK and Cu²⁺ in the solution. Its full spectra before and after adsorption are shown in Figure 13a. It is found that there are eight peaks in the whole spectrum before adsorption, namely, O 1s, C 1s, N 1s, Si 2s, Si 2p, Al 2s, Al 2p, and Mg 2p. The presence of the N 1s peak confirms the presence of KH550 on the surface of MCK, which is well consistent with FTIR characterization. Apparently, the new peak at 942.2 eV attributed to Cu 2p is observed in the survey scan spectrum of XPS after the

Figure 11. Adsorption kinetic model fitting of MCK: (a) linear curve of the pseudo-first-order kinetic model; (b) nonlinear curve of the pseudo-first-order kinetic model; (c) linear curve of the pseudo-second-order kinetic model; (d) nonlinear curve of the pseudo-second-order kinetic model (pH = 5, dosage: 0.8 g, initial Cu²⁺ concentration: 30 $\text{mg}\cdot\text{L}^{-1}$, temperature: 298 K).

Table 3. Adsorption Kinetic Parameters for Cu²⁺ Adsorption on MCK

type		linear model	nonlinear model
pseudo-first-order	k_1 (min ⁻¹)	0.0116	0.0555
	q_e (mg·g ⁻¹)	8.39	17.91
	R^2	0.8657	0.9843
pseudo-second-order	k_2 (g·mg ⁻¹ min ⁻¹)	0.0042	0.0039
	q_e (mg·g ⁻¹)	19.88	20.03
	R^2	0.9994	0.9987

adsorption of Cu²⁺, which confirms the adsorption of Cu²⁺ onto the surface of MCK. In Figure 13b, the characteristic peaks appearing at 941.3 and 961.2 eV were attributed to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively; Cu 2p_{1/2} shock peaks also appeared at 951.2 eV. Usually, the special vibration peak of Cu²⁺ is related to the d⁹ configuration of Cu. The C 1s spectra of MCK in Figure 13c shows two peaks at 284.8 and 286.3 eV corresponding to C–C/C–H and C–N, respectively. After the adsorption of Cu²⁺ in Figure 13e, the binding energy of C–N shifted to 285.7 eV, which indicated that the C–N was involved in the adsorption mechanisms. Figure 13d,f is the N 1s spectra of MCK and Cu–MCK. The binding energy at 398.5 eV is assigned to the N 1s of C–N. After adsorption of Cu²⁺, the peak shifted to 404.8 eV. This is because the N atom donates the lone pair of electrons to the copper ion and the resulting electron density of the N atom decreases and binding energy increases. All data evidence the stronger interaction between Cu²⁺ with the –NH₂ group, indicating that the main adsorption process is chemical adsorption.

2.3. Desorption and Regeneration. After cyclic adsorption for five times, the removal efficiency of the regenerated MCK is shown in Figure 14. It can be seen that the removal efficiency of MCK remains stable during five adsorption–desorption cycles. The Cu²⁺ removal efficiency decreases approximately 4 and 7% (after five cycles) compared with the first adsorption by using EDTA-2Na and HCl, respectively, because Cu²⁺ forms a more stable chelate complex with EDTA-2Na. The removal efficiency loss can be ascribed to desorption process incompleteness. In view of the above results, it was clear that the adsorbent MCK exhibited excellent reusability.

2.4. Comparison of Cu²⁺ Removal with the Literature. Table 5 includes the Cu²⁺ adsorption capacity of MCK and related materials. The maximum adsorption capacity shows the outperformance of MCK, indicating the beneficial effect of grafting KH550 to the adsorbent. The higher adsorption capacity together with other suitable features such as easy synthesis, availability, easy separation, reusability, and being environmentally friendly makes MCK an efficient adsorbent.

3. CONCLUSIONS

In this study, a porous ceramic-based adsorbent (MCK) with high Cu²⁺ adsorption capability was fabricated through molten salt reaction and silane coupling reaction. The chemical structure and adsorption characteristics of MCK were analyzed through several instrumental techniques. The main conclusions are summarized as follows:

- (1) Various factors affecting the adsorption property such as reaction time, pH, temperature, adsorbent dosage, and initial Cu²⁺ concentration were evaluated. The adsorption process was relatively fast; the equilibrium could be

Figure 12. Adsorption isotherm models for Cu²⁺ adsorption: (a) linear curve of the Langmuir model; (b) nonlinear curve of the Langmuir model; (c) linear curve of the Freundlich model; (d) nonlinear curve of the Freundlich model (pH = 5, dosage: 0.8 g, contact time: 120 min, temperature: 298 K).

Table 4. Adsorption Parameters of Langmuir and Freundlich Isotherm Models

type		linear model	nonlinear model
Langmuir	q_m ($\text{mg}\cdot\text{g}^{-1}$)	54.94	55.32
	K_L ($\text{L}\cdot\text{mg}^{-1}$)	0.8273	0.6765
	R^2	0.9861	0.9628
Freundlich	K_F ($(\text{mg}\cdot\text{g}^{-1})\cdot(\text{mg}\cdot\text{L}^{-1})^{-n}$)	20.6252	22.2536
	n	0.3934	0.3425
	R^2	0.9895	0.9917

reached within 120 min, and the maximum removal efficiency is observed at pH 5, with a dosage of 0.8 g, and the initial concentration was $30 \text{ mg}\cdot\text{L}^{-1}$ at room temperature.

- (2) The adsorption of Cu^{2+} onto MCK was a spontaneous endothermic process from thermodynamic studies. The adsorption kinetic studies showed that Cu^{2+} adsorption onto MCK was best fitted with a pseudo-second-order kinetic model. The adsorption isotherm studies showed that the Freundlich models can well fit the adsorption process of Cu^{2+} onto MCK, which indicated that the adsorption of Cu^{2+} occurs on heterogeneous surfaces by multilayer adsorption. The chemisorption process was

Figure 14. Regeneration studies of MCK.

- further confirmed from XPS analysis because of the strong interaction between Cu^{2+} with the $-\text{NH}_2$ group.
- (3) MCK has good stability and regeneration performance and Cu^{2+} could be desorbed by HCl solution or EDTA-2Na solution. The Cu^{2+} removal efficiency decreases approximately by 4 and 7% (after 5 cycles) compared with the first adsorption by using EDTA-2Na and HCl,

Figure 13. XPS spectra of MCK and Cu-MCK: (a) full spectra of MCK and Cu-MCK; (b) Cu 2p spectrum of Cu-MCK; (c) C 1s spectra of MCK; (d) N 1s spectra of MCK; (e) C 1s spectra of Cu-MCK; (f) N 1s spectra of Cu-MCK.

Table 5. Comparison of Maximum Adsorption Capacities (q_m), Isotherm, Order of Reaction, and Reaction Time for Cu^{2+} by Different Adsorbents

adsorbents for Cu^{2+}	time	capacity ($\text{mg}\cdot\text{g}^{-1}$)	isotherm	order of reaction	refs
chitosan/clay/magnetite composite	24 h	17.20	Freundlich	pseudo-second	50
chitosan–zeolite composite (CZ)	60 min	25.88	Langmuir	pseudo-second	51
magnetic iron oxide@graphene composites	150 min	50.40	Freundlich	na	52
magnesium ferrite nanoparticle	60 min	29.44	Langmuir	na	53
modified wheat bran	2 h	4.33	Langmuir	pseudo-second	54
pristine natural zeolite	24 h	14.93	Langmuir	pseudo-second	55
polydopamine-treated zeolite	24 h	28.58	Langmuir	pseudo-second	55
Ca–Mg phosphate sorbent (PD-2)	10 min	264.16	na	pseudo-second	56
non-apatite Ca–Mg phosphate sorbent	5 min	240.20	Freundlich	na	57
polyamine-functionalized polystyrene adsorption resin (PSAPA)	600 min	112.14	Freundlich	pseudo-second	58
egg-shell glass beads	100 min	81.33	Langmuir	pseudo-second	59
Hydroxyapatite	24 h	7.68	na	pseudo-second	60
metakaolin-based geopolymer	24 h	48.78	Langmuir	pseudo-second	61
activated carbon prepared from grape bagasse	3 h	43.47	Langmuir	pseudo-second	62
MCK	120 min	55.32	Freundlich	pseudo-second	this work

respectively. MCK has great potential application in the metal ion removing field.

4. MATERIALS AND METHODS

4.1. Materials. All the chemicals were analytically pure. Porous cordierite ceramics was purchased from Kelley Chemical Packing Co., Ltd. (Jiangxi, China); γ -aminopropyl triethoxysilane (KH550) was purchased from Youpu Chemical Co., Ltd. (Nanjing, China); absolute ethanol, aluminum sulfate, diatomaceous earth, sodium sulfate, copper sulfate, disodium edetate ($\text{EDTA}\cdot 2\text{Na}$), sodium hydroxide, and hydrochloric acid were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Double distilled water was used throughout the experiment.

4.2. Methods. **4.2.1. Preparation of Mullite Whiskers/Cordierite Porous Ceramics (MC).** First, $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ was sintered at 400 °C for 3 h to remove the crystallization water to obtain anhydrous $\text{Al}_2(\text{SO}_4)_3$ in a muffle furnace. Then, $\text{Al}_2(\text{SO}_4)_3$ was used as the aluminum source, diatomaceous earth was used as the silicon source, and sodium sulfate was used as the molten salt. The reagents were accurately weighed in a proper amount with a mixing mass ratio of 5:2:14 for $\text{Al}_2(\text{SO}_4)_3$ /diatomaceous earth/sodium sulfate. The mixed powders of the above raw materials were ball-milled in a high-energy planetary balling machine at a rotation speed of 180 rpm for 30 min. After milling, the mixture was dried and filtered with a 100-mesh sieve. Then, the mixture was covered on the cordierite block at the bottom of the corundum crucible. The samples were heated to 1000 °C at the rate of 5 °C/min and then kept at 1000 °C for 2 h. After cooling to room temperature, the sulfate adhering to the base of cordierite was removed by washing with 100 °C double distilled water. Then, the product was dried in a vacuum oven at 100 °C for 24 h, and the obtained product was denoted as MC.

4.2.2. Modification of Mullite Whiskers/Cordierite Porous Ceramics (MCK). Mullite whisker/cordierite porous ceramic activation process: a certain amount of mullite whiskers/cordierite porous ceramic was put in 2.5 mol·L⁻¹ hydrochloric acid with a solid–liquid ratio of 1:10 in a 90 °C water bath for 2 h. Subsequently, the remaining hydrochloric acid from mullite whiskers/cordierite porous ceramic was removed, washed several times with double distilled water, and dried

under vacuum at 50 °C to get the active mullite whiskers/cordierite porous ceramics. Modification: 80 mL of absolute ethanol and 10 mL of γ -aminopropyl triethoxysilane (KH550) were mixed by magnetic stirring for 1 h at room temperature. Then, the mixture and 12 g of active mullite whiskers/cordierite porous ceramic was added into the polytetrafluoroethylene reactor and hydrothermally treated at 70 °C for 24 h. After cooling to room temperature, the modified product was washed several times with absolute ethanol and dried in a vacuum oven at 60 °C for 24 h to obtain the surface-modified mullite whiskers/cordierite porous ceramic denoted as MCK.

4.3. Characterization. The crystalline phases of the samples were determined by an X-ray diffractometer (D8, Bruker, Germany) using $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA. Bonds of samples were identified by FT-IR (Nicolet 5700, Thermo, America) in the wavenumber range of 4000–400 cm⁻¹. The morphologies of the samples were determined by SEM (S-4800, Japan). The specific surface area and pore size distributions of the sample were measured by the means of the BET method via an accelerated surface area and porosimetry analyzer (Micromeritics USA, ASAP 2020) with N_2 adsorption analysis. XPS spectra were recorded on an ESCALAB 250 electron energy spectrometer (Thermo Fisher Scientific, USA) using monochromated Al K-alpha 150 W as the X-ray excitation source. The concentration of copper ions was measured by atomic absorption spectrophotometry (AAS, WFX-120, Beijing Rayleigh Analytical Instrument Co., Ltd.). In addition, the open porosity of porous cordierite ceramic was measured in accordance with Archimedes' principle using distilled water as the liquid medium. The distribution of pore sizes of the porous cordierite ceramic was determined by using an automatic mercury porosimeter (AutoPore IV9500, Micromeritics Instrument Corp., America).

4.4. Batch Adsorption Experiment. The adsorption experiments were carried out in a 150 mL stoppered conical flask which contained a certain number of adsorbents (0.8 g) and Cu^{2+} solution (30 mg·L⁻¹) in a 180 rpm thermostatic oscillator at 298 K. Kinetics ($t = 0$ –180 min), thermodynamics ($T = 293$ –313 K), and adsorption isotherms ($c_0 = 10$ –110 mg·L⁻¹) were studied. For these studies all parameters were fixed and only one parameter is changed. All adsorption experiments were repeated three times, and their mean values were used in the data analysis. The required pH was adjusted with 0.1 M

HCl and 0.1 M NaOH solutions. The residual concentration of Cu^{2+} after adsorption was determined by AAS. The sample of adsorption Cu^{2+} onto MCK (Cu–MCK) was obtained after washing with double distilled water and drying. The removal efficiency (eq 1) and the adsorption capacity (eq 2) of Cu^{2+} were calculated by the following equations

$$\varphi = \frac{c_0 - c}{c_0} \times 100\% \quad (1)$$

$$q = \frac{(c_0 - c) \times v}{w} \quad (2)$$

where φ is the removal efficiency (%), q is the adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), c_0 and c are the initial and equilibrium concentrations of Cu^{2+} solutions ($\text{mg}\cdot\text{L}^{-1}$), respectively, v is the volume of the adsorption solution (mL), and w is the dosage of the adsorbent (g).

The thermodynamic parameters can be calculated according to the laws of thermodynamics using the following eqs 3–5.

$$\Delta G^\circ = -RT \ln k_c \quad (3)$$

$$k_c = \frac{c_\partial}{c_e} \quad (4)$$

$$\ln k_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

where R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), k_c is the thermodynamic equilibrium constant, c_∂ is the concentration of the metal ions on the adsorbent ($\text{mg}\cdot\text{L}^{-1}$), and c_e is the equilibrium concentration of residual metal ions ($\text{mg}\cdot\text{L}^{-1}$); the thermodynamic parameters can be obtained from the slope and intercept of $\ln k_c$ versus $1/T$, respectively.

The adsorption kinetics of Cu^{2+} adsorption were fitted by a pseudo-first-order kinetic model⁶³ and a pseudo-second-order kinetic model.⁶⁴ The pseudo-first-order kinetic model can be expressed in nonlinear (eq 6) and linear forms (eq 7) and the pseudo-second-order kinetic model (eq 8) in linear forms (eq 9).

$$q_t = q_e(1 - e^{-k_1 t}) \quad (6)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where q_e and q_t are the adsorption capacities ($\text{mg}\cdot\text{g}^{-1}$) at equilibrium and at time t (min), respectively. k_1 is the rate constant of the pseudo-first-order kinetic equation (min^{-1}), and k_1 and q_e can be obtained from the slope and intercept of $\ln(q_e - q_t)$ versus t , respectively. k_2 is the rate constant of the pseudo-second-order kinetic equation ($\text{g}\cdot\text{mg}^{-1} \text{ min}^{-1}$). The values of q_e and k_2 can be obtained from the slope and intercept of t/q_t versus t , respectively.

The adsorption isotherms of Cu^{2+} were fitted by the Langmuir model⁶⁵ and the Freundlich model.⁶⁶ The nonlinear form of the Langmuir model is described in eq 10 and its linearized form is shown in eq 11. The nonlinear and linear

forms of the Freundlich equation can be expressed as shown in eqs 12 and 13, respectively.

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad (10)$$

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \quad (11)$$

$$q_e = K_F c_e^n \quad (12)$$

$$\log q_e = \log K_F + n \log c_e \quad (13)$$

where q_e is the equilibrium adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), q_m is the maximum adsorption capacity corresponding to the complete monolayer coverage ($\text{mg}\cdot\text{g}^{-1}$), c_e is the equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$), and K_L is the Langmuir adsorption equilibrium constant ($\text{L}\cdot\text{mg}^{-1}$). K_F is the Freundlich constant ($(\text{mg}\cdot\text{g}^{-1})\cdot(\text{mg}\cdot\text{L}^{-1})^{-n}$) and n (dimensionless) is the Freundlich intensity parameter. The values of q_m and K_L can be derived from the slope and intercept of c_e/q_e versus c_e . K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The values of n and K_F can be obtained from the slope and intercept of $\log q_e$ versus $\log c_e$.

4.5. Desorption Experiment. The desorption study was carried out using HCl (0.1 $\text{mol}\cdot\text{L}^{-1}$) and EDTA-2Na (0.5 $\text{g}\cdot\text{L}^{-1}$) solutions. Cu–MCK was added in 20 mL of 0.1 $\text{mol}\cdot\text{L}^{-1}$ HCl solution and 20 mL of 0.5 $\text{g}\cdot\text{L}^{-1}$ EDTA-2Na solution under stirring at 180 rpm up to 4 h for desorption, respectively. Then, the mixture was washed with double distilled water, and the consecutive adsorption–desorption cycle was carried out five times to investigate regeneration property.

AUTHOR INFORMATION

Corresponding Author

Wei Wang – Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region of the Ministry of Education and School of Water and Environment, Chang'an University, Xi'an 710054, China; orcid.org/0000-0002-0540-1810; Phone: +86-29-82339052; Email: wwchem@126.com; Fax: +86-29-82335485

Authors

Yaoyao Zhang – Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region of the Ministry of Education and School of Water and Environment, Chang'an University, Xi'an 710054, China

Zhengwen Wei – Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region of the Ministry of Education and School of Water and Environment, Chang'an University, Xi'an 710054, China

Mengyao Li – School of Water and Environment, Chang'an University, Xi'an 710054, China

Xishe Wu – School of Water and Environment, Chang'an University, Xi'an 710054, China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.0c02085>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (51678059), the Key Research and Development Program of Shaanxi Province (2019GY-179), the Fundamental Research Funds for the Central Universities (300102298202), and the Open Foundation of Key Laboratory of Shaanxi Provincial Land Rehabilitation (2018-JC10).

■ REFERENCES

- (1) Ma, X.; Li, Q.; Zhang, Y.; Wang, W.; Guo, Y.; Zhang, C. Facile Synthesis of Polymeric Schiff Base Metal Complex as Electrode for High-performance Supercapacitors. *J. Electrochem. Soc.* **2020**, *167*, 090544.
- (2) Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* **2011**, *92*, 407–418.
- (3) Li, P.; Qian, H.; Howard, K. W. F.; Wu, J.; Lyu, X. Anthropogenic pollution and variability of manganese in alluvial sediments of the Yellow River, Ningxia, northwest China. *Environ. Monit. Assess.* **2014**, *186*, 1385–1398.
- (4) Li, P.; Qian, H.; Howard, K. W. F.; Wu, J. Heavy metal contamination of Yellow River alluvial sediments, northwest China. *Environ. Earth Sci.* **2015**, *73*, 3403–3415.
- (5) Li, P.; Wu, J.; Qian, H.; Zhou, W. Distribution, enrichment and sources of trace metals in the topsoil in the vicinity of a steel wire plant along the Silk Road economic belt, northwest China. *Environ. Earth Sci.* **2016**, *75*, 909.
- (6) He, S.; Wu, J. Hydrogeochemical Characteristics, Groundwater Quality, and Health Risks from Hexavalent Chromium and Nitrate in Groundwater of Huanhe Formation in Wuqi County, Northwest China. *Exposure Health* **2019**, *11*, 125–137.
- (7) He, X.; Wu, J.; He, S. Hydrochemical characteristics and quality evaluation of groundwater in terms of health risks in Luohe aquifer in Wuqi County of the Chinese Loess Plateau, northwest China. *Hum. Ecol. Risk Assess.* **2019**, *25*, 32–51.
- (8) Paulino, A. T.; Minasse, F. A. S.; Guilherme, M. R.; Reis, A. V.; Muniz, E. C.; Nozaki, J. Novel adsorbent based on silkworm chrysalides for removal of heavy metals from wastewaters. *J. Colloid Interface Sci.* **2006**, *301*, 479–487.
- (9) Gupta, A.; Mumper, R. J. Elevated copper and oxidative stress in cancer cells as a target for cancer treatment. *Cancer Treat. Rev.* **2009**, *35*, 32–46.
- (10) Jomova, K.; Valko, M. Advances in metal-induced oxidative stress and human disease. *Toxicology* **2011**, *283*, 65–87.
- (11) Li, P.; Wu, J. Drinking water quality and public health. *Exposure Health* **2019**, *11*, 73–79.
- (12) Li, P.; Wu, J. Sustainable living with risks: meeting the challenges. *Hum. Ecol. Risk Assess.* **2019**, *25*, 1–10.
- (13) Chen, Q.; Yao, Y.; Li, X.; Lu, J.; Zhou, J.; Huang, Z. Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates. *J. Water Process Eng.* **2018**, *26*, 289–300.
- (14) Ali, R. M.; Hamad, H. A.; Hussein, M. M.; Malash, G. F. Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecol. Eng.* **2016**, *91*, 317–332.
- (15) Oehmen, A.; Vergel, D.; Fradinho, J.; Reis, M. A. M.; Crespo, J. G.; Velizarov, S. Mercury removal from water streams through the ion exchange membrane bioreactor concept. *J. Hazard. Mater.* **2014**, *264*, 65–70.
- (16) Barakat, M. A.; Schmidt, E. Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater. *Desalination* **2010**, *256*, 90–93.
- (17) Tonini, G. A.; Ruotolo, L. A. M. Heavy metal removal from simulated wastewater using electrochemical technology: optimization of copper electrodeposition in a membraneless fluidized bed electrode. *Clean Technol. Environ.* **2017**, *19*, 403–415.
- (18) Li, C.; Duan, H.; Wang, X.; Meng, X.; Qin, D. Fabrication of porous resins via solubility differences for adsorption of cadmium (II). *Chem. Eng. J.* **2015**, *262*, 250–259.
- (19) Burakov, A. E.; Galunin, E. V.; Burakova, I. V.; Kucherova, A. E.; Agarwal, S.; Tkachev, A. G.; Gupta, V. K. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicol. Environ. Saf.* **2018**, *148*, 702–712.
- (20) Da'na, E.; Sayari, A. Adsorption of copper on amine-functionalized SBA-15 prepared by co-condensation: Equilibrium properties. *Chem. Eng. J.* **2011**, *166*, 445–453.
- (21) Faghiliani, H.; Naghavi, M. Synthesis of Amine-Functionalized MCM-41 and MCM-48 for Removal of Heavy Metal Ions from Aqueous Solutions. *Sep. Sci. Technol.* **2014**, *49*, 214–220.
- (22) Shariati, S.; Khabazipour, M.; Safa, F. Synthesis and application of amine functionalized silica mesoporous magnetite nanoparticles for removal of chromium(VI) from aqueous solutions. *J. Porous Mater.* **2017**, *24*, 129–139.
- (23) Kumar, R.; Barakat, M. A.; Daza, Y. A.; Woodcock, H. L.; Kuhn, J. N. EDTA functionalized silica for removal of Cu(II), Zn(II) and Ni(II) from aqueous solution. *J. Colloid Interface Sci.* **2013**, *408*, 200–205.
- (24) Lopes, C. B.; Oliveira, J. R.; Rocha, L. S.; Tavares, D. S.; Silva, C. M.; Silva, S. P.; Hartog, N.; Duarte, A. C.; Pereira, E. Cork stoppers as an effective sorbent for water treatment: the removal of mercury at environmentally relevant concentrations and conditions. *Environ. Sci. Pollut. Res.* **2014**, *21*, 2108–2121.
- (25) Loganathan, P.; Shim, W. G.; Sountharajah, D. P.; Kalaruban, M.; Nur, T.; Vigneswaran, S. Modelling equilibrium adsorption of single, binary, and ternary combinations of Cu, Pb, and Zn onto granular activated carbon. *Environ. Sci. Pollut. Res.* **2018**, *25*, 16664–16675.
- (26) Tan, P.; Hu, Y.; Bi, Q. Competitive adsorption of Cu²⁺, Cd²⁺ and Ni²⁺ from an aqueous solution on graphene oxide membranes. *Colloids Surf., A* **2016**, *509*, 56–64.
- (27) Chen, Y.; Zhao, W.; Zhang, J. Preparation of 4-vinylpyridine (4VP) resin and its adsorption performance for heavy metal ions. *RSC Adv.* **2017**, *7*, 4226–4236.
- (28) Andrejkovičová, S.; Sudagar, A.; Rocha, J.; Patinha, C.; Hajjaji, W.; Silva, E. F.; Velo, A.; Ro-cha, F. The effect of natural zeolite on microstructure, mechanical and heavy metals adsorption properties of metakaolin based geopolymers. *Appl. Clay Sci.* **2016**, *126*, 141–152.
- (29) Mende, M.; Schwarz, D.; Steinbach, C.; Boldt, R.; Schwarz, S. Simultaneous adsorption of heavy metal ions and anions from aqueous solutions on chitosan-Investigated by spectrophotometry and SEM-EDX analysis. *Colloids Surf., A* **2016**, *510*, 275–282.
- (30) Ohji, T.; Fukushima, M. Macro-porous ceramics: Processing and properties. *Int. Mater. Rev.* **2012**, *57*, 115–131.
- (31) Yao, Y.; Ochiai, T.; Ishiguro, H.; Nakano, R.; Kubota, Y. Antibacterial performance of a novel photocatalytic-coated cordierite foam for use in air cleaners. *Appl. Catal., B* **2011**, *106*, 592–599.
- (32) Neyertz, C. A.; Miró, E. E.; Querini, C. A. K/CeO₂ catalysts supported on cordierite monoliths: Diesel soot combustion study. *Chem. Eng. J.* **2012**, *181–182*, 93–102.
- (33) Soghrati, E.; Kazemeini, M.; Rashidi, A. M.; Jozani, K. J. Preparation and characterization of Co-Mo catalyst supported on CNT coated cordierite monoliths utilized for naphta HDS process. *Procedia Eng.* **2012**, *42*, 1484–1492.
- (34) Shyam, A.; Lara-Curzio, E.; Pandey, A.; Watkins, T. R.; More, K. L. The thermal expansion, elastic and fracture properties of porous cordierite at elevated temperatures. *J. Am. Ceram. Soc.* **2012**, *95*, 1682–1691.
- (35) Zhang, X.; Fang, D.; Lin, B.; Dong, Y.; Meng, G.; Liu, X. Asymmetric porous cordierite hollow fiber membrane for micro-filtration. *J. Alloys Compd.* **2009**, *487*, 631–638.
- (36) Li, Y.; Qian, H.; Cheng, X.; Zhang, R.; Zhang, H. Fabrication of dense cordierite ceramic through reducing Al₂O₃ mole ratio. *Mater. Lett.* **2014**, *116*, 262–264.

- (37) Acimović-Pavlović, Z.; Andrić, L.; Milošević, V.; Milićević, S. Refractory coating based on cordierite for application in new evaporate pattern casting process. *Ceram. Int.* **2011**, *37*, 99–104.
- (38) Wang, S.; Zhou, D.; Hou, Z.; Wang, M.; Hu, X.; Liu, X. Low-temperature sintering, low-dielectric cordierite ceramic tapes for high frequency application. *Ceram. Int.* **2013**, *39*, 9505–9509.
- (39) Wang, S.; Kuang, F. Sol-gel preparation and infrared radiation property of Boron-substituted cordierite glass-ceramics. *J. Mater. Sci. Technol.* **2010**, *26*, 445–448.
- (40) Meng, B.; Peng, J. Effects of in situ synthesized mullite whiskers on flexural strength and fracture toughness of corundum-mullite refractory materials. *Ceram. Int.* **2013**, *39*, 1525–1531.
- (41) Nouri Khezrabadi, M.; Naghizadeh, R.; Assadollahpour, P.; Mirhosseini, S. H. An investigation on the properties and micro-structure of mullite bonded cordierite ceramics. *J. Ceram. Process. Res.* **2007**, *8*, 431–434.
- (42) Yang, H.; Gao, Q.; Xie, Y. T.; Chen, Q.; Ouyang, C. F.; Xu, Y. M.; Ji, X. T. Effect of SiO₂ and TiO₂ nanoparticle on the properties of phenyl silicone rubber. *J. Appl. Polym. Sci.* **2015**, *132*, 42806.
- (43) Boparai, H. K.; Joseph, M.; O'Carroll, D. M. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *J. Hazard. Mater.* **2011**, *186*, 458–465.
- (44) Wei, Z.; Zhang, Y.; Wang, W.; Dong, S.; Jiang, T.; Wei, D. Synthesis of Cost-Effective Pomelo Peel Dimethoxydiphenylsilane-Derived Materials for Pyrene Adsorption: From Surface Properties to Adsorption Mechanisms. *ACS Omega* **2020**, *5*, 9465–9476.
- (45) Mi, X.; Huang, G.; Xie, W.; Wang, W.; Liu, Y.; Gao, J. Preparation of graphene oxide aerogel and its adsorption for Cu²⁺ ions. *Carbon* **2012**, *50*, 4856–4864.
- (46) Ge, F.; Li, M.-M.; Ye, H.; Zhao, B.-X. Effective removal of heavy metal ions Cd²⁺, Zn²⁺, Pb²⁺, Cu²⁺ from aqueous solution by polymer-modified magnetic nanoparticles. *J. Hazard. Mater.* **2012**, *211–212*, 366–372.
- (47) Ma, L.; Wang, Q.; Islam, S. M.; Liu, Y.; Ma, S.; Kanatzidis, M. G. Highly Selective and Efficient Removal of Heavy Metals by Layered Double Hydroxide Intercalated with the MoS₄²⁻ Ion. *J. Am. Chem. Soc.* **2016**, *138*, 2858–2866.
- (48) Tan, P.; Sun, J.; Hu, Y.; Fang, Z.; Bi, Q.; Chen, Y.; Cheng, J. Adsorption of Cu²⁺, Cd²⁺ and Ni²⁺ from aqueous single metal solutions on graphene oxide membranes. *J. Hazard. Mater.* **2015**, *297*, 251–260.
- (49) Wen, Y.; Ma, J.; Chen, J.; Shen, C.; Li, H.; Liu, W. Carbonaceous sulfur-containing chitosan-Fe(III): A novel adsorbent for efficient removal of copper (II) from water. *Chem. Eng. J.* **2015**, *259*, 372–380.
- (50) Cho, D.-W.; Jeon, B.-H.; Chon, C.-M.; Kim, Y.; Schwartz, F. W.; Lee, E.-S.; Song, H. A novel chitosan/clay/magnetite composite for adsorption of Cu(II) and As(V). *Chem. Eng. J.* **2012**, *200–202*, 654–662.
- (51) Wan Ngah, W. S.; Teong, L. C.; Toh, R. H.; Hanafiah, M. A. K. M. Utilization of chitosan-zeolite composite in the removal of Cu(II) from aqueous solution: Adsorption, desorption and fixed bed column studies. *Chem. Eng. J.* **2012**, *209*, 46–53.
- (52) Yang, Z.-F.; Li, L.-Y.; Hsieh, C.-T.; Juang, R.-S.; Gandomi, Y. A. Fabrication of magnetic iron Oxide@Graphene composites for adsorption of copper ions from aqueous solutions. *Mater. Chem. Phys.* **2018**, *219*, 30–39.
- (53) Ivanets, A. I.; Srivastava, V.; Roshchina, M. Y.; Sillanpää, M.; Prozorovich, V. G.; Pankov, V. V. Magnesium ferrite nanoparticles as a magnetic sorbent for the removal of Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ from aqueous solution. *Ceram. Int.* **2018**, *44*, 9097–9104.
- (54) Renu; Agarwal, M.; Singh, K. Removal of Copper, Cadmium, and Chromium from Wastewater by Modified Wheat Bran using Box-Behnken Design: Kinetics and Isotherm. *Sep. Sci. Technol.* **2018**, *53*, 1476–1489.
- (55) Yu, Y.; Shapter, J. G.; Popelka-Filcoff, R.; Bennett, J. W.; Ellis, A. V. Copper removal using bio-inspired polydopamine coated natural zeolites. *J. Hazard. Mater.* **2014**, *273*, 174–182.
- (56) Ivanets, A. I.; Kitikova, N. V.; Shashkova, I. L.; Oleksienko, O. V.; Levchuk, I.; Sillanpää, M. Using of phosphatized dolomite for treatment of real mine water from metal ions. *J. Water Process Eng.* **2016**, *9*, 246–253.
- (57) Ivanets, A. I.; Srivastava, V.; Kitikova, N. V.; Shashkova, I. L.; Sillanpää, M. Non-apatite Ca-Mg phosphate sorbent for removal of toxic metal ions from aqueous solutions. *J. Environ. Chem. Eng.* **2017**, *5*, 2010–2017.
- (58) Meng, Q.; Liu, J.; Jiang, Y.; Teng, Q. Branched Polyethyleneimine-Functionalized Polystyrene Resin: Preparation and Adsorption of Cu²⁺. *J. Chem. Eng. Data* **2019**, *64*, 2618–2626.
- (59) Shen, C.; Wang, Y.; Xu, J.; Lu, Y.; Luo, G. Preparation and ion exchange properties of egg-shell glass beads with different Surface morphologies. *Particuology* **2012**, *10*, 317–326.
- (60) Ivanets, A. I.; Kitikova, N. V.; Shashkova, I. L.; Roshchina, M. Y.; Srivastava, V.; Sillanpää, M. Adsorption performance of hydroxyapatite with different crystalline and porous structure towards metal ions in multicomponent solution. *J. Water Process Eng.* **2019**, *32*, 100963.
- (61) Cheng, T. W.; Lee, M. L.; Ko, M. S.; Ueng, T. H.; Yang, S. F. The heavy metal adsorption characteristics on metakaolin-based geopolymer. *Appl. Clay Sci.* **2012**, *56*, 90–96.
- (62) Demiral, H.; Güngör, C. Adsorption of copper(II) from aqueous solutions on activated carbon prepared from grape bagasse. *J. Cleaner Prod.* **2016**, *124*, 103–113.
- (63) Lagergren, S. About the theory of so-called adsorption of soluble substances. *K. Sven. Vetenskapsakad. Handl.* **1898**, *24*, 1–39.
- (64) Blanchard, G.; Maunaye, M.; Martin, G. Removal of heavy metals from waters by means of natural zeolites. *Water Res.* **1984**, *18*, 1501–1507.
- (65) Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403.
- (66) Freundlich, H. Über die adsorption in Lösungen. *Z. Phys. Chem.* **1907**, *57U*, 385–470.