Preparation and Characterization of Amino-Functionalized Geopolymer Microspheres

M L Chen, Y Y Ge, G H Xue, M X Xu and X M Cui*

Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Guangxi Nanning, 530004 China

* Corresponding author: cui-xm@tsinghua.edu.cn

Abstract: Geopolymer microspheres have the advantages of environmentally friendly, cost-effective, easily to synthesize and regenerate, which can be applied for adsorption of heavy metal ions from aqueous solution. In this study, the amino-functionalized metakaolin-based geopolymer microspheres (NH2-MGS) were synthesized by coupling agent method using N-β-aminoethyl-γ-aminopropyltrimethoxysilane (AEAPTS). The influences of AEAPTS dosage and temperature on modification efficiency were investigated in detail, and the properties of NH2-MGS were characterized by SEM, EDS, BET, XRD and FTIR analysis. It is shown that amino groups were grafted onto the surface of geopolymer microspheres successfully, and the amount of amino groups grafted increased as the AEAPTS dosage further increasing to 15 wt% and the temperature to 70 °C. The BET specific surface area of NH2-MGS increased significantly from 23.78 to 63.78 m²/g with a corresponding increase of micropores and porosity, which have great potential as adsorbent for removal of heavy metal ions.

1. Introduction
Geopolymer, a new kind of inorganic polymer material with three-dimensional network gel structure, which is composed of aluminosilicate minerals that undergo condensation polymerization under the excitation of alkali metals, to form the silicon-oxygen tetrahedron and aluminum-oxygen tetrahedron [1-3]. Geopolymers have the excellent properties of both ceramic and cement such as low-cost, materials widely, environmentally friendly, rapid hardening and have excellent resistance to chemical attack [4, 5], which have been widely applied in construction materials, wastewater treatment, paint coating etc., especially played a major role in heavy metal wastewater treatment as adsorbents [6].

Adsorbents classified by chemical structure can be divided into inorganic absorbents, organic highpolymer adsorbents and carbonaceous adsorbents [7]. Recently, as an emerging material of inorganic adsorbents, geopolymer has been researched extensively. Cheng [8] condensed a mixture of metakaolin and water glass and then crashed to powder adsorbents to eliminate the Pb²⁺, Cu²⁺, Cr³⁺ and Cd²⁺ in aqueous solution. Tang [9] fabricated porous metakaolin-based geopolymer spheres as adsorbents by a suspension and solidification method, which exhibited excellent removal efficiency for Cu²⁺, Pb²⁺ and Ca²⁺. The spherical geopolymer adsorbents have overcome the shortcomings of powder adsorbent that are nonrenewable, non-reusable and cannot be used in columns for continuous treatment, suggesting it is an ideal adsorbent for waste water treatment in industry [10]. But the inorganic adsorbent is limited in narrow applicable range and single adsorption mechanism of ion exchange in comparison to organic macromolecular adsorbent [11]. In order to improve the
performance of the inorganic adsorbents, the researchers are focusing on organic modification via surface physical coating method and chemical modification method include coupling agent method, etherification reaction method and surface grafting modification method [12]. Tsuda [13] first modified the amorphous silica gel with the diaminosilane and triaminosilane to prepared adsorbents. Du [14] prepared six kinds of amino functionalized nano-silica materials by introduce tetraethylenepentamine and polyethyleneimine with polyacrylic acid as chain extender. It’s known that S, N, C and O are coordination atoms, which can strongly complex with heavy metal ions to form stable chelates. Thus the materials grafted amino group and dithiamine group demonstrated outstanding ability to remove a wide variety of heavy metal ions such as Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Cr$^{6+}$ and Cd$^{2+}$ from aqueous solutions [15-17].

In this study, N-$\beta$-aminoethyl-$\gamma$-aminopropyltrimethoxysilane (AEAPTS) was used to modify the metakaolin-based geopolymer microspheres by coupling agent method. The influences of AEAPTS dosage and temperature were investigated, and the properties were characterized by SEM, EDS, BET, XRD and FTIR, indicating that the geopolymer microspheres were functionalized successfully.

2. Materials and Methods

2.1. Materials
Metakaolin was obtained from the Chaopai Company, Inner mongolia of China. The chemical compositions of metakaolin were SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ and the relative contents measured by XRF (X-ray Fluorescence) were 56.91 mass%, 42.35 mass% and 0.33 mass%, respectively. Water glass with an industrial grade was supplied by Guangxi Chunxu chemical company, China. The module (n$_{SiO_2}$/n$_{Na_2O}$) of water glass and solid content were 3.3 and 38.7 wt%, respectively. The dimethyl silicone oil was industrial grade and had a kinematic viscosity of 2000 mm$^2$/s. The analytical grade hydrochloric acid was supplied by Chengdu Cologne Chemicals co., Ltd. N-$\beta$-aminoethyl-$\gamma$-aminopropyltrimethoxysilane with a content of 97 % was purchased from Nanjing Chuangshi Chemical Regent co., Ltd. The analytical grade sodium hydroxide, ethanol and deionized water were also used in this experiment.

2.2. Characterizations
The specific surface area and pore size distribution were tested by Micromeritic Gemini 2390 surface area and porosity analyzer (America). Hatachi S-3400N Scanning Electron Microscope (SEM) (Japan) was used to observe the morphology of geopolymer microspheres and the elemental content was analyzed using energy dispersive analysis (EDS, EDAX PV8200) (Japan). Infrared spectra were obtained on a Nicolet 6700 Fourier Transform Infrared Spectrophotometer (Thermo Nicolet 510, United States) using a KBr disk method in the 4000-400 cm$^{-1}$ region with a resolution of 4 cm$^{-1}$, by accumulating 16 scans. The crystalline phases of these geopolymer microspheres were identified via Rigaku Mini Flex 600 X-ray diffractometer (XRD) (Japan) with a CuK$_\alpha$ source operating at 40 kV and 15 mA. The scanning range (2$\theta$) was from 10° to 70°, at a step size of 0.02° and a rate of 10°/min.

2.3. Synthesis of amino-functionalized geopolymer microspheres

2.3.1. Preparation of metakaolin-based geopolymer microspheres. The metakaolin-based geopolymer microspheres were prepared by suspension dispersion solidification method as described in literature [18]. NaOH was dissolved in water glass with a molar ratio of SiO$_2$/Na$_2$O = 1.5. Then metakaolin powder and deionized water were added into alkaline solution with molar ratio of Na$_2$O/Al$_2$O$_3$ = 0.7 and H$_2$O/Na$_2$O = 21, mechanism stirring for 6 minutes to obtain the homogeneous slurry. The slurry continuously injected into silica oil that heated to 60 °C by syringe and broken into small droplets and then formed their spherical shape by stirring with dispersion machine. After treated through
vacuum filtering, washing and curing in oven, the metakaolin-based geopolymer microspheres (MGS) were obtained.

2.3.2. Amino-modification of geopolymer microspheres. The amino-modification process of geopolymer microspheres were composed with two parts. Part I: Acidification of MGS: the geopolymer microspheres were first activated with 2 mol·L⁻¹ hydrochloric acid by heated in 90 °C water bath for 2 hours. Then the acidified microspheres were washed with deionized water, dried and sealed for later experiment. Part II: Amino-modification of MGS: 25 mL deionized water and 25 mL ethanol were well mixed in a erlenmeyer flask of total volume 100 mL followed by adding 10 wt%, 15 wt%, 20 wt%, 30 wt% AEAPTS into the erlenmeyer flask respectively and the pH of the modified solution was checked and adjusted to 5 by manually dropwise adding hydrochloric acid. Afterwards 0.1 g geopolymer microspheres dispersed in the modified solution and the erlenmeyer flask was placed in water bath shaker with a shaking speed of 250 rpm at 25 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C for 10 hours, respectively. The final products, amino-functionalized metakaolin-based geopolymer microspheres (NH₂-MGS), were washed with ethanol and deionized water and dried overnight in 60 °C.

![Figure 1. Schematic of the preparation of amino-functionalized geopolymer microspheres.](image)

3. Results and discussions

3.1. Effect of AEAPTS dosage
The elemental content analyzed by EDS was illustrated in Figure 2. The content (express as relative weight percent) of N of NH₂-MGS was higher than that before modification, demonstrated that amino groups were grafted onto the microspheres. The content of N increased as the dosage of AEAPTS further increasing to 15 wt% and then decreased with the dosage of AEAPTS increasing. The highest relative content of N element was 3.61 wt% with the AEAPTS dosage of 15 wt% which presented in Figure 3.

The dosage of coupling agent was a critical factor for the efficiency of amino modification. In the modified solution, AEAPTS first hydrolyzed to siloxanols, which interacted with the silica hydroxyl group of the geopolymer microspheres and introduced the amino group into the surface of the
geopolymer microspheres [19]. With the increase of AEAPTS dosage, the amount of siloxanol generated by hydrolysis increased, and the amount of amino group grafted onto the surface of geopolymer microspheres increased simultaneously, that was the content of N element increased. However, the self-condensation of excessive hydrolytic products of AEAPTS which hindered the interaction between hydrolytic products and hydroxyl on the surface of geopolymer microspheres decreased the coupling efficiency consequently [20, 21].

![Figure 2. Influence of AEAPTS dosage on the amount of amino groups grafted in NH2-MGS.](image)

![Figure 3. EDS analysis of NH2-MGS with 15 wt% AEAPTS.](image)

### 3.2. Effect of temperature

Temperature is also a major factor affecting the modification efficiency. As can be seen in Figure 4, when the reaction temperature was lower than 70 °C, the content of N increased with the increase of temperature, while when the reaction temperature was higher than 70 °C, the content of N decreased with the increase of temperature. This could be ascribed to low temperature was not conducive to the formation of Si-O bond. In a certain range, the higher the temperature was, the more the number of activated molecules increased, the more complete the chemical reaction would be. In contrast, when
the temperature was too high, the self-condensation of hydrolyzed products of AEAPTS occurred, making the modification reaction impossible [22]. Therefore, 70 °C was the optimum reaction temperature under which the content of N reached maximum of 3.61 wt%.

Figure 4. Influence of temperature on the amount of amino group grafted in NH$_2$-MGS.

Figure 5. Pore diameter distribution of (a) MGS; and (b) NH$_2$-MGS.
3.3. Characterization of amino-functionalized geopolymer microspheres

3.3.1. BET analysis. Figure 5 showed the pore diameter distribution before and after the modification of geopolymer microspheres calculated by the BJH method. It can be seen that the pore diameter distribution of MGS was in the range of 1-185 nm which centralized in 103 nm. On the contrary, the pore diameter of NH$_2$-MGS decreased and mainly distributed in 15 nm, which suggested it contains many mesopores and micropores. The pore volume of NH$_2$-MGS decreased from 0.25 to 0.12 cm$^3$/g while the BET surface area increased from 28.78 to 63.78 cm$^2$/g, providing more active sites for the adsorption of heavy metal ions [18]. Given that the acidification process improved the surface activity of geopolymer microspheres and changed the pore structure, which was more conducive to the subsequent modification and adsorption applications [23].

3.3.2. SEM analysis. The morphology of MGS and NH$_2$-MGS were observed in Figure 6. It showed that MGS had good sphericity roughly 150 μm in diameters. Further magnified, there were many pits on the surface of MGS and abundant pores in the channel structure which provided abundant active sites for adsorption of heavy metal ions in aqueous solution[24]. No significant change in the shape or sphericity was observed after modified with AEAPTS although the interface energy of the microspheres did decrease in modified solution [25]. The surface of the MGS-NH$_2$ was more loosened and the presence of more micropores verified the results from BET analysis.

![SEM images of (a) MGS; (b) magnified image of (a); (c) NH$_2$-MGS; (d) magnified image of (c).](image)

3.3.3. XRD analysis. As can be seen in Figure 7, the XRD pattern of the MGS had only a broad peak in the region of 20-30°, indicating the presence of fully amorphous geopolymer. After modification, the diffraction patterns of the geopolymer microspheres did not change and still no features observed
indicative of crystalline phases, demonstrated that the modification process did not change the noncrystalline structure of geopolymer.

3.3.4. FTIR analysis. The FTIR spectra of geopolymer microsphere before and after modified were shown in Figure 8. Notably, compared to the unmodified microspheres, a new characteristic feature of NH$_2$-MGS was alicyclic C-H bond stretching frequencies at 2917 cm$^{-1}$ and 2849 cm$^{-1}$, making a conclusion that organic functional group had been grafted onto the surface of MGS. The sharp feature at 1079 cm$^{-1}$ correspond to the stretching vibration of C-N bond which overlapped with the Si-O-T (T presents Al or Si) asymmetric stretching vibration at 1060 cm$^{-1}$ in the geopolymer materials. There was no feature of the N-H bond in the FTIR spectra of NH$_2$-MGS because it was obscured by the strong stretching vibration peaks of O-H in geopolymer microsphere around 3452 cm$^{-1}$ [15, 17].

![Figure 7. XRD patterns of MGS and NH$_2$-MGS.](image1)

![Figure 8. FTIR spectra of MGS, NH$_2$-MGS and AEAPTS.](image2)
4. Conclusions
In this work, the amino-functionalized metakaolin-based geopolymer microspheres were synthesized successfully by coupling agent method using AEAPTS. The occurrence of modification proved by the FTIR analysis and it did not change the noncrystalline structure of geopolymer. The modification efficiency was strongly affected by the AEAPTS dosage and modified temperature which reached the optimum with the AEAPTS dosage of 15 wt% and the temperature of 70 °C. The SEM and BET analysis confirmed that NH₂-MGS have porous structure with the pore diameter mainly distributed in 15 nm, and the specific surface area increased significantly after modified, which provided abundant active sites for adsorption of heavy metal ions. Efforts are currently underway to extending the functional groups toward the modification of geopolymer microspheres on the basis of amino graft to provide better properties for the adsorption of heavy metal ions in aqueous solution.

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