



Role of modification of natural zeolite in removal of manganese from aqueous solutions



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ABSTRACT

The natural zeolite (NZ) was obtained from Sivas-Yavu of Turkey and modified by ion-exchange (NH_4NO_3), alkali treatment (NaOH) and addition of aluminum ($\text{Al}_2(\text{SO}_4)_3$). The natural and modified samples were characterized by XRF, XRD, N_2 sorption, FTIR, NH_3 -TPD, particle size distribution, SEM and TGA. Ion-exchange with NH_4^+ of NZ results in the exchange of the Na^+ and Ca^{2+} cations and the partial exchange of the Fe^{3+} and Mg^{2+} cations. While the treatment of the NZ with NaOH leads to insignificant change of almost all cations, it causes significant dealumination and desilication of the NZ. FTIR and TGA results showed that decationization, dealumination and desilication give rise to a decrease in hydrophilic nature of NZ. However, manganese adsorption of samples enhances their hydrophilic nature. Ion exchange and aluminum introduction increase surface area and pore volume of samples as well as surface acidity, whereas alkali treatment with NaOH decreases them due to partial collapse of structure with significant desilication and dealumination. All modifications, ion exchange, alkali treatment, and aluminum introduction, increased two times the manganese adsorption capacity of natural zeolites. The Freundlich isotherm model was best fitted to the isotherm data obtained due to a heterogeneous surface existence.

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1. Introduction

Manganese is an abundant material in the Earth's crust and its presence in drinking water is a result of leaching process depending on rock types. The pyrolusite (MnO_2) and manganese bromide (MnBr_2) minerals exist in the Sivas region of Turkey and they dissolve in drinking water and exceed the maximum contaminant level depending on seasonal variations. In addition, manganese mineral may come from various industrial sources such as electroplating, metal finishing, metallurgy, chemical manufacturing, mining, and battery manufacturing. In Turkey, the maximum level of Mn^{2+} permitted in drinking water is $0.1 \text{ mg} \cdot \text{L}^{-1}$ whereas for the United States Environmental Protection Agency (EPA) this concentration must be lower than $0.05 \text{ mg} \cdot \text{L}^{-1}$. Because of health legislations, the level of manganese in drinking water must be reduced and therefore the conventional methods applied can be listed as follows: membrane filtration [1,2], chemical precipitation [2], and ion exchange [3] with silica [4] and active carbon [5]. In addition, the adsorption process provides an attractive alternative treatment because of its more economic and easy operation if a suitable adsorbent is chosen or designed. Some natural materials such as zeolites, chitosan and clay have been considered as alternative low cost adsorbents [6].

A summary of manganese adsorption over various adsorbents is listed in Table 1. The highest manganese adsorption capacity is

observed in the iron loaded clinoptilolite. The adsorption capacity of clinoptilolite-rich natural zeolites varies depending on their source. For example, the adsorption capacity of the clinoptilolite obtained from Greece is higher than that of Turkey, showing that the adsorption capacity of the zeolite mostly depends on the characteristics of the zeolite such as composition, the size and distribution of pores and crystal structure. However, unmodified natural zeolites for removal of manganese have low adsorption capacity as seen in Table 1. Therefore, to allow them to be used, the characteristics of natural zeolites have to be improved by various methods such as ion exchange with alkali bases and aluminum introduction [7–17].

Our previous study showed that NH_3 treatment of the zeolites leads to mostly exchange of Na^+ and Ca^{2+} with NH_4^+ and partly exchange of Fe^{3+} and Mg^{2+} in zeolites [8]. Based on previous studies in references [10,11,13,17], the treatment of zeolites with NaOH leads to dissolution of silica and partial removal of aluminum, resulting in an increase in the ratio of Si/Al and the formation of mesopores. The removal extent of silica and the formation of mesopores are a function of the concentration of NaOH used [9,13,25–27]. Mostly, the treatment of zeolites with alkali solutions is an effective method for selective silica removal without significant changes in their acidity and crystal structure [28]. The formation of mesopores via removal of silica from structure has been performed for several synthetic zeolites such as ferrierite (FER) [29], beta [30], ZSM-22 [31], mordenite [32], and ZSM-5 [33–38]. Groen et al. [29,32,35–37] reported that the formation of mesopores necessitates a range of 25–50 of Si/Al. Then, Verboekend et al. [38] showed

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the formation of mesoporosity in a range of 12–200 of Si/Al after mild acid treatment following NaOH treatment.

The participation of aluminum into zeolites was studied by Kamali et al. [15] using aluminum sulfate and sodium aluminates as aluminum sources and natural zeolite as a silica source and increased adsorption capacity of the zeolite.

Based on the aforementioned results, this study deals with the modification of natural zeolite originated from Sivas-Yavru of Turkey via ion exchange with NH_3 , treatment with NaOH and introduction of aluminum for removal of manganese from aqueous solution. Chemical and physical properties of natural and modified zeolites were characterized by various techniques such as XRF, XRD, N_2 sorption, FTIR, NH_3 -TPD, particle size distribution, SEM and TGA. The influence of specific adsorption parameters on removal of manganese from aqueous solution was studied and the data obtained were applied to isotherm models.

2. Experimental

2.1. Material

The natural zeolite obtained from the Sivas-Yavru (NZ) region of Turkey was examined. The zeolite was first ball milled to particle size in a range of 0.25–0.5 mm and dried in an oven at 120 °C overnight. The zeolite was transformed to the NH_4 -form by a twofold exchange with a 0.5 M NH_4NO_3 solution at 80 °C. After washing and drying, the sample was calcined at 500 °C for 2 h and denoted as NH_4 -NZ.

After washing and drying, 1 g of the NZ was mixed with sodium hydroxide and water with 5:50 mass ratios for 1 h at 90 °C and then the mixture was filtered and the filtrate was denoted as Na-NZ.

Preparation of aluminum introduced zeolite is based on the study of Kamali et al. [15]. For preparation of aluminum solutions, sodium chloride, aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) and water with 1:5.4:10 mass ratios were mixed to make a clear solution (solution A). Aluminum sulfate, sodium hydroxide and water with 1:1.5:7.8 mass ratios were mixed and heated to make a clear solution (solution B). The A, Na-NZ and B with 1:7.1:1 mass ratios were mixed at 90 °C for 2 h with a mixing rate of 500 rpm. The product was filtered, washed and dried at 80 °C. The product was denoted as Al-NZ.

2.2. Characterization of samples

The chemical composition of the zeolites was investigated using an X-ray fluorescence (XRF, PANalytical) analyzer.

X-ray powder diffraction (XRD) patterns of zeolites were recorded on a Rigaku SmartLab X-ray diffractometer using non-monochromotographic $\text{Cu K}\alpha$ 1-radiation (40 kV, 40 mA, $\lambda = 1.5$). Scanning was in the range of 5–65 °C of 2θ .

The morphology of the natural and modified zeolites was examined by a LEO440 Scanning Electron Microscope (SEM).

The specific surface area and micropore volume of the samples were measured using N_2 adsorption–desorption (AUTOSORB 1C) at –196 °C. Prior to adsorption, the samples were evacuated until a pressure of 66.6 Pa at room temperature was reached, then heated up to 350 °C and evacuated until a pressure of 1.3 Pa was reached. This condition was maintained overnight. The surface area, pore volume and micropore volume were determined by multipoint BET, DFT (Density Functional Theory) and DR (Dubinin–Radushkevich), respectively.

Infrared absorption measurements were carried out using a Fourier transform infrared (FTIR) spectrophotometer (Perkin-Elmer Spectrum One). The FTIR spectra were obtained in the wavenumber range of 650–4000 cm^{-1} with the use of ATR.

The temperature-programmed desorption with ammonia (NH_3 -TPD) was carried out in Autochem II-2920, Micromeritics. The samples were saturated with a flow of 15 (v/v)% NH_3 in He at 50 °C. Subsequently, NH_3 was desorbed in a He flow of 25 $\text{cm}^3 \text{min}^{-1}$ up to a temperature of 700 °C with ramp rate of 10 K min^{-1} .

Table 1
Manganese adsorption capacity of different materials.

Material	Mn uptake ($\text{mg} \cdot \text{g}^{-1}$)	Reference
Clinoptilolite–Fe system	27.2	[18]
Clinoptilolite of Greece	7.69	[18]
Clinoptilolite of Turkey	4.22	[19]
Na-montmorillonite	3.22	[20]
Granular activated carbon	2.54	[21]
Dolomite	2.21	[22]
Marble	1.20	[22]
Quartz	0.06	[22]
Brazilian natural scolecite	37.5	[23]
Natural zeolite of Turkey	19.0	[24]

Thermogravimetric analysis (TGA) of fresh and manganese adsorbed adsorbents was carried out using the TGA-50 analyzer (Shimadzu) at a heating rate of 10 K min^{-1} from ambient temperature to 900 °C. Manganese adsorbed NZ (NZ-Mn_x) and Al-NZ (Al-NZ-Mn_x) are prepared by mixing adsorbents with manganese solutions for 24 h in which x denotes concentrations of manganese solutions.

The particle size distribution of samples in solutions was measured using a Malvern particle size analyzer (Mastersizer 3000 MS).

2.3. Adsorption experiments

Batch adsorption experiments were carried out in a glass flasks (0.1 L) using a magnetic shaker at 25 °C at a constant agitation of 200 rpm. In the kinetic studies suspensions containing a range of 25–250 $\text{mg} \cdot \text{L}^{-1}$ of Mn^{2+} were stirred for different periods of time at initial pH of 6. After the reaction, suspensions were centrifuged at 5000 rpm for 3 min in order to separate the solution and the solids. The initial and non-adsorbed concentrations of Mn^{2+} in supernatants were determined by atomic absorption spectroscopy (AAS).

Adsorption studies of Mn^{2+} onto NZ, NH_4 -NZ and Al-NZ were conducted using the same procedure in sufficient time for attaining equilibrium, 240 min for NZ and NH_4 -NZ and 24 h for Al-NZ, and for varying feed solution concentrations (25–200 $\text{mg} \cdot \text{L}^{-1}$). All results were averaged values of duplicate tests.

The adsorption capacity (q_e , $\text{mg} \cdot \text{g}^{-1}$) and removal percent (%) of Mn^{2+} were determined using following equations:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2.1)$$

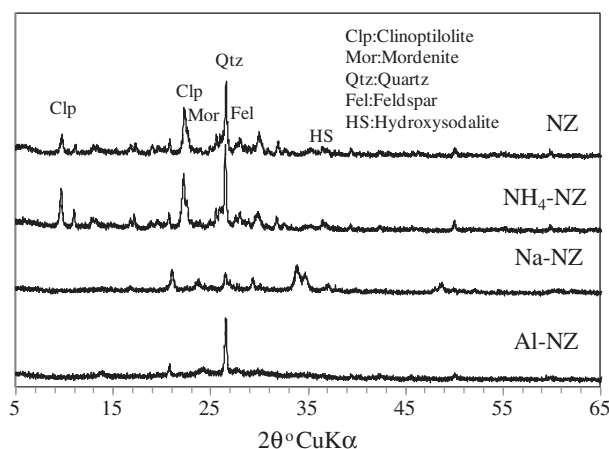


Fig. 1. XRD patterns of natural and modified zeolites.

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