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Short communication

# Modification of synthesized β-zeolite by ethylenediamine and monoethanolamine for adsorption of $Pb^{2+}$

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ABSTRACT

β-Zeolite was synthesized and modified with monoethanolamine (MEA) and ethylenediamine (EDA). The synthesized materials were characterized by X-ray diffraction, FT-IR, TG/DTG and SEM techniques. The adsorbents were used for removal of $Pb^{2+}$ from aqueous solutions. The effect of the solution pH, contact time, metal ions concentration, and temperature was studied. The results indicated that adsorption of $Pb^{2+}$ on the surface of the adsorbents depended on the solution pH and was maximized at pH = 4.0. The adsorption isotherms were evaluated with reference to Langmuir and Freundlich models. Thermodynamic studies showed that the adsorption process was endothermic and spontaneous.



## 1. Introduction

Zeolites constitute an important class of material and are found wide application in the environment. Zeolites, especially β-type zeolite, have been widely used in many aspects, such as separation and catalysis [1]. β-Zeolite has been known since 1967, when it was synthesized by using tetraethyl ammonium ion as structure directing agent [2]. It is a high-silica zeolite possessing a three-dimensional system of large rings (rings of 12 oxygen atoms as the minimum 2 constricting apertures).

Considerable attention has been paid to the functionalization of mesoporous silicas because of their large surface areas, uniform mesopores and tuneable pore size [3]. Most of the studies in adsorbent modification have been concerned to the functionalization with thio-groups for mercury removal from aqueous solutions. However many other heavy metals are efficiently adsorbed on adsorbent modified with organic chains containing one or more amino group [4–6]. Functionalization of clinoptilolite by cysteamine and propylamine for removal of $Pb^{2+}$ has been reported [7]. Rios et al. reported caesium and cobalt removal by functionalized ZSM-5 and Y-zeolite [8,9]. The aim of this research was to prepare a new adsorbent with high adsorption capacity and with regeneration ability for removal of $Pb^{2+}$ from aqueous solutions. Therefore β-zeolite which has received much attention because of its regular porous structure with excellent stability was employed and was functionalized by ethylenediamine and monoethanolamine. The adsorption capacity of the functionalized adsorbents was studied under different experimental conditions.

## 2. Experimental

### 2.1. Synthesis and modification of β zeolite

β-Zeolite was synthesized by hydrothermal method. A mixture containing 120 g of tetraethyl ammonium hydroxide (20 wt% in water), 2.23 g of $NaAlO_2$, 0.90 g of KCl and 0.15 g of NaOH was stirred until became transparent. Then 32.60 g of aerosil-200 was added to the mixture. The resulting homogeneous sol was transferred into a Teflon-lined stainless-steel autoclave and heated to 170 °C statically. After 40 h, the autoclave was quenched, the content filtered, and the solid was washed with deionised water. After drying at 96 °C overnight, the product was calcined at 540 °C for 20 h [1].

To prepare amine functionalized adsorbent, 5.0 g of β-zeolite was mixed with 60 mL or monoethanolamine or ethylenediamine solution in a 250 mL reaction flask. The mixture was refluxed for 36 h. The reaction mixture was poured into cold water and the solid was filtered and washed with 0.1 M NaCl solution until the filtrate was free from amine. The remaining NaCl was washed with water followed by methanol. The functionalized adsorbents were dried at 70 °C and designated as β-zeolite-MEA and β-zeolite-EDA

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for the sample functionalized respectively with monoethanolamine and ethylenediamine.

### 2.2. Characterization of the adsorbent

Zeolite and the modified samples were characterized by a series of complementary analytical techniques. The XRD patterns were prepared by X-ray diffractometer (Bruker, Diffraktometer D8 ADVANCE, Germany) using CuKα as radiation source and Ni as filter. The range of scanning angle ($2\theta$) was between 3° and 70° with scanning rate of 5°/min. Infrared Fourier transform spectroscopy was carried out (Nicolet 400 D Impact spectrum single FT-IR machine) at wavenumbers of 400–4000 $cm^{-1}$ by using KBr pellet. The thermal curves were obtained using a Setar Am TG-DTG thermobalance (range 25–700 °C). The atmosphere was pure nitrogen and the heating rate of 10 °C $min^{-1}$ was used [10,11].

### 2.3. Adsorption experiments

Batch adsorption experiments were conducted in 100 mL stoppered reagent bottles. A measured amount (0.10 g) of the adsorbents was placed into the bottles, which containing 25 mL of various concentrations of $Pb^{2+}$ solution. The solution pH was adjusted to the desired value by adding hydrochloric acid or ammonia solution and the bottles were shaken at room temperature for a prescribed length of time to attain equilibrium. After filtration, the concentration of $Pb^{2+}$ was measured using GF-AAS. The effect of the initial ion concentration (150–4000 mg $L^{-1}$), contact time (30–1660 min) and solution pH (2.0–5.0) on the adsorption of $Pb^{2+}$ was studied.

### 2.4. Reusability of the adsorbent

To regenerate the adsorbent, the used adsorbent loaded with $Pb^{2+}$ was equilibrated with 0.2 M $HNO_3$ solution. The mixture was filtered and the $Pb^{2+}$ concentration was measured in the solution. The regenerated adsorbent was reused for adsorption of $Pb^{2+}$ at the optimized conditions. This procedure was repeated for four consecutive adsorption–desorption cycles.

## 3. Results and discussion

### 3.1. Characterization of synthesized adsorbents

The XRD patterns of the parent and the modified zeolite are given in Fig. 1. The location of diffraction lines which remained unchanged indicated that the structure of β-zeolite was well preserved after introduction of the amines. Nevertheless, the intensity of diffraction lines decreased as the amines were introduced. That was in agreement with the results reported by Xia and Xu results [1,2].

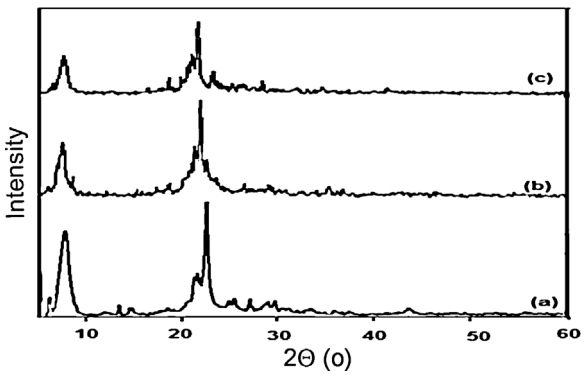


**Fig. 1.** XRD patterns of (a) β-zeolite, (b) β-zeolite-MEA and (c) β-zeolite-EDA.

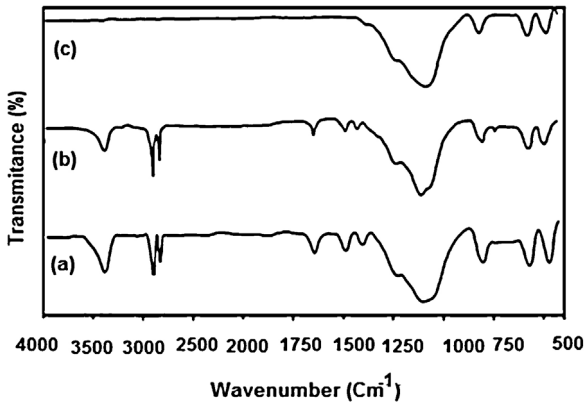


**Fig. 2.** F T-IR spectra of (a) β-zeolite, (b) β-zeolite-MEA and (c) β-zeolite-EDA.

The FT-IR spectra of β-zeolite and modified samples are provided in Fig. 2. The characteristic band at 1080–1090 $cm^{-1}$ which was observed in all spectra was attributed to the Si–O stretching of Si–O–Si structure. The absorption band due to H–O–H bending vibration of zeolite water was appeared at 1600–1645 $cm^{-1}$. The broad band appeared around 3100–3600 $cm^{-1}$, was assigned to $NH_2$. In the amine modified samples the N–H bending vibration was observed at 792–795 $cm^{-1}$ and $NH_2$ symmetric bending vibration at 1485–1579 $cm^{-1}$ [10,12,13].

In the TG/DTG profiles of β-zeolite (Fig. 3), a single continuous weight loss step from room temperature to 150 °C was observed which was attributed to desorption of water molecules. In the profiles of the modified samples three distinct weight loss steps at 90, 250 and 380 °C were recorded. Since MEA and EDA have the boiling point of 170.8 and 182 °C respectively, the second and third peaks were attributed to volatilization and degradation of MEA and EDA [14].

SEM method was used to study the morphology of the samples (Fig. 4). The images revealed that the surface morphologies of the zeolite and the modified samples were different. In β-zeolite massive, aggregated morphology and some large flakes were observed. After modification, the zeolite surface was changed to a loss-aggregated morphology and there are a large number of small white flakes with severely crumpled structures. The morphological changes of the samples were attributed to the change in the surface charge of the particles after zeolite was modified with amines species [14].

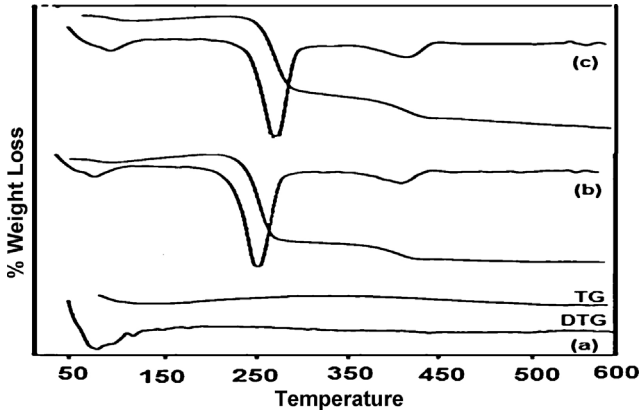


**Fig. 3.** Thermal curves (TG–DTG) of (a) β-zeolite, (b) β-zeolite-MEA and (c) β-zeolite-EDA.