Materials Research Express

PAPER

Synthesis of a novel magnetic nano-zeolite and its application as an efficient heavy metal adsorbent

Xiao Zhang1,3, Ting Cheng1–2, Chen Chen3,4, Lei Wang1, Qin Deng1, Gang Chen1 and Chenhao Ye1
1 School of Environmental Ecology, Jiangsu City Vocational College, Nanjing 210036, People’s Republic of China
2 Nanjing University and Yancheng Academy of Environmental Technology and Engineering, Yancheng 224000, People’s Republic of China
3 School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212005, People’s Republic of China

E-mail: chenc@just.edu.cn

Keywords: nano-zeolite, magnetic, magnetic sphere, adsorbent

Abstract
A novel magnetic nano-zeolite (MNZ@MS) is successfully synthesized, characterized and applied to adsorb heavy metals from solution. In the synthesis of MNZ@MS, the fly ash magnetic sphere (MS) and [C18H37(CH2)3-N+-(CH2)3-N+-(CH3)2C18H37]Cl2 is used as carrier and directing agent, respectively. The characterization results of XRD, XRF, XPS and SEM demonstrate that the nano-scale (200–600 nm) Linde F(K) zeolite completely wraps the magnetic spherical fly ash particle, and the saturation magnetization value of MNZ@MS is around 17.7 emu g−1. MNZ@MS exhibits a favorable and efficient adsorption performances on heavy metals, and the maximum adsorption capacity of Cu, Cd and Pb on MNZ@MS is 59.9 mg g−1, 188.6 mg g−1 and 909.1 mg g−1, respectively. The higher pH value in solution is more conducive to the adsorption process of heavy metals on MNZ@MS. The adsorption is a fast process, well represented by the pseudo-second-order model. Concerning the equilibrium behavior, Langmuir isotherm model are more suitable for describing the adsorption. Furthermore, in competitive adsorption system, the adsorption process of Pb is the most difficult to be interfered, and the order of adsorption advantage is Pb>Cu>Cd. MNZ@MS may be applied as a low-cost and efficient magnetic adsorbent for wastewater treatment to remove heavy metals.

1. Introduction

With the development of chemical industries, a large amount of pollutants are discharged into the environment, and governments pay more attention to problems of various pollution, including water pollution. Heavy metals are common water pollutants which are harmful to environment and human health [1–5]. Wastewater containing heavy metal mainly comes from some modern industries such as car manufacturing, battery production, metal plating, mining and tannery industries [6, 7]. Through transformation and accumulation of food chain, heavy metal elements contained in wastewater will eventually be transferred to human body, thus causing harm to human health [8, 9]. The long-term intake of heavy metals are detrimental to human body including bladder, brain, liver, kidney damage and other various neurodegenerative diseases [10, 11]. According to China’s sewage discharge standards (GB8978/1996), the concentration of Cu, Cd and Pb in effluent must be lower than 0.5 mg l−1, 0.1 mg l−1 and 1.0 mg l−1, respectively [12]. Therefore, it is necessary to remove heavy metals from wastewater before discharge.

Nowadays, main methods for removing heavy metals from wastewater are as follows: chemical precipitation, ion exchange, membrane filtration, electrolysis, adsorption and etc [13–15]. Among these methods, the adsorption has become one of hot research methods due to its relatively cheap and simple operation. In addition, the adsorbent is the core of adsorption method [16–18]. Zeolite material is a general term for a class of alumino-silicate crystalline materials. Many studies have shown that zeolite materials obtain better adsorption effect on heavy metals [19]. For example, the needle-like nano-crystalline zeolites was applied for
efficient removal of Cu and Pb from solutions [20]. The modified synthetic clinoptilolite was used for the removal of Zn, Pb, Cd and Cu from aqueous solutions, and the maximum adsorption capacity of modified synthetic clinoptilolite for heavy metals was higher than that of unmodified natural clinoptilolite [21]. The Linde F (K) zeolite was synthesized and its efficient adsorption for heavy metals was proved [22–24]. Moreover, the adsorption mechanism of Cu, Ni and Cd on zeolite was studied [25].

In recent years, to improve the adsorption efficiency of zeolite as much as possible, more attention has been paid to the synthesis of nano-zeolite materials. For instance, different diquaternary ammonium-type surfactants were utilized as structure directing surfactants to the synthesis of nano-zeolites [26–28]; An ultrasound assisted hydrothermal method that could convert fly ash to nanozeolite X was developed, and the products was used for heavy metals adsorption [29]. Furthermore, the zeolite nanoparticles could also be synthesized through a hydrothermal method [30].

On the other hand, the decreasing size of zeolite materials makes it difficult to be separated from solutions, which leads to nano-zeolite material could not be widely used for wastewater treatment. In order to overcome these difficulties, many scholars have studied ways to make magnetic zeolite materials. For example, The silica-coated magnetic nanocomposites were synthesized and applied for Pb\(^{2+}\) removal from aqueous solution [31]; the magnetic zeolite NaA was prepared from loading Fe\(_3\)O\(_4\) and applies for adsorption of Cu and Pb from solutions [32]. Then, through in situ co-precipitation method, zeolite/Fe\(_3\)O\(_4\) magnetic nanocomposit was synthesized [33, 34]. In above studies, Fe\(_3\)O\(_4\) is used as magnetic source, which increases the cost of magnetic zeolite materials. Thus, an economical and effective magnetic zeolite material needs to be developed.

Fly ash is a kind of solid waste produced by coal combustion power plants. The main component of fly ash is glass spheres mainly composed of silica-alumina oxides. The glass spheres with high iron content (magnetic spheres) often have relatively strong magnetism, which is proved in related literatures [35–38]. For example, a novel magnetic fly ash/ acrylic acid composite microgel was prepared and utilized for selective adsorption of Pb [39]. However, studies on the preparation of magnetic adsorbents using fly ash magnetic spheres as carriers are very limited at present.

Hence, based on previous research, this paper focuses on the following points: (1) A nano-zeolite adsorbent with obvious magnetic properties (MNZ@MS) is synthesized using fly ash magnetic spheres (MS) as carrier and [C\(_{18}\)H\(_{37}\)(CH\(_3\))\(_2\)–N\(^+\)-(CH\(_2\))\(_2\)–N\(^-\)-(CH\(_3\))\(_2\)C\(_{18}\)H\(_{37}\)]Cl\(_2\) as directing agent. (2) The various measurements including XRF, XRD, SEM, FT-IR, XPS, magnetic hysteresis loop and Zeta potential are performed for the contrastive characterization of MNZ@MS and MS. (3) The synthetic material of MNZ@MS is applied to adsorption heavy metals (Cu, Cd and Pb) from solution. The effects of solution pH, adsorption time and initial concentration on adsorption performances are studied. (4) On the basis of the results obtained, the adsorption kinetics and isotherm for adsorption process of heavy metals on MNZ@MS are investigated. (5) The adsorption behaviors of heavy metals in competitive adsorption system are also carried out. The aims of this paper are to provide an efficient and inexpensive magnetic treatment material for heavy metal wastewater and promote the comprehensive utilization of fly ash.

2. Experiments and methods

2.1. Adsorbent synthesis

The fly ash magnetic spheres used in this experiment were purchased from a company in Kunming, Yunnan Province, China. The samples of fly ash from power plants were treated by magnetic separation method in the company. Potassium silicate (Analytically pure) and potassium hydroxide (Analytically pure) used in the experiment are purchased from China national pharmaceutical chemical reagent Co. Ltd. Partial potassium aluminate (Chemical purity) is purchased from Shandong Luke chemical industry Co. Ltd, China. [C\(_{18}\)H\(_{37}\)(CH\(_3\))\(_2\)–N\(^+\)-(CH\(_2\))\(_2\)–N\(^-\)-(CH\(_3\))\(_2\)C\(_{18}\)H\(_{37}\)]Cl\(_2\) (98%) is purchased from Henan Daochun Chemical Technology Co., Ltd, China. The synthesis system of MNZ@MS is as follows: 6.1087 g potassium silicate, 2.744 g partial potassium aluminate and 0.1819 g directing agent are added into a Teflon bottle which contains potassium hydroxide (240 ml, 10 mol l\(^{-1}\)) solution. A water bath reaction device installed with an electric blender keep the reaction temperature around 75 °C. During the synthesis process, magnetic stirrer maintains stirring the reaction system, and the reaction time is 10 h. When the reaction lasts for 5 h, 3 grams of MS is added to the synthetic system. Then, the reaction continues for another 5 h. The electric blender keeps reaction mixtures in suspension. After the synthesis reaction is finished, deionized water is used to wash the reaction products until the pH value of filtrate liquor is around 7. Ultimately, the reaction product is dried under 105 °C and the final product is MNZ@MS.
2.2. Adsorption experiments
The Copper nitrate (Analytically pure), Cadmium nitrate (Analytically pure), Lead nitrate (Analytically pure), sodium hydroxide (Analytically pure) and hydrochloric acid (37.5%) used in the experiment are purchased from China national pharmaceutical chemical reagent Co. Ltd. The adsorption experiments are conducted as typical batch trials in single solute systems. In each adsorption trial, a quantity of MNZ@MS is dispersed in 10 ml heavy metal solution in a 20-mL Teflon bottle. The bottles are subsequently immersed in a water bath and agitated at 200 rpm. Following the adsorption, each dispersion is filtered through a 0.45 μm membrane and the concentration of heavy metals in the filtered solution are determined by an Atomic Absorption Spectrometer. For studying the influence of solution pH, the initial concentration of Cu, Cd and Pb is 60 mg l⁻¹, 180 mg l⁻¹ and 500 mg l⁻¹, respectively. The different initial concentration for Cu, Cd and Pb is determined by exploratory experiment for evaluating the adsorption capacity of MNZ@MS. The solution pH ranges from 3 to 9. The adsorption dosage of MNZ@MS is 1 g l⁻¹, the adsorption temperature is 25 °C, and the adsorption time is 60 min. For investigating the influence of adsorption time and adsorption kinetics, the initial concentration of Cu, Cd and Pb is also 60 mg l⁻¹, 180 mg l⁻¹ and 500 mg l⁻¹, respectively. The dosage of MNZ@MS is 1 g l⁻¹, the adsorption temperature is 25 °C, and the adsorption time ranges from 20 min to 480 min. For studying the influence of initial concentration and adsorption isotherm, the initial concentration of Cu and Cd ranges from 20 mg l⁻¹ to 280 mg l⁻¹, and the initial concentration of Pb ranges from 100 mg l⁻¹ to 600 mg l⁻¹. The dosage of MNZ@MS is 1 g l⁻¹, the adsorption temperature is 25 °C, and the adsorption time is 60 min. For studying the interactions between heavy metals, adsorption experiments are conducted as typical batch trials in single and competitive solution systems. The initial concentration of three heavy metals ranges from 20 mg l⁻¹ to 280 mg l⁻¹, the dosage of MNZ@MS is 1 g l⁻¹, the adsorption temperature is 25 °C, and the adsorption time is 60 min.

The calculation of the mass of heavy metals adsorbed per unit mass of MNZ@MS at time t and the equilibrium are as equations (1) and (2).

\[
Q_t = \frac{(C_0 - C_t) V}{m}
\]  
\[
Q_e = \frac{(C_0 - C_e) V}{m}
\]

Where, V(ml) is the solution volume, m (g) is the mass of the adsorbent, \( Q_t \) (mg g⁻¹) is the mass of heavy metals adsorbed per unit mass of zeolite at time t, \( Q_e \) (mg g⁻¹) is the mass of heavy metals adsorbed per unit mass of zeolite at adsorption equilibrium, \( C_0 \) (mg l⁻¹) is the initial concentration of heavy metals, \( C_t \) (mg l⁻¹) is the concentration of heavy metals at time t, \( C_e \) (mg l⁻¹) is the concentration of heavy metals at adsorption equilibrium.

2.3. Materials characterization
The MS and MNZ@MS are characterized by x-ray diffraction (XRD), X-ray fluorescence, Scanning electron microscopy-energy dispersive spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, Microiontophoresis apparatus and x-ray photoelectron spectroscopy, and liquid specific surface area measuring instrument.

X-ray fluorescence is analyzed using ARL-9800 X-ray fluorescence analyzer from Swiss ARL. The XRD patterns of powder samples are acquired using a Shimadzu XD-3A diffractometer, employing Cu-Kα radiation (\( \lambda = 1.540 56 \) Å). The morphologies of the composites are observed with a HITACHI(S-3400 N) scanning electron microscope, and FT-IR spectra are recorded on a Nicolet iS5 FT-IR spectrometer using pressed KBr discs. The surface zeta potential is determined by IS94H microiontophoresis apparatus (POWEREACH). The x-ray photoelectron spectroscopy spectra are recorded on a PHI 5000 VersaProbe XPS equipment. The liquid specific surface area is determined by Xigo liquid specific surface area measuring instrument.

3. Results and discussions
3.1. Liquid specific surface area
The liquid specific surface area results of MS (a) and MNZ@MS was deducted based on the fitting results of computer, which is shown in figure 1. The liquid specific surface area of MS and MNZ@MS is 699.4 m² g⁻¹ and 2123.6 m² g⁻¹, respectively. The liquid specific surface area of MNZ@MS is larger than that of pure nano zeolite [40]. This demonstrates that the liquid specific surface area of composite material can be increased through coating nano zeolite on MS.
3.2. XRD and XRF
The X-ray diffraction patterns of original MNZ@MS and MS are shown in figure 2(a). The XRD pattern of MS exhibited a series of diffraction peaks at 18.3° (1 1 1), 20.8° (1 0 0), 25.9° (1 2 0), 26.2° (2 1 0), 26.6° (1 1 1), 30.2° (2 2 0), 33.2° (1 0 4), 35.6° (3 1 1)/ (1 1 0), 40.9° (1 1 3), 43.2° (4 0 0), 49.7° (0 2 4), 53.8° (4 2 2), 54.2° (1 1 6), 57.2° (2 1 0) and 62.8° (4 4 0). The diffraction peaks of 20.8° and 26.6° can be indexed as quartz crystal phase (SiO2 PDF46-1045); The diffraction peaks of 30.2°, 35.6°, 43.2°, 53.8°, 57.2° and 62.8°, can be identified as magnetite crystal phase (Fe3O4 PDF19-0629); The diffraction peaks of 33.2°, 35.6°, 40.9°, 49.7° and 54.2° can be verified as hematite crystal phase (Fe2O3 PDF 33-0664). In addition, the overlapping of two peaks including magnetite (35.6° / 3 1 1) and hematite (35.6° / 1 1 0) could be observed. Two weak peaks of 25.9° and 26.2° can be attributed to mullite crystal phase (Al6Si2O13 PDF 15-0776). The quartz and mullite crystal phase originate from fly ash particles [41]. The abundant magnetite and hematite crystal phase comes from magnetic separation operation and often exists in iron-rich fly ash sphere [37]. The XRD patterns of MNZ@MS is also depicted in figure 2(a), several new sharper and stronger peaks (12.7°/11 0, 13.4°/0 0 2, 18.6°/1 1 2, 25.6°/2 2 0, 28.7°/3 1 0, 28.9°/2 2 2, 30.1°/1 1 4, 31.8°/3 1 2, 33.5°/3 2 1 and 39.9°/3 1 4) reveal the formation of new crystal phase. The new crystal phases are consistent with the Linde F (K) zeolite (KAlSiO4·1.5H2O PDF 38-0216), which proves that the zeolite has been successfully synthesized. Besides zeolite, the peaks of quartz, magnetite and hematite are also observed in the XRD pattern of MNZ@MS, which implies that the crystal phases are retained in the reaction products. The magnetic could bring magnetic properties to MNZ@MS.

Figure 2(b) shows the XRF results of MNZ@MS and MS. The main compositions (oxide form) of MS are SiO2 (38.3%), Fe2O3 (32.7%), Al2O3 (20.1%), CaO (3.2%), K2O (1.8%), MgO (1.59%), TiO2 (0.92%), SO3 (0.77%), Na2O (0.2%), MnO (0.13%), and others (0.26%). All of components are common elements in fly ash [42], and the results are consistent with main crystal phase (quartz, mullite, magnetite and hematite). Furthermore, the main compositions (oxide form) of MNZ@MS are SiO2 (35.3%), Fe2O3 (12.3%), Al2O3 (30.48%), CaO (0.93%), K2O (19.8%), MgO (0.13%), TiO2 (0.3%), SO3 (0.019%), Na2O (0.41%), MnO (0.049%) and others (0.32%). The composition growth of K2O and Al2O3 may come from the formation of reaction products (Linde F (K) zeolite/KAlSiO4·1.5H2O).

3.3. SEM
The micromorphology and micro-composition of MNZ@MS and MS are characterized by SEM and EDX. Figure 3 shows the SEM images and EDS results of MS. The spherical particles with abundant micro crystal on
the surface can be observed in the figures 3(a) and (b). The detail of abundant micro crystal could be seen with large magnification (figures 3(c) and (d)). The micromorphology of MS is typical magnetic iron-rich fly ash sphere, and the crystal on its surface might be the magnetite [35, 36]. The results of EDS suggest that, the main compositions (oxide form) of crystal are as follow: Fe2O3 (70.68%), SiO2 (21.71%), Al2O3 (6.44%), which are basically in accord with our speculation.

Figure 4 shows the SEM images and EDS results of MNZ@MS. Contrast with figure 3, the spherical particle is changed to spheroid shape (figures 4(a) and (b)) and the surface is completely encapsulated by reaction products (figures 4(c) and (d)). The details of reaction products could be observed in figures 4(c) and (d), which dipicts the microstructures of nano-zeolite. The nano-zeolite has tetragonal crystal structure and the size ranges from 200 nm to 600 nm. The results indicate that the addition of [C18H37(CH3)2-N\(^{+}\)-(CH2)3-N\(^{+}\)-(CH3)2C18H37] Cl2 effectively reduces the size of zeolite crystals [26–28]. Moreover, the results of EDS indicates the main compositions (oxide form) of nano-zeolite are as follow: K2O (22.41%), SiO2 (35.27%), Al2O3 (39.77%), which are corresponded to Linde F(K) zeolite/KAlSiO4.1.5H2O. Therefore, the nano-zeolite is successfully coated on the surface of MS through synthetic reaction.

3.4. FT-IR

Figure 5 shows the FT-IR spectra of MS and MNZ@MS. For MS, the strong and broad peak around 1093 cm\(^{-1}\) should be designated to T–O bond (where T is Si or Al) stretching bands [24, 41]; the minor peaks at 789 cm\(^{-1}\) and 585 cm\(^{-1}\) might be assigned to quartz double bands and the O–Si (Al)–O bending mode; the low but broad peak around 3454 cm\(^{-1}\) should be belonged to stretching vibration of O–H [41, 43]. For MNZ@MS, the strong and broad peaks around 3487 cm\(^{-1}\) and 1698 cm\(^{-1}\) should be ascribed to the stretching and bending vibration of O–H [24], which originates from the adsorbed water and crystal water in MNZ@MS. The low sharp peaks at 598 cm\(^{-1}\) could also be designated to the O–Si (Al)–O bending mode of MS [41, 43]. The strong sharp peaks at
1001 cm$^{-1}$ can be designated to the Si(Al)–O–Si(Al) stretching vibration, which reveals the formation of Si(Al)–O tetrahedron in Linde F(K) zeolite [24].

### 3.5. Magnetic hysteresis loop

Figure 6 shows the magnetic properties of MNZ@MS and MS. The saturation magnetization value (SMV) of MS and MNZ@MS is about 27.5 emu g$^{-1}$ and 17.7 emu g$^{-1}$, respectively. Such magnetism is comparable to many magnetic materials [44–48]. The coercivities of MS and MNZ@MS are around $-70.1$ Oe and $-60.2$ Oe, respectively, which indicates that the magnetic sphere has weak residual magnetism. In addition, the SMV and coercivity subtraction of MNZ@MS should be attributed to the coating of some non-magnetic zeolite on the surface of MS. Figure 7 shows the magnetic separation performance of MNZ@MS. In the absence of environmental magnetic force, MNZ@MS can be stably suspended in the solution. However, after adding external magnet, the MNZ@MS could be well separated from solution, which proves the excellent magnetic ability of MNZ@MS.

### 3.6. XPS

The surface properties of MNZ@MS and MS are analyzed by x-ray photoelectron spectroscopy (XPS), and the results are shown in figures 8 and 9. Survey scan of MS depicts two strong and sharp peaks at 284 eV and 531 eV, which could be attributed to C 1s and O 1s, respectively. Four low peaks are found at 73 eV, 100 eV, 118 eV and 149 eV, which are corresponded to Al 2p, Si 2p, Al 2s and Si 2s. Figure 8(a) suggests that MS contains abundant Si, Al and O, which is consistent with the results of XRF. Besides, two faint peaks at 710 eV and 846 eV imply the existence of Fe in MS.

Figures 8(c) and (b) shows the high-resolution scans of Al 2p, Si 2p for MS. There are two different types of silicon in Si 2p peaks including 99.6 eV and 102.1 eV. The two silicon peaks should originate from Si in quartz and mullite crystal phases. In addition, the peaks of Al 2p (73 eV) could be separated to two peaks at 73.5 eV and 73.9 eV. The two peaks represent the aluminum in mullite crystal phase and glass phase of MS.
Moreover, the survey scan of MNZ@MS is shown in figure 9(a). Comparing with figure 8(a), two additional peaks at 377 eV and 294 eV can be observed, which are corresponded to K 2s and K 2p. Besides, changes are consistent with the analytical results of XRF and XRD, confirming the formation of Linde F (K) zeolite (KAlSiO₄·1.5H₂O). Through the analysis of high-resolution scans of Al 2p and Si 2p peaks at 73 eV and 100 eV, it could be observed that there are three different types of silicon (100.3 eV, 100.7 eV and 101.3 eV) and aluminum...
(71.8 eV, 72.8 eV and 73.2 eV) in Al 2p and Si 2p peaks of MNZ@MS. Compared with figures 8(b) and (c), the additional types of silicon and aluminum should also mainly due to the formation of reaction products.

### 3.7. Solution pH

The solution pH is one of important factors affecting the adsorption process. Figure 10 shows the effect of solution pH on the adsorption capacity of Cu, Pb and Cd on MNZ@MS. From figure 10(a), the adsorption capacity of three heavy metals is obviously improved with the increase of solution pH. This phenomenon is often reported by other literatures related to heavy metals adsorption process [49–54]. In addition, the maximum adsorption capacity of Cu, Pb and Cd reaches around 60 mg g⁻¹, 180 mg g⁻¹ and 500 mg g⁻¹, respectively. This experimental results could be explained as follows: a. The measurement results of Zeta potential of MNZ@MS. Figure 10(b) shows the Zeta potential of MNZ@MS. It could be observed that the Zeta potential of MNZ@MS continuous decreases with the increase of solution pH, and the point of zero charge (PZC) of MNZ@MS is about 3.3. Because of the positive charge of hydrated heavy metal ions, the adsorption process would become difficult when solution pH is lower than 3.3. However, when solution pH is higher than 3.3, the continuously decreasing Zeta potential would accelerate the adsorption process. b. The competitive effect of H⁺ in solution. When solution pH is lower than 7, the competitive adsorption process would happen between H⁺ and heavy metals, resulting in the decrease of adsorption capacity. c. The precipitation reaction in the system. As we know, heavy
metals reacts with OH$^-$ and forms hydroxide precipitation at high solution pH, which might enhance the apparent adsorption efficiency.

3.8. Adsorption time and kinetics

The kinetics equations used to investigate the adsorption kinetics are showed as follows [55–57]:

The pseudo-first-order model:

$$
\ln(Q_{e-exp} - Q_t) = \ln(Q_{e-cal}) - k_1 t
$$

(3)

$Q_t$ (mg g$^{-1}$) is the mass of heavy metals adsorbed per unit mass of the zeolite at time $t$. $Q_{e-exp}$ (mg g$^{-1}$) and $Q_{e-cal}$ (mg g$^{-1}$) are the mass of heavy metals adsorbed per unit mass of the zeolite at adsorption equilibrium obtained from experimental work and model calculations. $k_1$ (min$^{-1}$) is the rate constant of the first-order model.
The pseudo-second-order model [15, 18]:

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_{e-cal}^2} + \frac{t}{Q_{e-cal}}
\]

(4)

\(Q_t\) (mg g\(^{-1}\)) is the mass of heavy metals adsorbed per unit mass of the zeolite at time t. \(Q_{e-cal}\) (mg g\(^{-1}\)) is the mass of heavy metals adsorbed per unit mass of the adsorbent at adsorption equilibrium obtained from model calculations. \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant of the second-order model.

Figure 11(a) shows the effect of adsorption time on the adsorption capacity of heavy metals. The initial concentration of Cu, Cd and Pb is 60 mg l\(^{-1}\), 180 mg l\(^{-1}\) and 500 mg l\(^{-1}\), respectively; the adsorption time ranges from 20 min to 480 min; the dosage of MNZ@MS is 1 g l\(^{-1}\). From figure 11(a), the adsorption process of heavy metals on MNZ@MS is very fast, and it almost reaches adsorption equilibrium in 20 min. These results may be ascribed to the abundant active adsorption sites on MNZ@MS.

Figure 9. XPS spectra of MNZ@MS ((a), survey scan spectra of MNZ@MS; (b), high resolution spectra of Si 2p for MNZ@MS; (c), high resolution spectra of Al 2p for MNZ@MS).
The adsorption kinetics profiles of heavy metals on MNZ@MS are depicted in figures 11(b) and (c), which shows the fitting results of pseudo-first-order model and pseudo-second-order model on adsorption process, respectively. Compared figures 11(b) with figure 11(c), it can be seen that the pseudo-second-order model better describes the adsorption reaction process of heavy metals on MNZ@MS. Furthermore, we calculate the kinetics parameters of pseudo-first-order model and pseudo-second-order model, and the results are shown in table 1. From the results of calculated adsorption capacity ($q_{cal}$) and $R^2$ value, we also believe that the pseudo-second-order model presents suitable fitting results, based on the higher value of $R^2$ and the closer value between $q_{exp}$ (experimental adsorption capacity) and $q_{cal}$.

3.9. Adsorption isotherm

The equation of Langmuir isotherm is as follow [55, 58, 59];

$$\frac{C_e}{Q_e} = \frac{1}{k_L Q_m} + \frac{C_e}{Q_m}$$

(5)

Where $Q_e$ and $C_e$ are the amount adsorbed (mg g$^{-1}$) and the concentration of heavy metals in solution (mg l$^{-1}$), both at equilibrium; $k_L$ (l mg$^{-1}$) is the Langmuir constant related to the energy of adsorption; $Q_m$ (mg g$^{-1}$) is the maximum adsorption capacity.

The equation of Freundlich isotherm is as follow [60–62];

$$\ln(Q_e) = \ln(k_F) + \frac{1}{n} \ln(C_e)$$

(6)
Where $Q_e$ and $C_e$ are the amount adsorbed (mg g$^{-1}$) and the concentration of heavy metals in solution (mg l$^{-1}$), both at equilibrium; $k_F$ and $n$ are constants for Freundlich isotherm, and they are indicative of the adsorption capacity (mg g$^{-1}$) and adsorption intensity.

Figure 12 and table 2 presents the adsorption isotherm (Langmuir isotherm and Freundlich isotherm) fitting results of heavy metals on MNZ@MS, with the initial concentration of Cu and Cd ranging from 20 mg l$^{-1}$ to
280 mg l\(^{-1}\), the initial concentration of Pb ranging from 100 mg l\(^{-1}\) to 600 mg l\(^{-1}\), the dosage of MNZ@MS is 1 g l\(^{-1}\). Compared the fitting curve of Langmuir isotherm (figure 12(a)) with that of the Freundlich isotherm, the Langmuir adsorption isotherm is more suitable than the Freundlich adsorption isotherm to describe the adsorption process of heavy metals on MNZ@MS. The R\(^2\) value in table 2 also provides us similar results. As the basic assumptions of Langmuir adsorption isotherm, the adsorption process of heavy metals on MNZ@MS

Table 1. Pseudo-first-order and pseudo-second-order rate constants calculated from experiment data.

|          | \(q_{exp}\) (mg g\(^{-1}\)) | \(k_1\) (/min) | \(q_{cal}\) (mg g\(^{-1}\)) | \(R^2\) |
|----------|-------------------------------|----------------|-----------------------------|---------|
| Cu       | 50                            | 0.008          | 48.99                       | 0.9641  |
| Cd       | 119                           | 0.0053         | 25.03                       | 0.9029  |
| Pb       | 450                           | 0.0083         | 99.83                       | 0.7435  |

|          | \(q_{exp}\) (mg g\(^{-1}\)) | \(k_2\) (g/mg-min) | \(q_{cal}\) (mg g\(^{-1}\)) | \(R^2\) |
|----------|-------------------------------|--------------------|-----------------------------|---------|
| Cu       | 50                            | 0.000 179          | 58.47                        | 0.9892  |
| Cd       | 119                           | 0.000 072          | 119.04                       | 0.9982  |
| Pb       | 450                           | 0.000 024          | 454.5                        | 0.9984  |

Figure 12. (a) The adsorption isotherm analysis with Langmuir model; (b) The adsorption isotherm analysis with Freundlich model.
could be considered as a monolayer adsorption process. In addition, according to the computational results on table 2, the maximum adsorption capacity of heavy metals for Cu, Cd and Pb on MNZ@MS is 59.9 mg g\(^{-1}\), 188.6 mg g\(^{-1}\) and 476.1 mg g\(^{-1}\), respectively.

### 3.10. Competitive adsorption system

In industrial wastewater, multiple heavy metals often exist at the same time. Due to the interaction of heavy metals, the adsorption efficiency will be different from that of a single adsorption system.

\[
\text{reduction} = \frac{Q_0 - Q_1}{Q_0} \times 100\%
\]

(7)

\(Q_0\) is the equilibrium adsorption capacity under a single adsorption system. 

\(Q_1\) is the equilibrium adsorption capacity under a competitive adsorption system.

Figure 13 depicts the effect of initial concentrations on the reduction rates of heavy metals in competitive adsorption system, with the initial concentrations of heavy metals ranging from 20 to 280 mg l\(^{-1}\), and the dosage of MNZ@MS is 1 g l\(^{-1}\). The reduction rate of Cd is the highest among three heavy metals, and it maintains around 70% regardless of the changes of initial concentration. In addition, the reduction rate of Pb is the lowest, and it improves with the increase of initial concentrations. Besides, the reduction rate of Cu appears between Pb and Cd, and the variation trend is similar with that of Pb. This experiment results suggest that, under competitive adsorption system, the adsorption process of Pb is the most difficult to be interfered, while the adsorption process of Cd is the most susceptible to the interference from other heavy metals. Under low initial concentration system, the adsorption advantages of Pb and Cu appear more obviously at low initial concentrations.

![Figure 13. The effect of initial concentration on the reduction rate of heavy metals in competitive adsorption system.](image-url)
4. Conclusions

In this paper, the MNZ@MS is successfully prepared using MS as carrier and [C_{12}H_{25}(CH_{3}2)N^+-\text{(CH}_{3})\text{-N}^+-\text{(CH}_{2})(C_{29}H_{37})\text{Cl}_{2}] as directing agent. The characterization results of materials exhibit that the surface of spherical MS particles are completely wrapped by nano-scale Linde F(K) zeolite. The MNZ@MS presents favorable magnetic properties, and the saturation magnetization value of MNZ@MS is around 17.7 emu g⁻¹. The Zeta potential result indicates that MNZ@MS is suitable to the adsorption of heavy metals from solution. In addition, the higher solution pH is beneficial to the adsorption process of heavy metals on MNZ@MS. The pseudo-second-order model are more suitable for fitting the adsorption process of heavy metals on MNZ@MS. Isotherm study suggests that the adsorption process follows the Langmuir isotherm model. Moreover, the maximum adsorption capacity of heavy metals on MNZ@MS is 59.9 mg g⁻¹, 188.6 mg g⁻¹ and 476.1 mg g⁻¹, respectively. Under competitive adsorption system, the adsorption process of Pb is most difficult to be interfered, while the adsorption process of Cd is most susceptible to the interference from other heavy metals. The results proved that MNZ@MS is a low-cost and efficient magnetic adsorbent, and it has great potential for the application in heavy metal wastewater treatment.

Acknowledgments

This work is supported by 2016 University of Jiangsu Province Blue Project of young academic leader training objects, Science Foundation of Jiangsu Colleges and Universities (Grant No. 17KJD610001, 17KJD610002).

ORCID iDs

Chen Chen https://orcid.org/0000-0003-3714-7076

References

[1] Azizi M and Seidi S 2018 A novel N, N'-bis(acetylamido) ethylenediamine functionalized silica-core-shell magnetic nanosorbent for manetic dispersive solid phase extraction of copper in cereal and water samples Food Chem. 249 30
[2] Zhu J and Wei S 2012 One-pot synthesis of magnetic graphene nanocomposites decorated with core-double-shell nanoparticles for fast chromium removal Environ. Sci. Technol. 46 977
[3] Islam M A and Angove M J 2019 Recent innovative research on chromium (VI) adsorption mechanism Environ. Nanotechnol. Monit. Manag. 12 100267
[4] Ghashghaee M and Ghambarian M 2020 Theoretical insights into sensing of hexavalent chromium on buckled and planar polymeric carbon nitride nanosheets of heptazine and triazine structures Mol. Simulat. 46 1
[5] Ghashghaee M and Ghambarian M 2019 Adsorption of toxic mercury, lead, cadmium, and arsenic ions on black phosphorous nanosheet: first-principles calculations Struct. Chem. 30 1
[6] Dinari M and Tabatabaeian R 2018 Ultra-fast and highly efficient removal of cadmium ions by magnetic layered double hydroxide/ guar gum bianonanocomposites Carbohydr. Polym. 192 317
[7] Manatungu D C and De Silva R M 2016 Natural polysaccharides leading to super adsorbent hydroxyapatite nanoparticles for the removal of heavy metals and dyes from aqueous solutions RSC Adv. 6 105618
[8] Yang F and Sun S 2016 Mg-Al layered double hydroxides modified clay adsorbents for efficient removal of Pb^{2+}, Cu^{2+} and Ni^{2+} from water Appl. Clay Sci. 123 134
[9] Kumar R and Sharma R K 2017 Cellulose based grafted biosorbents-Journey from lignocellulose biomass to toxic metal ions sorption applications-a review J. Mol. Liq. 232 62
[10] Ali L A and Ibrahim W A W 2015 New chrysin-functionalized silica-core-shell magnetic nanoparticles for the magnetic solid phase extraction of copper ions from water samples Talanta 148 191
[11] Tobiasz A and Walas S 2014 Solid-phase-extraction procedures for atomic spectrometry determination of copper Trend Anal. Chem. 62 106
[12] 1996 Chinese Integrated wastewater discharge standard GB 8978-1996, National Standards of People’s Republic of China, Ministry of Ecological Environment of the People’s Republic of China
[13] Huang Q and Chen Y 2018 Magnetic graphene oxide/MgAl-layered double hydroxide nanocomposite: one-pot solvothermal synthesis, adsorption performance and mechanisms for Pb^{2+}, Cd^{2+}, and Cu^{2+} Chem. Eng. J. 341 1
[14] Yu S and Wang X 2017 Macroscopic, spectroscopic, and theoretical investigation for the interaction of phenol and naphthal on reduced graphite oxide Environ. Sci. Technol. 51 3278
[15] Heraldyoa E and Rahmawati F 2019 Fabrication of Mg-Zn-Al hydroxalite and its application for Pb^{2+} removal Acta Polytex. 59 3
[16] Fan H and Ma X 2019 Highly efficient removal of heavy metal ions by carboxymethyl celluloseimmobilized Fe_{3}O_{4} nanoparticles prepared via high-gravity technology. Carbohydr. Polym. 213 39
[17] Cheng M and Wang Z 2018 Preparation of amino-functionalized Fe_{3}O_{4}@mSiO_{2}-core-shell magnetic nanoparticles and their application for aqueous Fe^{3+} removal J. Hazard. Mater. 341 198
[18] Melichová Z and Hromada L 2013 Adsorption of Pb^{2+} and Cu^{2+} ions from aqueous solutions on natural bentonite Pol. J. Environ. Stud. 22 457
[19] Ghashghaee M and Farzaneh V 2016 Removal of Cr(VI) species from aqueous solution by different nanoporous Materials. Iran. J. Toxicol. 10 6
[20] Luo H and Law Y W W 2018 Hydrothermal synthesis of needle-like nanocrystalline zeolites from metakaolin and their applications for efficient removal of organic pollutants and heavy metals Microporous Mesoporous Mat. 272 8
[21] Li Y and Bai P 2019 Removal of Zn\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), and Cu\(^{2+}\) from aqueous solution by synthetic clinoptilolite Microporous Mesoporous Mat. 273 203

[22] Chen C and Cheng T 2014 Adsorption of Cu (II) from aqueous solution on fly ash based Linde F (K) zeolite Iran. J. Chem. Chem. Eng. 33 29

[23] Chen C and Cheng T 2014 Removal of Zn\(^{2+}\) in aqueous solution by Linde F (K) zeolite prepared from recycled fly ash Indian Chem. Soc. 91 285

[24] Cheng T and Chen C 2018 Competitive adsorption of Cu, Ni, Pb, and Cd from aqueous solution onto fly ash-based Linde F (K) zeolite Iran. J. Chem. Eng. 37 61

[25] Hong M and Yu L 2019 Heavy metal adsorption with zeolites: the role of hierarchical pore architecture Chem. Eng. J. 359 363

[26] Choi M and Na K 2019 Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived catalysts Nature 461 246

[27] Jo C, Park W and Ryou R 2017 Synthesis of mesoporous zeolites in fluoride media with structure-directing multiammonium surfactants Microporous Mesoporous Mat. 239 19

[28] Han S W and Kim J 2017 Dry-gel synthesis of mesoporous MFI zeolite nanosponges using a structure-directing surfactant Microporous Mesoporous Mat. 240 123

[29] Sivamani S and Suji S 2018 Rapid ultrasound assisted hydrothermal synthesis of highly pure nanozelite X from fly ash for efficient treatment of industrial effluent Chemosphere 210 816

[30] Yilmaz Y 2019 Determination of adsorption characteristics of synthetic NaX nanoparticles J. Hazard. Mater. 378 120743

[31] Nicola R, Costori O, Cíopec M, Negrea A and Putz A M 2020 Silica-coated magnetic nanocomposites for Pb\(^{2+}\) removal from aqueous solution Applied Sciences 10 2726

[32] Liu H and Peng S 2013 Magnetic zeolite NaX: synthesis, characterization based on metakaolin and its application for the removal of Cu\(^{2+}\), Pb\(^{2+}\) Chemosphere 119 1539

[33] Mesadghinia A and Azari A 2017 Removal of phthalate esters (PAEs) by zeolite/Fe\(_2\)O\(_3\) in investigation on the magnetic adsorption separation, catalytic degradation and toxicity bioassay. J. Mol. Liq. 233 378

[34] Xie W M and Zhou F P 2018 Accelerated crystallization of magnetic 4A-zeolite synthesized from red mud for application in removal of mixed heavy metal ions J. Hazard. Mater. 358 641

[35] Yang J and Zhao Y 2014 Physical–chemical characteristics and elements enrichment of magnetospheres from coal fly ashes Fuel 135 15

[36] Baha U and Sapkota B 2008 Micro-scale grain-size analysis and magnetic properties of coal-fired power plant fly ash and its relevance for environmental magnetic pollution studies Atmos. Environ. 42 8359

[37] Gomes S and François M 1999 Characterization of magnetite in silico-aluminous fly ash by SEM, TEM, XRD, magnetic susceptibility, and Mössbauer spectroscopy. Cem. Concr. Res. 29 1705

[38] Veneva I and Hoffmann V 2004 Rock magnetic, mineralogical and microstructural characterization of fly ashes from Bulgarian power plants and the nearby anthropogenic soils Phys. Chem. Earth. 29 1011

[39] Jiang L and Liu P 2014 Novel magnetic fly ash/poly(acrylic acid) composite microgel for selective adsorption of Pb(II) ion: synthesis and evaluation. Ind. Eng. Chem. Res. 53 2924

[40] Chen C and Cheng T 2019 Synthesis of an efficient Pb adsorption nano-crystal under strong alkaline hydrothermal environment using a gemini surfactant as directing agent J. Chem. Soc. Pak. 41 6

[41] Chen C and Li Q 2012 Feasibility of manufacturing geopolymer bricks using circulating calcined ash Mater. Res. Express 9 015083

[42] Chen C and Gong W 2011 Kinetics of fly ash leaching in strongly alkaline solutions J. Mater. Sci. 46 590

[43] Fernández-Jiménez A and Palomo A 2005 Mid-infrared spectroscopic studies of alkaline-activated fly ash/graphene oxide@Fe\(_3\)O\(_4\) gel beads for adsorbing heavy metal ions Carbohydr. Polym. 216 119

[44] Li Y and Bi H Y 2018 Adsorption behavior and mechanism of core–shell magnetic rhombohedral-layered double hydroxide nanohybrid for phenolic compounds from heavy metal–phenol pollutants Appl. Clay Sci. 162 230

[45] Fan C and Li K 2018 Evaluation of magnetic chitosan beads for adsorption of heavy metal ions Sci. Total Envi. 627 1396

[46] Son E B and Poo K M 2018 Heavy metal removal from aqueous solutions using engineered magnetic biochars derived from waste engineering materials J. Hazard. Mater. 378 120743

[47] Cui L M and Guo X Y 2015 Removal of mercury and methylene blue from aqueous solution by xanthate functionalized magnetic nanoparticles J. Mater. Sci. 41 6

[48] Guo S and Duan N 2018 g-C\(_3\)N\(_4\) modified graphene oxide@Fe\(_3\)O\(_4\) composite microgel for selective adsorption of Pb(II) ion: synthesis and evaluation. Ind. Eng. Chem. Res. 53 2924

[49] Wu Z and Deng W 2019 Novel magnetic polysaccharide/graphene oxide@Fe\(_3\)O\(_4\) gel beads for adsorbing heavy metal ions Carbohydr. Polym. 216 119

[50] Li Y and Bi H Y 2018 Adsorption behavior and mechanism of core–shell magnetic rhombohedral-layered double hydroxide nanohybrid for phenolic compounds from heavy metal–phenol pollutants Appl. Clay Sci. 162 230

[51] Alqadami A A and Khan M A 2018 A magnetic nanocomposite produced from camel bones for an efficient adsorption of toxic metals from water J. Clean. Prod. 178 293

[52] Zhang Y and Nie S 2019 Ultrafast adsorption of heavy metal ions onto functionalized lignin–based hybrid magnetic nanoparticles Bio-adsorbent Mater. Sci. Technol. 101 42

[53] Nejadshafiee V and Islami M R 2019 Adsorption capacity of heavy metal ions using sulfonated-modified magnetic activated carbon as a bio-adsorbent Mater. Sci. Eng. C 96 0

[54] Lukman S and Essa M H 2013 Adsorption and desorption of heavy metals onto natural clay material: influence of initial pH J. Environ. Sci. Technol. 61 1

[55] Abdulla A and Alwan L H 2020 Thermodynamic and kinetic studies of Eriochrome black adsorption on activated charcoal prepared from lemon leaves Mater. Res. Express 6 015088

[56] Shahzad A, Jang J, Lim S R and Lee D S 2020 Unique selectivity and rapid uptake of molybdenum-diisulfide functionalized MXene nanocomposite for mercury adsorption Environ. Sci. 182 109005

[57] Alqadami A A and Khan M A 2018 Development of citric anhydride anchored mesoporous MOF through post synthesis modification to sequester potentially toxic lead (II) from water Microporous Mesoporous Mat. 261 198

[58] Begum J, Hussain Z and Noor T 2020 Adsorption and kinetic study of Cr(VI) on ZIF-8 based composites Mater. Res. Express 7 015083

[59] Khan B, Nawaz M and Wasem M 2019 Adsorption of methylene blue onto size controlled magnetite nanoparticles Mater. Res. Express 6 095511
[60] Li A and Huang W 2020 Porous carbon prepared from lotus leaves as potential adsorbent for efficient removal of rhodamine B Mater. Res. Express 7 055505
[61] Ouakouak A, Rihani K and Youcef I 2020 Adsorption characteristics of Cu(II) onto CaCl2 pretreated algerian bentonite Mater. Res. Express 7 025045
[62] Zheng T, Xu Y and Yan C 2019 Functional group driven adsorption of neutral red by boron nitride nanoparticles: experimental and theoretical studies Mater. Res. Express 6 095001