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Investigation on natural and pretreated Bulgarian clinoptilolite for ammonium ions removal from aqueous solutions

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ABSTRACT

The possibilities for ammonium ions removal from aqueous solutions by natural and NaCl pretreated Bulgarian clinoptilolite from Beli plast deposit were studied. Experiments were carried out using batch method. The adsorption of NH_4^+ was investigated as a function of the solution pH, dosage of adsorbent, initial ammonium concentration and temperature. The results clearly showed that the treatment with NaCl improved both the adsorption capacity and the removal efficiency of natural clinoptilolite. The equilibrium experimental data for adsorbed NH_4^+ ions on clinoptilolite samples were correlated better by the Langmuir isotherm model. The maximum adsorption capacities for ammonium ions shown by natural and pretreated clinoptilolites (CL_Na and CL_Na(t)) were 7.85, 12.29 and 18.40 mg/g, respectively. The results indicated a significant potential of the natural and conditioned clinoptilolites as adsorbents for ammonium removal.

1. Introduction

Nitrogen compounds are very essential elements for living organisms. The presence of excess N compounds causes environmental pollution. Therefore, the control on them is important for the protection of public health. Ammonia and ammonium ions are the more commonly encountered N compounds in waste water and groundwater. There are different methods for removing ammonium ions from wastewaters: air stripping, chemical treatment, selective ion exchange, adsorption and biological nitrification–denitrification [1–7]. Previously we reported that carbon obtained from Bulgarian lignite from Chukurovo deposit by one-step steam pyrolysis-activation followed by oxidative modification gave comparable results despite its worse texture parameters as compared with Norit GAC 1240 oxidized in an analogous way and was a more promising adsorbent as a means of ammonia removal from aqueous solutions [8].

Clinoptilolite, which has a high affinity for the ammonium ion, is one of the most important natural zeolites because it is found in large deposits worldwide. The various aspects of removal from aqueous solutions by clinoptilolite have been investigated by many researchers [6,7,9–15]. It is reported to have a classical alumina silicate age-like structure. The general formula of a zeolite is as follows:

$$(M_x{}^{+}, M_y{}^{2+})(Al_{(x+2y)}Si_{n-(x+2y)}O_{2n})\cdot mH_2O$$

where M^+ and M^{2+} are univalent and divalent cations such as Na^+, K^+, and Ca^{2+},Mg^{2+}, Ba^{2+}, respectively. They are called exchangeable cations. Al^{3+} and Si^{4+} are known as structural cations. They make the framework of the structure with O [13]. Pretreatment of natural zeolites by acids, bases, surfactants, etc. is an important method to improve their ion-exchange capacity [15–19]. The chemical treatment of clinoptilolite is aimed at removing certain cations from its structure and locating more easily the removable ones, prior to its application. Conditioning with NaCl causes an increase in Na^+ and a decrease in Ca^{2+} concentrations in clinoptilolite, this leading to an increase of the ratios Na^+/Ca^{2+}. Despite the large number of different studies on the removal of ammonium ions from aqueous solutions using clinoptilolite, every special material requires individual research. Therefore, such studies are important for future practical use of this natural material in wastewater treatment. The purpose of this paper is to investigate the removal efficiency of ammonium ions from aqueous solutions using natural and treated Bulgarian clinoptilolite and to characterize equilibrium isotherms.

2. Materials and methods

2.1. Characterization of clinoptilolite

A sample of clinoptilolite was taken from Beli plast deposit in Eastern Rhodopes, Bulgaria. The chosen clinoptilolite was crushed and classified to a size range of 0.2–1.0 mm. Then it was washed

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to remove the water-soluble residues and other undesirable material, and dried in an oven at 378 K for 24 h before its use in the experiments. The clinoptilolite sample was characterized by X-ray diffraction (XRD) and chemical analysis. The chemical composition was determined by analytical methods usual for silicate materials. Characterization of the texture parameters of clinoptilolite was carried out by low-temperature adsorption of nitrogen (77 K) using a conventional volumetric-measuring apparatus. The nitrogen adsorption isotherms were analyzed to evaluate the following parameters: the specific surface areas, the total pore volume and average pore diameter. The clinoptilolite sample was outgassed at 473 K for 6 h under vacuum (10^{-3} Torr) before N_2 adsorption.

2.2. Pretreatment procedure of clinoptilolite

Ammonium ions adsorption studies were carried out using three different clinoptilolite forms, natural and treated samples:

- Sample 1 (CL): natural clinoptilolite.
- Sample 2 (CL_Na): natural clinoptilolite treated with 2 mol/L NaCl solution at 293 K. An aliquot of 10 g was transferred to a conical flask containing 100 mL of 2 mol/L NaCl solution. The suspension was magnetically stirred over a period of 24 h and was separated from the supernatant by filtration. The clinoptilolite sample was then washed with deionized water until no more Cl^- was detected in the washing water. The pretreated sample was dried at 378 K for 6 h and stored in a desiccator until further use.
- Sample 3 (CL_Na(t)): the third sample of clinoptilolite was prepared by treating clinoptilolite with 2 mol/L NaCl solution (clinoptilolite/solution ratio of 100 g/L) at 363 K over a period of 7 h in thermostat. After a cool-down period, the sample was filtered and washed with distilled water. After washing, the Na-modified clinoptilolite was dried at 378 K for 6 h.

2.3. Adsorption studies

Batch experiments were performed in a stirred system at 293 K except for the experiment on the effect of temperature. The experiments were carried out in plugged 50-mL Erlenmeyer flasks containing 0.25 g clinoptilolite sample and 25 mL NH_4Cl solution. On reaching equilibrium the adsorbent was eliminated by filtering through a Millipore filter (0.2 μm). Initial and equilibrium concentrations of ammonium ions were determined spectrophotometrically with a Berthelot reactive using a Spekol 11 apparatus. The amount of NH_4^+ ions adsorbed by the clinoptilolite sample at equilibrium (Q_e, mg/g) was calculated using the expressions:

$$Q_e = (C_0 - C_e) \times \frac{V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of NH_4^+ (mg/L), respectively. V is the solution volume (L) and m is the adsorbent weight (g).

Analytical grade ammonium chloride (NH_4CI) and deionised water were used for the preparation of the stock NH_4^+ solutions. The working solutions containing different concentrations of NH_4^+ in the range 50–250 mg/L were prepared by stepwise dilution of the stock solutions. The initial pH value was adjusted by addition of NaOH or HCl to the designed value.

3. Results and discussion

3.1. Characterization of clinoptilolite

The chemical and mineralogical composition and the main texture parameters of the natural clinoptilolite are presented in Table 1.

Table 1
Chemical, mineralogical and structural characteristics of natural Bulgarian clinoptilolite.

Parameter	Value
Chemical analysis	
SiO_2, %	70.43
Al_2O_3, %	11.11
Fe_2O_3, %	1.89
Na_2O, %	1.35
K_2O, %	3.62
CaO, %	2.36
MgO, %	0.38
H_2O, %	6.92
Other, %	1.94
Si/Al	5.3
XRD analysis	
Clinoptilolite, %	83
Cristobalite, %	5
Heulandite, %	7
Quartz, %	2
Albite, %	2
Microcline, %	1
Surface area, m^2/g	26.0
Total pore volume, cm^3/g	0.082
Average pore radius, nm	20.4

As can be seen from Table 1, it contained significant amounts of SiO_2 (70.4%) and Al_2O_3 (11.1%), while the contents of other metal oxides were less than 11%. Cristobalite, heulandite, quartz, albite and microcline are the main mineral admixtures (17%). The low-temperature nitrogen adsorption on natural clinoptilolite (Fig. 1) is expressed by IV-type isotherm with a hysteresis loop of the type H3 by IUPAC classification [20]. This type isotherm is typical for micro-mesoporous materials. The average pore diameter is 20.4 nm, corresponding to mesopores. It is established that the type H3 of hysteresis loop is usually given by the aggregates of particles or adsorbent containing slit-like pores [21]. The sharp rise of the isotherm under the lowest relative pressures may be caused by the presence of free micropores in the clinoptilolite sample. The specific surface area of Bulgarian clinoptilolite is 26.0 m^2/g. The relatively low values of specific surface area and pore volume found for CL (26.0 m^2/g and 0.082 cm^3/g, respectively) are due to the fact that N_2 cannot enter into the pores of the natural clinoptilolite and it is mainly adsorbed on the external surface of the solid.

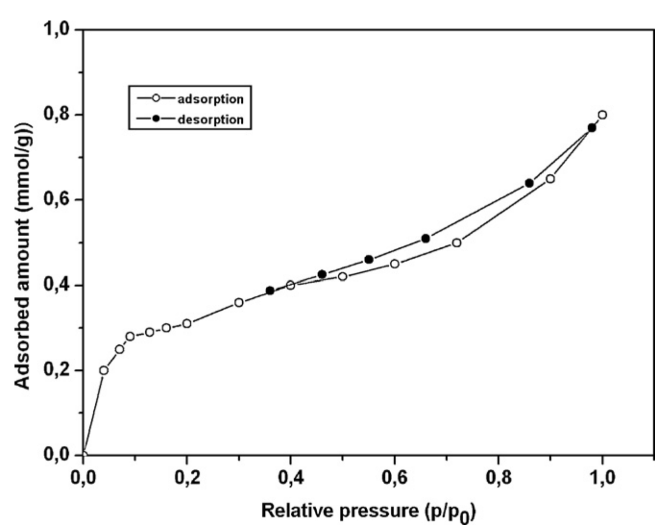

Fig. 1. Nitrogen adsorption/ desorption isotherms for initial clinoptilolite.