Hydrothermal synthesis of magnetic zeolite P from fly ash and its properties

Peng Wang¹, Qi Sun², Yujiao Zhang³ and Jun Cao¹
¹ College of Materials and Metallurgy, Guizhou University, Guiyang 550025, People’s Republic of China
² State key laboratory of advanced processing and recycling of nonferrous metals, Lanzhou University of Technology, Lanzhou, 730050, People’s Republic of China
E-mail: qsun@gzu.edu.cn
Keywords: fly ash, magnetic zeolite P, hydrothermal method, synthesis

Abstract
Magnetic zeolite P with the spherical form was successfully synthesized from low-grade fly ash via hydrothermal synthesis method. These samples were characterized by XRD, XRF, FTIR, BET, VSM, SEM and TEM. The textural properties of magnetic zeolite P were further studied by N₂ adsorption-desorption technique. In addition, the vibrating sample magnetometer study confirmed that the saturation magnetization is 11.99 emu·g⁻¹, indicating that magnetic zeolite P has sufficiently magnetic property to be attracted by a permanent magnet. Moreover, this facile approach to study saturation adsorption capacity and percentage removal of the magnetic zeolite P for Pb (II) and Cu (II) ions might expand the application of magnetic zeolite P in the adsorption of heavy metal ions, and it may be further extended to other magnetic zeolite materials.

1. Introduction

As is all known, our living standard has been improved greatly which profit from the industrialized development. However, the industrialization also bring about plenty of severe problems which made the environment polluted [1, 2]. Recently, due to the heavy metal pollutants are released into environment without restraint, the concentration of heavy metal pollutants has increased sharply by years. Heavy metal ions equipped with the character of high toxicity and enrichment that would threaten not only human-beings and animals but also the whole biogeocenose badly [3–7]. In summary, disposing the heavy metals waste water reasonably is an urgent solution.

Currently, the technologies for removing heavy metals from waste water mainly include chemical precipitation [8], filtration [9], ion exchange [10], membrane separation [11–14], electrochemical precipitation [11], etc. However, these technologies have some native defect such as extravagant price but low efficiency.

Zeolite has been widely used all the time because of its predominant adsorption performance. Therefore, zeolite as an excellent adsorption material is often used in the area of heavy metal removal. However, zeolite is not easy to be separated from the adsorbed heavy metal ions, there is a problem about the reuse of zeolite after adsorbing heavy metal waste water. Such difficulty could be resolved through preparation the magnetically modified zeolite which would not only preserving the all useful properties of zeolite but also the adsorbent can be separated conveniently from the solutions merely using an external magnet [13, 15]. Uthain et al [16] first put forward the magnetic carrier technology when researching the waste-water treatment in 1940s. The main idea about the magnetic carrier technology is even scattered magnetic material on the substrate surface that usually present weak magnetic or non-magnetic and equipped with special function. All of that could separate adsorbed material with the substrate by the field of the external magnetic force [17].

In this study, magnetic zeolite P was synthesized from low-grade fly ash through hydrothermal method and the saturated adsorption capacity and removal percentage of the magnetic zeolite P for Pb(II) and Cu(II) ions were studied by controlling the adsorption time under the optimal conditions. The starting material and final product were analyzed by XRD, XRF, FTIR, BET, VSM, SEM and TEM.
2. Experimental

2.1. Materials
The chemicals used in our study are as follows: sodium hydroxide pellets (NaOH, AR), hydrochloric acid (HCl, AR), ammonia (NH₃, AR) 25%, ferric chloride hexahydrate (FeCl₃·6H₂O, AR), ferrous chloride tetrahydrate (FeCl₂·4H₂O, AR), copper nitrate (Cu(NO₃)₂, AR), lead nitrate (Pb(NO₃)₂, AR) and deionized water. A certain concentration of heavy metal ion solution was prepared in the laboratory. The fly ash was provided by a Thermal Power Plant in China. Zeolite P was prepared from fly ash in the laboratory. The fly ash is passed through 80-mesh sieve for the synthesis of zeolite.

2.2. Sample characterization
Fourier infrared spectroscopy of the sample was performed using the American Thermo Scientific Nicolet i550 infrared spectrometer. The phase and crystallinity of the sample were analyzed by German Bruker AXS D8-Focus, the instrument was Cu target, λCuKα = 0.15418 nm, tube voltage/current 30 kV/30 mA, monochromator Ni, scanning step size 0.02°, integration time 0.2 s. The magnetization curves of the magnetic zeolite P and the magnetic particles were recorded by a Lake Shore 7410 VSM vibrating sample magnetometer manufactured by Quantum Dsign, USA. The microscopic morphologies of the sample were performed by using a Hitachi SU8010 field emission scanning electron microscope. The chemical composition of the sample was determined using a Dutch PANalytical B.V., AXIOSmAX type fluorescence spectrometer. The textural properties of final product were measured using ASAP2020 specific surface area analyzer (Micromeritics, America). The concentration of heavy metal ions in the filtrate was measured using an ICP spectrometer (ICP, DSG-III).

2.3. Synthesis of magnetite particles
Magnetite particles were prepared by the method presented by Ranjbakhsh et al [18]. Typically 13.60 g of FeCl₃·4H₂O and 22.10 g of FeCl₂·6H₂O were dissolved in a certain amount of deionized water under nitrogen gas with vigorous stirring at 65 °C for 2 h; the pH of the solutions was adjusted by adding 25% NH₃·H₂O. After static crystallization reaction on 90 °C for 12 h the black precipitates were collected by a permanent magnet and using deionized water washed twice.

2.4. Synthesis of adsorbents
We weighed 10 g of fly ash and a certain amount of magnetic particles. Then a certain amount of solid sodium hydroxide was weighed to prepare a solution having an alkali concentration of 3 mol l⁻¹. The fly ash and the sodium hydroxide solution as well as magnetic particles were mixed uniformly. The mixed solution was transferred to a PTFE-lined stainless steel reactor and placed in a dry box for reaction at 90 °C for 24 h. After that, the mixture was filtered, washed and dried. Eventually, we obtain the magnetic zeolite P.

2.5. Adsorption experiments
The Pb(NO₃)₂ and Cu(NO₃)₂, were used for preparation Pb (II) and Cu (II) solutions. The final volume of the solutions was 50 ml and the pH was adjusted by 1.0 mol l⁻¹ HCl and NaOH solutions. A series of adsorption experiments were proposed by the multivariate method. In the next step, magnetic zeolite P was separated by an external magnet and residual solutions were analyzed by ICP spectrometer. To compare the adsorption efficiency of the adsorbent in different conditions, the removal percentage Q and adsorbed amounts per mass of adsorbent q (mg g⁻¹) were calculated as follows: [13, 19]

\[
q = \frac{(C_0 - C_e)}{m} \times V \tag{1}
\]

\[
Q = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}
\]

where C₀ and Cₑ (mg l⁻¹) are initial and equilibrium concentrations of the cations, respectively. V (L) is the volume of the solution and m (g) is the mass of adsorbents.

3. Results and discussion

3.1. Structural and chemical composition analysis
Figure 1 shows the XRD patterns of fly ash, zeolite P, magnetic zeolite P and magnetic particles. From the 2θ values of the diffraction peaks in fly ash, it is known that the main component of fly ash is amorphous structure which including anatase, quartz and mullite that has shown in figure 1 (d). From the 2θ values of the diffraction peaks in zeolite P, magnetic zeolite P and magnetic particles, it is revealed that the main component of the adsorbent is anatase, quartz and mullite.
peaks in magnetic particles, it is known that magnetic Fe$_3$O$_4$ has been successfully synthesized that is shown in figure 1(a). From figure 1(c), it can be observed that the characteristic reflections for zeolite P, synthesized in the absence of magnetic particles, are appeared at $2\theta = 12.6^\circ$, $17.8^\circ$, $21.8^\circ$, $28.3^\circ$ and $33.5^\circ$ [20, 21]. For zeolite P, sharp peaks are shown in the diffractogram, indicating that zeolite P is a high crystalline phase. From figure 1(b), it can be seen that diffraction peak intensity of the magnetic zeolite P is reduced, indicating that crystallinity of magnetic zeolite P is weakened. Meanwhile, it can be seen that the diffraction peaks of Fe$_3$O$_4$ appear, but its existence form in the magnetic zeolite P cannot be determined. Comparing the XRD pattern in figures 1(b) and (c), it can be seen that the diffraction peak of magnetic zeolite P is consistent with that of zeolite P, indicating that introduction of magnetic particles has not change characteristic diffraction peaks of zeolite P. It can be further illustrated that the zeolite P structure does not change, and the framework structure of zeolite P maintains steady. The diffraction line at 20 angle of 31.1$^\circ$ and 36.2$^\circ$ corresponds to magnetic Fe$_3$O$_4$ [22]; therefore, the synthesized composite is consisting of zeolite P and magnetic Fe$_3$O$_4$. In summary, we have successfully synthesized magnetic zeolite P.

FTIR spectra provide additional informations to the structural analysis performed by XRD [23]. Figure 2 shows the spectra of fly ash, zeolite P, magnetic zeolite P and magnetite particles severally. The FTIR spectrum of fly ash is presented in figure 2(d). The bands at 1093 cm$^{-1}$, 805 cm$^{-1}$, 573 cm$^{-1}$ and 469 cm$^{-1}$ are assigned to asymmetric stretching vibration of Si–O, bending vibration of Si–O, bending vibration of Al–O and bending vibration of O–Si–O, respectively. It is possible to synthesize zeolite from fly ash because of the existence of these silica-alumina skeletons. The band observed at 579 cm$^{-1}$ is assigned to Fe–O–Fe [24], in the spectra of magnetite particles, as could be seen in figure 2(b). Compared figures 2(a) and (c), it can be observed that the position of absorption peak caused by the antisymmetric stretching vibration of Si–O in the magnetic zeolite P is moved from 1008 cm$^{-1}$ of the zeolite P to 995 cm$^{-1}$, indicating that iron ions are placed in zeolite P skeleton to form Fe–O–Si bonds. From figure 2(a), a significant vibrational peak appears at 681 cm$^{-1}$, which coincides with the infrared characteristic peak of Fe$_3$O$_4$. It is further confirmed that Fe$_3$O$_4$ is not simply attached to the surface of zeolite P, but forms a chemical bond with the zeolite P matrix during the preparation of zeolite P.

The chemical compositions of the magnetic zeolite P were obtained by the XRF technique (table 1). The composite is consisting of 7.748%W iron oxide. According to the molar ratio, the molecular formula of the magnetic zeolite P is 6Na$_2$O·5.8Al$_2$O$_3$·18SiO$_2$·1.1Fe$_2$O$_3$·12H$_2$O.

### 3.2. Morphology analysis

Following that, SEM technique was applied to study the detailed morphologies of fly ash and zeolite P, as could be seen in figure 3. Figures 3(a) and (b) shows the micrograph of fly ash, which presents pseudo-spherical shape, and amorphous substance is distributed on the surface of the sphere. Figures 3(c) and (d) shows the micrograph of zeolite P, which presents spherical and smooth morphology. Figure 4 shows the TEM images of magnetite particles and magnetic zeolite P. It can be seen from the figures 4(a) and (b) that spherical magnetite particles have a uniform particle size, and most of magnetite particles are gathered together. It is apparent that magnetite particles are in nanosize with the average particle size of about 10 nm. From figures 4(c) and (d), it can be seen that magnetic zeolite P is spherical, and crystal form does not change greatly. Meanwhile, magnetite

![Figure 1. XRD patterns of (a) magnetite particles, (b) magnetic zeolite P, (c) zeolite P, (d) fly ash.](image-url)
particles uniformly adhere to the surface of zeolite P, and no agglomeration occurs. Combined with figures 1(b) and 2(a), it is further confirmed that magnetite particles are bound to the aluminosilicate framework of the zeolite P.

3.3. Analysis of physicochemical properties

3.3.1. BET analysis

\( \text{N}_2 \) adsorption-desorption isotherms of magnetic zeolite P and zeolite P measured with nitrogen gas at 77 K are depicted in figure 5(a), which shows a typical type II behavior [25]. As can be seen from the figure 5(a) that there is a significant hysteresis loop, indicating the presence of mesoporosity [26]. The low pressure isotherm provides information about the micro porosity. The micro pore surface area and micro pore volume are obtained by the t-plot method [27]. The specific surface area values are calculated by BET method. The size distribution of pore

| Compound          | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | CaO | Na\(_2\)O | K\(_2\)O | TiO\(_2\) | P\(_2\)O\(_5\) | MnO |
|-------------------|-----------|----------------|----------------|-----|-----------|---------|----------|--------------|-----|
| Fly ash           | 52.60     | 18.09          | 0.40           | 0.40| 0.03      | 0.39    | 4.33     | 0.38         | 0.49|
| Magnetic zeolite P| 41.90     | 23.10          | 7.75           | 0.05| 14.42     | 0.05    | 0.03     | 0.003        | 0.005|

Figure 2. FTIR spectra of (a) magnetic zeolite P, (b) magnetite particles, (c) zeolite P, (d) fly ash.

Figure 3. SEM images of (a), (b) fly ash, and (c), (d) zeolite P.
has been determined by using the BJH equation showed in figure 5(b). The BJH average pore diameter of magnetic zeolite P and BJH average pore diameter of zeolite P are 11.61 nm and 12.60 nm, respectively. Textural properties of magnetic zeolite P and zeolite P are listed in table 2. As can be seen from the table 2, the micro pore volume is almost zero. The main reason is that the zeolite has small pores and it is difficult for nitrogen molecules to enter the microchannel structure. From table 2, it can be seen that textural properties of magnetic zeolite P change a little, indicating that the structure and surface morphology of synthesized composite almost unchanged, which is in agreement with the FTIR, XRD and TEM results.

![Figure 4](image_url) **Figure 4.** TEM images of (a), (b) magnetite particles, and (c), (d) magnetic zeolite P.

![Figure 5](image_url) **Figure 5.** (a) N\textsubscript{2} adsorption-desorption isotherm and (b) pore size distribution of magnetic zeolite P and zeolite P.

| Adsorbents       | BET surface area (m\textsuperscript{2}·g\textsuperscript{-1}) | Micro pore surface area (m\textsuperscript{2}·g\textsuperscript{-1}) | Micro pore volume (cm\textsuperscript{3}·g\textsuperscript{-1}) |
|------------------|---------------------------------------------------------------|-----------------------------------------------------------------|---------------------------------------------------------------|
| Magnetic zeolite P | 29.52                                                         | 1.89                                                            | 0.0003                                                        |
| Zeolite P        | 22.39                                                         | 4.23                                                            | 0.0017                                                        |

Table 2. Textural properties of zeolite P and magnetic zeolite P.
3.3.2. Magnetic analysis

Facile separation and recycle of magnetic sorbents from solutions is possible by the applied magnetic field, so the magnetization power of sorbents is essential. The magnetic hysteresis loops of magnetite particle and magnetic zeolite P measured using a VSM at room temperature are shown in figure 6. Figure 6(a) shows the magnetization curve of magnetic zeolite P as a function of the applied magnetic field at room temperature. The magnetic curve of S shaped behavior shows no hysteresis loop and no remanence which indicates that magnetic zeolite P has good superparamagnetic property [28]. The zero remanence ensures that magnetic zeolite P does not retain magnetization after exposure to an external magnetic field, which allows magnetic zeolite P to be redispersed when the magnetic field is removed [22]. In the absence of magnetic field, magnetization value is zero and the saturation magnetization is at 11.99 emu g$^{-1}$, which indicates that magnetic zeolite P has sufficiently magnetic property to be attracted by a permanent magnet. The magnetic parameters of magnetite particle and magnetic zeolite P are listed in table 3.

![Figure 6. The hysteresis loops of magnetite particles and magnetic zeolite P. (a) Magnetic zeolite P curve, (b) Magnetite particles curve.](image)

| Adsorbents          | Saturation magnetization (emu g$^{-1}$) | Coercivity (Oe) |
|---------------------|----------------------------------------|-----------------|
| Magnetic zeolite P  | 11.99                                  | 20.67           |
| Magnetite particle  | 75.77                                  | 30.08           |

Table 3. The magnetic parameters of magnetite particle and magnetic zeolite P.

| Adsorbents          | Q(mg g$^{-1}$) | Q (%)         |
|---------------------|---------------|---------------|
|                     | Cu(II)        | Pb(II)        | Cu(II) | Pb(II) |
| Zeolite P           | 29.85         | 27.50         | 39.80  | 36.67  |
| Magnetic Zeolite P  | 25.20         | 20.38         | 33.60  | 27.17  |

Table 4. The saturation adsorption capacity and percentage removal of Cu(II) and Pb(II) ions using synthesised samples.

3.3.2. Magnetic analysis

Facile separation and recycle of magnetic sorbents from solutions is possible by the applied magnetic field, so the magnetization power of sorbents is essential. The magnetic hysteresis loops of magnetite particle and magnetic zeolite P measured using a VSM at room temperature are shown in figure 6. Figure 6(a) shows the magnetization curve of magnetic zeolite P as a function of the applied magnetic field at room temperature. The magnetic curve of S shaped behavior shows no hysteresis loop and no remanence which indicates that magnetic zeolite P has good superparamagnetic property [28]. The zero remanence ensures that magnetic zeolite P does not retain magnetization after exposure to an external magnetic field, which allows magnetic zeolite P to be redispersed when the magnetic field is removed [22]. In the absence of magnetic field, magnetization value is zero and the saturation magnetization is at 11.99 emu g$^{-1}$, which indicates that magnetic zeolite P has sufficiently magnetic property to be attracted by a permanent magnet. The magnetic parameters of magnetite particle and magnetic zeolite P are listed in table 3.

3.3.3. Adsorption analysis

The saturated adsorption capacity and removal percentage of synthesised samples for Pb(II) and Cu(II) ions were studied by controlling the adsorption time under the optimal conditions. The saturation adsorption capacity and percentage removal of synthesised samples for Pb (II) and Cu (II) ions are shown in table 4. The saturation adsorption capacity of magnetic zeolite P for Pb (II) and Cu (II) is 20.38 mg g$^{-1}$ and 25.20 mg g$^{-1}$, respectively. The percentage removal of magnetic zeolite P for Pb (II) and Cu (II) are 27.17% and 33.60%, respectively. In combination with table 2, it can be concluded that the magnetic zeolite P has a unique pore structure and a high specific surface area as well as a certain number of adsorption sites.
A comparative study is carried out from the point of view of the time of adsorption of lead and copper ions for assessment of the performance of the synthesised samples. From table 5, it can be seen that the advantages of the presented magnetic zeolite P over other adsorbents are readily apparent. It is clearly observed that the magnetic zeolite P exhibits a much higher saturation adsorption capacity at the lowest time for removal of the selected ions.

4. Conclusions

In summary, by careful tuning of the synthetic conditions, magnetic zeolite P sample with spherical form was successfully synthesized from low-grade fly ash by using hydrothermal method. The XRF study confirmed that the molecular formula of the magnetic zeolite P was $6\text{Na}_2\text{O} \cdot 5.8\text{Al}_2\text{O}_3 \cdot 18\text{SiO}_2 \cdot 1.1\text{Fe}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$. The $N_2$ adsorption-desorption technique indicated the micro pore volume, BET surface area, micro pore surface area of the magnetic zeolite P were $0.0005 \text{ cm}^3 \cdot \text{g}^{-1}$, $29.52 \text{ m}^2 \cdot \text{g}^{-1}$ and $1.89 \text{ m}^2 \cdot \text{g}^{-1}$, respectively. The VSM study confirmed that the saturation magnetization was $11.99 \text{ emu} \cdot \text{g}^{-1}$, indicating that magnetic zeolite P has sufficiently magnetic property to be attracted by a permanent magnet. In addition, this facile approach to study saturation adsorption capacity and percentage removal of the magnetic zeolite P for Pb (II) and Cu (II) ions might expand the application of zeolite P in adsorption of heavy metal ions, and it may be further extended to other magnetic zeolite materials. Further studies on the mechanism of how the magnetic zeolite P adsorbs heavy metal ions are under investigation in our lab at present.

Acknowledgments

This work was supported by the Guizhou Science and Technology Plan Project [(2017) No. 7247].

ORCID iDs

Qi Sun @ https://orcid.org/0000-0003-2570-4568

References

[1] Cheng T, Chen C and Xu W 2016 Fly Ash Comprehensive Utilization 5 12–20
[2] Zhang R and Ying G E 2011 Environmental Pollution and Control 33 41–45
[3] Hena S and Mater J H 2010 J. Hazard. Mater. 181 474–479
[4] Pillai S S, Mullasser J D and Fernandez N B 2013 Ecotox. Environ. Safe 92 199–205
[5] Chauhan D, Jaitswal M and Sankaramakrishnan N 2012 Carbohydr. Polym. 88 670–675
[6] Gaffer A, Kahlawy A A A and Amann D 2017 Egyptian Journal of Petroleum 26 995–999
[7] Kousalya G N, Rajiv G M and Meenakshi S 2010 Int. J. Bio. Macromol. 47 308–315
[8] Figueras G V, Parga J R and Valenzuela J L 2016 JOM 68 540–547
[9] Baharuddin N H, Sulaiman N M N and Aroua M K 2015 Environ. Prog. Sustain. 34 359–367
[10] Pepe F, Gennaro B D and Aprea P 2013 Chem. Eng. J. 219 37–42
[11] Zen G, He Y and Zhan Y 2016 J. Hazard. Mater. 317 60–72
[12] Şerife P, Yar A and Aci I 2016 Water. Treat. 57 16177–16183
[13] Khodadadi M, Ansarizad M and Malekpour A 2017 Micropor. Mesopor. Mater. 248 256–265
[14] Dong B, Fishgold A and Lee P 2016 J. Hazard. Mater. 318 379–387
[15] Liu H, Peng S and Shu L 2013 Chemosphere 91 1539–1546
[16] Anshits A G 2001 Catal. Today. 64 59–67
[17] Nah J W, Hwang K Y and Shul Y G 2007 Powder. Technol. 177 99–101
[18] Chen X and Lam K F 2009 Phys. Chem. C 113 9804–9813
[19] Malekpour A and Khodadadi M 2016 Rsc Adv. 6 14705–14711
[20] Wang F, Wu D Y and He S B 2005 J. Mater. Eng. 8 47–50
[21] Berkgaat V and Singer A 1996 Appl. Clay. Sci. 10 369–378

Table 5. Comparison of magnetic zeolite P with reported data in uptake of Pb (II) and Cu (II) ions.

| Adsorbents                     | $Q$(mg g$^{-1}$) | Time(min) | References               |
|-------------------------------|------------------|-----------|--------------------------|
| Natural zeolite               | 8.53             | 1200      | [29]                     |
| Iron coated Australian zeolite| 9.33             | 1200      | [29]                     |
| Coconut dregs residus          | 2.76             | 60        | [22]                     |
| Magnetic zeolite P            | 25.20            | 60        | This study               |

\[Q_{\text{Cu(II)}}(\text{mg g}^{-1})\ 
\text{Pb(II)}(\text{mg g}^{-1})]
[22] Faghihian H, Moayed M and Firooz A 2013 J. Colloid Interf. Sci. 393 445–451
[23] Nguyen T C, Loganathan P and Nguyen T V 2015 Chem. Eng. J. 270 393–404
[24] Faghihian H, Moayed M and Firooz A 2014 CR. Chim. 17 108–117
[25] Bessa R D A, Costa L D S and Oliveira C P 2017 Micropor. Mesopor. Mater. 245 64–72
[26] Iqbal A, Sattar H, Haider R and Munir S 2019 J. Clean. Prod. 219 258–267
[27] Garshasbi V 2017 Appl Surf. Sci. 393 225–233
[28] Kamari A and Yusoff S N M 2015 J. Pharmaceut. Biomed. 107 244–250
[29] Kamari A and Yusoff S N M 2014 Chem. Eng. J. 2 1912–1919