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Accelerated crystallization of magnetic 4A-zeolite synthesized from red mud for application in removal of mixed heavy metal ions

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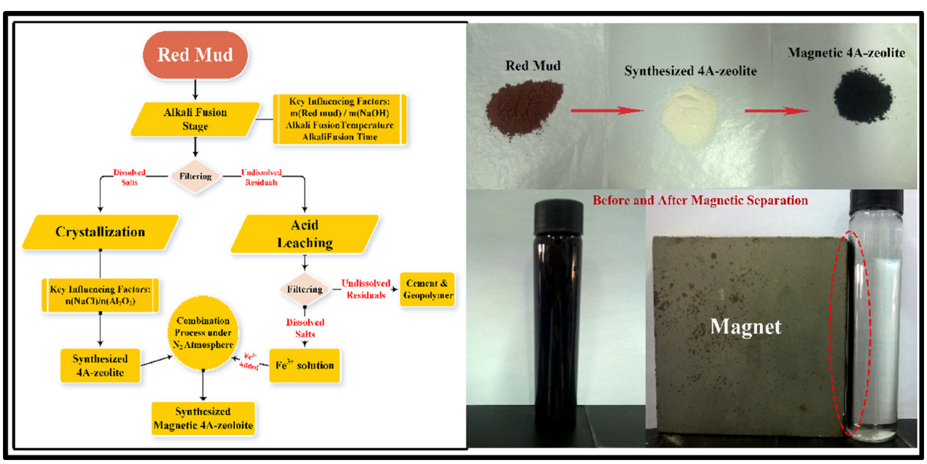
GRAPHICAL ABSTRACT

Magnetic 4A-zeolite was synthesized from red mud alone based on the comprehensive technique route and used for mixed heavy metals removal.



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ABSTRACT

To cope with the increasing environmental issues of red mud, an integrated technological route for its comprehensive utilization was developed through the extraction of valuable components and the synthesis of magnetic 4A-zeolite. To accelerate the crystallization process of the synthesized 4A-zeolite, sodium chloride (NaCl) was innovatively employed under hydrothermal treatment. The effects of various parameters, including mass ratio of red mud/NaOH, alkali fusion temperature, alkali fusion time and molar ratio of $NaCl/Al_2O_3$, were systematically investigated. The results showed that approximately 81.0% Al, 76.1% Si and 95.8% Fe were utilized from red mud using alkali fusion and acid leaching methods. The optimal conditions of the alkali fusion process were determined as: mass ratio of red mud/NaOH = 1/2, alkali fusion temperature of 800 °C, and time of 90 min. Furthermore, when the molar ratio of $NaCl/Al_2O_3$ was kept at 1.5, the crystallization time reduced from 240 min to 150 min, and particle size distributions narrowed from 20–100 μm to 1–10 μm. The practical

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applications in removal of mixed heavy metal ions (Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+}) from wastewater indicated that the as-synthesized magnetic 4A-zeolite is a promising candidate for heavy metals adsorption.

1. Introduction

Red mud is a by-product of alumina production issued during alkaline-leaching of bauxite ores using the Bayer process. Approximately 0.8–1.5 tons of red mud are generated per ton of alumina production depending on the used bauxite ores and operating conditions [1]. The disposal of red mud in landfills and sea created large negative environmental impact. The safe disposal and storage of red mud are currently under international focus and better reduction of large quantities is by reusing it [2,3]. Recent developments in red mud explored a range of industrial, environmental and engineering processes, such as adsorption of toxic gasses and heavy metals [4–8], catalysis [9,10], soil remediation [11], and framework for sewage sludge conditioning [12]. However, due to the high alkalinity of red mud, neutralization process has to be employed by seawater [13], fungus [14], or CO_2 [15] before utilization, preventing its large-scale practical application. Thus, new approaches are needed for reducing large quantities of red mud. On the other hand, red mud could be considered as a reusable secondary resource instead of waste since it contains potential valuable compounds, such as Al_2O_3, SiO_2 and Fe_2O_3. With the development of technology, various strategies have been investigated for recovering the major components of red mud. For example, Li et al. [16] used a high gradient superconducting magnetic separation (HGSMS) system to separate the extremely fine red mud particles (< 100 μm) into the high and low iron content fractions. Li et al. [17] have successfully synthesized uniform hierarchical porous γ-AlOOH microspheres via a hydrothermal route using $NaAlO_2$ leached from red mud in the presence of urea. However, most of the researches were just focused on the recovery of monocomponent from red mud, and then little attention has been paid for the other components in the residue. Therefore, to develop a comprehensive technique routine for taking full advantage of red mud components especially for Al_2O_3, SiO_2 and Fe_2O_3 as secondary resource would be of inherent economic value. Among the methods employed for recycling valuable components from red mud, the synthesis of zeolite attracted a great deal of attention [18–22].

Among the different minerals possessing adsorbent properties, zeolite is promising for metal purification [23]. Zeolites are usually considered multiporous, referring to crystalline aluminosilicate or silica polymorph based on corner sharing TO_4 (T = Si and Al) tetrahedral. These form a three-dimensional four connected frameworks with uniformly sized pores of molecular dimensions [24]. Due to its unique pore size and framework structure, 4A-zeolite has widely been used in adsorbents [25,26], catalysis [27,28], and detergent builders [29,30]. Therefore, the synthesis of 4A-zeolite has attracted increasing interest. However, the costs of the raw materials based on pure chemical agents are relatively high for 4A-zeolite synthesis. Hence, various waste products from certain industries are being explored as ingredients to reduce production costs. Due to high SiO_2 and Al_2O_3 contents, kaolin and coal fly ash are used as the principal raw materials to reduce the cost of production and to reuse the waste materials [31–33]. In this context, red mud can be considered as a suitable alternative source due to its high silicon and aluminum contents. Although previous studies succeeded to synthesis 4A-zeolite red mud as raw materials, only Al_2O_3 and SiO_2 have been reutilized from red mud. This generated new contaminations since other elements remained in undissolved residuals. Moreover, the separation of the synthesized 4A-zeolite powder from the complex heterogeneous system remains a major challenge for large-scale industrial applications. Therefore, Fe_2O_3 as a major constituent of red mud could also be reutilized as main Fe^{3+} resources of magnetic particles for combination with the synthesized 4A-zeolite to form magnetic 4A-zeolite, which can be easily separated by simple magnetic field.

The synthesis of magnetic 4A-zeolite based on red mud alone has not yet been reported, and the most common method involves a hydrothermal process but limited by long crystallization time (4 h–13 h) [34–36]. The crystallization process of 4A-zeolite can be described through three steps, including polymerization, depolymerization, and repolymerization of the reactant gels in strong basic conditions. These steps comprise the formation, liberation and growth stages of the nuclei formed in the reactant gel, which were involved multiple equilibrium during the whole crystallization process. Some studies attempted to accelerate the polymerization/depolymerization process by adding various additives, such as TMAOH [37], TEA [38], oxyanions [39] and hydroxyl free radicals [40]. It seems that to improve the polymerization or depolymerization process of the gel can build up the repolymerization process, resulting in accelerated the crystallization. However, some of these additives are expensive and/or toxic to the environment.

Herein, sodium chloride (NaCl) with low biotoxicity and cost was innovatively employed in this study to accelerate the crystallization process of 4A-zeolite, resulting in improving the productivity. More importantly, to take full advantage of the constituents of red mud, an integrated route for comprehensive utilization of red mud was conceived, and the final undissolved residue can also be used as a potential by-product of geopolymer without further dealkaline treatment since acid digestion was employed. In our research, the effects of mass ratio of red mud/NaOH, alkali fusion temperature, alkali fusion time and molar ratio of $NaCl/Al_2O_3$, were systematically investigated. Finally, the adsorption of mixed heavy metals of the synthesized magnetic 4A-zeolite were also studied to extend their applications in terms of converting red mud into useful materials.

2. Experimental

2.1. Materials and reagents

The red mud used in this study was obtained from Zhengzhou, Henan Province, China. The chemical compositions of red mud were analyzed by X-ray fluorescence (XRF) (Table 1), and found to contain mainly Al_2O_3, SiO_2, Fe_2O_3 and Na_2O. Hydrochloric acid (HCl, analytical grade), sodium hydroxide pellets (NaOH, analytical grade) and ferrous chloride ($FeCl_2$, analytical grade) were used to prepare magnetic 4A-zeolite. The water used for preparing all solutions was obtained from Milli-Q deionized water system.

2.2. Synthesis of magnetic 4A-zeolite

Three steps were employed to produce magnetic 4A-zeolite from red mud. The first step was based on reutilizing Al, Si and Fe components from red mud by using alkali fusion and acid leaching methods. Different mass ratios of red mud/NaOH were prepared, placed in a graphite crucible and calcined in a muffle furnace. The alkali fusion

Table 1
Chemical compositions of red mud (wt.%).

	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	CaO	Others[a]	LOI[b]
Red mud	16.56	17.75	23.96	2.08	21.11	8.01	9.83

[a] K_2O, TiO_2, SO_3, MgO, MnO, and ZrO_2.
[b] LOI: Loss on ignition.