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Synthesis of magnetic zeolite at low temperature using a waste material mixture: Fly ash and red mud

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ABSTRACT

A low temperature environmentally friendly synthesis of magnetic zeolites by hydrothermal activation is reported. The novelty of the process is related to the use of a mixture of waste materials (fly ash (FA) and red mud (RM)) as precursors for the one-step synthesis (without passing through the additional synthesis of magnetic nanoparticles) of zeolites with good magnetic properties. The structural and magnetic investigation indicated that different types of zeolites were obtained for different FA/RM percentages and incubation temperatures, and all of these zeolites possess sufficiently high magnetic moments to enable their easy separation from the solution using an external magnet. Therefore, the time consuming and expensive high performance centrifugation processes, which are typically employed to recover zeolites, can be eliminated. In detail, sodalite and mixed Ti–Fe oxides formed using the 80% RM mixture, and a higher amount of A-type zeolites was observed for the 50% RM mixture. However, a mixture of A-, X- and ZK-5-type zeolites was obtained using 20% RM. The global magnetic properties of the newly formed minerals are discussed based on the magnetic properties of the precursors in which different magnetic behaviours were observed. A preliminary characterisation of the synthetic products was performed.

1. Introduction

Zeolites are hydrated aluminosilicate minerals consisting of a three-dimensional open structure with excellent ion exchange and sorption properties, which makes them notably useful for resolving the mobility of toxic elements in a number of environmental applications [1,2]. Their effectiveness is strictly connected to their typical structural characteristics, which facilitate pollutant adsorption and encapsulation. Magnetic zeolites have been successfully employed to remove contaminants from polluted water [3–10]. The main advantage of these zeolites is their easy removal from the medium using an external magnetic field [11]. Therefore, wastewater treatment becomes simpler than the conventional process, which involves a time and energy consuming centrifugation or filtration step. Zeolites can be synthesised using various processes [12–16]. However, two methods are primarily used to form magnetic zeolites. The first method involves the precipitation of magnetic nanoparticles on the zeolite surface [3,4], and the second one involves the modification of zeolites with magnetic particles [5–9]. In both cases, the addition of iron oxide magnetic nanoparticles is employed.

In this paper, a new method is proposed to synthesise magnetic zeolites with suitable magnetic properties without passing through the step involving the preparation of magnetic nanoparticles. Another interesting aspect of the proposed synthesis is that the precursors employed for the synthesis are waste materials, such as red mud (RM) and fly ash (FA), which are abundant, easy to recover and inexpensive. In addition, large amounts of FA and RM are deposited in landfills resulting in an increasing environmental problem.

The two waste materials were chosen for use in this synthesis because they both contain iron-based oxides, which are the most common magnetic materials used to induce magnetic properties in zeolites. In particular, RM is a waste material formed during the production of alumina when the bauxite ores are subjected to caustic leaching. The risk associated with red mud wastes is primarily due to the cumulative contamination of land and the surrounding dwellings. RM wastes are mineralogically characterised by the presence of iron oxy-hydroxides (i.e., primarily hematite

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and goethite) with a minor aluminium hydroxides (i.e., boehmite). Calcium oxides, titanium oxides, aluminosilicate minerals and sodalite occur as traces [17,18]. However, the RM mineralogical composition varies due to the differences in the bauxite ores and the refining processes employed [19–21]. To the best of our knowledge, much research has been focused on RM utilisation in different remediation technologies [22–25] as well as comprehensive characterisation of its properties. However, the use of this waste material for zeolite synthesis has not been previously reported. Fly ash is a by-product of thermal power plants and is used in concrete and cement manufacturing. FA is primarily composed of amorphous aluminosilicate and minerals, such as quartz and mullite. In addition, hematite, magnetite and carbon may also be present. More than half of fly ash is disposed of in landfills but in the last few years, much research has been focused on its use in solutions to environmental problems [26–31] as well as for the synthesis of zeolites [32–37].

In this study, the synthesis of zeolites using three mixtures of variable percentages of RM and FA is described. We synthesise magnetic zeolites at low temperatures without the addition of iron oxide magnetic nanoparticles. The magnetic properties of the precursors and final materials have been investigated to better understand the origin of the magnetic behaviour of these composites. The zeolites exhibited the desired magnetic properties, and they can be easily separated and recovered using an external magnet. A preliminary characterization of adsorption properties of the final synthetic products was performed to verify their potential application in addressing water pollution problems.

2. Materials and methods

A sample of FA from an Italian thermoelectric power plant, and RM from the aluminium extraction in an area close to the city of Podgorica (Montenegro) were used. Chemical analyses of the major elements of both source materials were performed using X-ray fluorescence (XRF) (Philips PW 1480). The mineralogical composition was determined by X-ray diffraction (XRD) using a Rigaku Rint 2200 powder diffractometer with Cu-Kα radiation and a graphite monochromator. Laboratory spectral analyses were performed on the RM. Reflectance spectra were recorded using an Analytical Spectral Devices (ASD) Field Spec Fr Pro spectroradiometer (details are available at: http://support.asdi.com). Radiance in the 350–2500 nm spectral range was measured and converted to reflectance using a calibrated Spectralon panel. The spectroradiometer was equipped with a contact probe containing a high-intensity (4.5 W) quartz–halogen lamp. The spectra were recorded in a dark room on sieved and oven dried samples that were approximately 3 cm thick and placed on Petri dishes from a vertical distance of approximately 3 cm. Ten replicated spectra were recorded and averaged, and the Petri dish was rotated for each measurement to reduce directional effects.

The pure mineral spectra (hematite, goethite and gibbsite) were measured on a custom-modified, computer-controlled Beckman spectrometer at the USGS Denver Spectroscopy Lab, USA. Wavelength accuracy was of the order of 0.5 nm in the near-IR and 0.2 nm in the visible. The full details of the spectral library and the descriptions of the samples are available at: http://speclab.cr.usgs.gov/. The zeolite synthesis was performed using three mixtures of FA and RM. The mixtures were fused at 600 °C with NaOH (1:1.2 weight ratio), mixed with distilled water and stirred overnight at room temperature [34,35]. Next, the solutions were incubated for 4 days at 25, 30, 35 and 40 °C. Then, the solids and solution were separated by centrifugation. The solids were washed with distilled water, dried and characterised using a high resolution scanning electron microscope (SEM; Zeiss Supra 40) equipped with an energy dispersive spectrometer (EDS), XRD and laboratory spectral analysis.

Table 2
Composition of fly ash (FA) and red mud (RM) mixtures.

	FA (%)	RM (%)	Si/Al
20RM	80	20	1.57
50RM	50	50	1.38
80RM	20	80	1.05

Field and temperature dependent magnetic properties were investigated using Quantum Design SQUID and VSM (Model 10 – Microsense) magnetometers.

The magnetic zeolite adsorption properties were determined using a batch adsorption test with Reactive Orange 16 (RO16).

The supernatant solutions were separated by applying a magnetic field. The absorbance was read at 493 nm with a UV–Vis-NIR 05E Cary spectrometer UV–visible spectrometer (Cary 500) on supernatant solutions. The adsorption percentage was determined by the following equation:

$$A\% = (A_i - A_f)/A_i \times 100$$

where $A\%$ is the adsorption percentage and A_i and A_f represent the initial (RO16 absorbance) and final absorbance (samples absorbance), respectively.

3. Results and discussion

Table 1 shows the chemical composition of both starting materials, and in Table 2, the weight percentage of fly ash and red mud in the mixtures is reported.

FA samples are characterised by 46.80% SiO_2 and 28.21% Al_2O_3, and the percentage of these oxides in RM is 7.89% and 11.46%, respectively. The amounts of MgO and K_2O are low and quite comparable in both samples, and the percentages of CaO and Na_2O are higher in FA and in RM, respectively. The chemical composition and relative Si/Al ratio make the FA and RM mixtures suitable for X- and A-type zeolite synthesis. In addition, the high percentage of Fe_2O_3 in FA and RM (i.e., 5.23% and 36.8%, respectively) indicates the possibility of their use for the synthesis of magnetic zeolite.

XRD patterns of the untreated fly ash and red mud are shown in Fig. 1. FA is mainly formed by amorphous aluminosilicates; mullite and quartz are also present. RM is primarily composed of hematite/goethite/pyrite and gibbsite. Calcite and sodalite are also present. The dominant RM spectral features in the visible and near-infrared (VNIR) region (400–1000 nm) are preliminary related to the iron oxides (hematite – α-Fe_2O_3 and goethite – FeO(OH)), and the short wave infrared (SWIR) range (2000–2500 nm) indicates the presence of gibbsite (Fig. 2) [38]. Regarding the iron oxides absorption features, hematite (Fe_2O_3) shows a spectral behaviour similar to the RM spectrum in the VNIR spectral range (from 450 to

Table 1
Chemical composition (major constituents-wt.%) of fly ash (FA) and red mud (RM) samples used for the experiments.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
FA	0.54	1.43	28.21	46.80	0.78	1.26	5.57	1.49	0.06	5.23
RM	4.03	0.21	11.46	7.89	0.09	0.45	3.53	4.82	0.21	36.8