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Removal of ammonium and phosphates from aqueous solutions by activated and modified Bulgarian clinoptilolite

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Results from a laboratory investigation on the capability of activated and modified Bulgarian clinoptilolite samples from Beli plast deposit in Eastern Rhodopes for removing ammonium and phosphates from aqueous solutions are presented in this report. A series of ion exchange batch experiments were carried out using model water composed of NH_4Cl and $Na_2HPO_4.12H_2O$. Total ion exchange capacity was determined by batch experiments as a function of initial ammonium and phosphates concentration, solution pH and temperature. The influence of the presence of Ca^{2+} on the removal of ammonia was investigated. It was found that the adsorption and ion exchange activity of natural clinoptilolite towards phosphate ions could be increased by chemical activation and modification.

Key words: Clinoptilolite, ammonium, phosphates, ion-exchange, sorption.

INTRODUCTION

Sources of ammonium and phosphates in wastewater are municipal, agricultural and industrial wastewater. Nitrogen is presented in the form of ammonium and organic nitrogen. Ammonium nitrogen decreases the dissolved oxygen required for the aquatic life and also accelerates the corrosion of metals and construction materials. Biological nitrification and denitrification, air sripping and ion exchange are the most preferred methods of removal of NH_4^+. The ion exchange method is preferred over the other methods since it is stable, suits automation and quality control and is easy to maintain. Phosphorus can exists like orthophosphates, three polyphosphates, pyrophosphates and organic phosphorus. Orthophosphates are the prevailing form in municipal wastewater (Hultman et al., 2000). Basic sources of contamination of groundwater and surface water with nitrogen and phosphorus are infiltration of rainfall in fertilised agricultural areas and leakage from municipal sewage. Traditional methods for removing phosphorus are chemical precipitation (with aluminium, iron and calcium salts), biological process that rely on

biomass growth (bacteria, algae, plants) or intracellural bacterial polyphosphate accumulation (De-Bashan and Bashan, 2004) and sorption (natural apatite, activated carbon, etc.) (Degs et al., 2001). In recent years considerable attention has been paid to the investigation of different types of low-cost sorbents, such as alum sludge (Galarneau and Gehr, 1997), red mud (Shiao and Akashi, 1977), fly ash (Oguz, 2005), calcite, goetite, apatite and zeolite (clinoptilolites) (Tillman et al., 2005).

The study aims to determine the optimal parameters of ion-exchange of ammonium ions and sorption of phosphate ions using activated and modified Bulgarian clinoptilolite.

MATERIALS AND METHODS

Pre-treatment procedure of clinoptilolite

Clinoptilolite is composed of rings of 8 and 10 elements or 5.6 Å unit window show an ideal molecular size for ammonium ion. The zeolite that was used for the experiments is clinoptilolite and comes from Bulgaria. It has been extracted from the site of Beli Plast in the

town of Kardjali, in the Rhodopi Mountains. The cation selectivity row of the used zeolite decreases in the sequence:

$Cs^+ > Tl^+ > Rb^+ > K^+ > NH_4^+ > Ag^+ > Na^+ > Ba^+ > Pb^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$
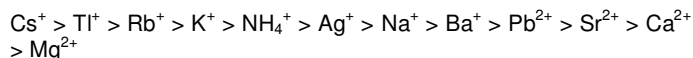
Practically the result of any pre-treatment operation is the increase of the content of a single cation what is called homoionic form. Therefore, pre-treatment aims to remove certain ions from the structure of the material and locate more easily removable ones, prior to any ion-exchange application of it (Semmens and Martin, 1998). Due to the high content of potassium ions in the structure of clinoptilolite, which block the capacity for NH_4^+ fixation, the natural material was previously exchanged with 1M solution of NaCl.

Ammonium ion-exchange studies were carried out using activated (modified) clinoptilolite samples. For the activation 100 g of a natural sample 1 M NaCl solution was used. The natural sample of clinoptilolite was treated 3 days at magnetic stir, then dried at 378 K for 5 h, washed with distilled water, dried at 378 K for 5 h and stored in a desiccator. Figure 1 shows two X-ray diffraction diagrams of natural and activated with 1M NaCl solution sample clinoptilolite.

Phospates ions adsorption studies were carried out using three types of modified clinoptilolite. Sample 1 (Cl -Al): 100 g of a natural sample of clinoptilolite was treated 3 days at magnetic stir with 1 M NaCl solution, then dried at 378 K for 5 h, washed with distilled water, treated with 6 g/LAl$_2$(SO$_4$)$_3$.18H$_2$O (500 mg/L Al^{3+}) in a batch system in a plexiglass column, dried at 378 K for 5 h, washed with 0.002 M NaOH pH=10.5 and 0.1 M HCl pH=3.5 dried at 378 K for 5 h and stored in a desiccator.

Sample 2 (Cl - Fe): 100 g of a natural sample of clinoptilolite was treated 3 days at magnetic stir with 1 M NaCl solution, then dried at 378 K for 5 h, washed with distilled water, treated with 1.5 g/L FeCl$_3$ (500 mg/L Fe^{3+}) in a batch system in a plexiglass column, dried at 378 K for 5 h, washed with 0.002 M NaOH pH=10.5 and 0.1 M HCl pH=3.5 dried at 378 K for 5 h and stored in a desiccator.

Sample 3 (Cl - Fe/Mn) 100 g of a natural sample of clinoptilolite was treated 3 days at magnetic stir with 1 M NaCl solution, then dried at 378 K for 5 h, washed with distilled water, treated with 1.5 g/L FeCl$_3$ (500 mg/L Fe^{3+}) and Mn Cl$_2$ (500 mg/L Mn^{2+}) in a batch system in a plexiglass column, dried at 378 K for 5 h, washed with 0.002 M NaOH pH=10.5 and 0.1 M HCl pH=3.5 dried at 378 K for 5 h and stored in a desiccator.

For the measurements of concentration of ammonium and phosphates the Hach-Lange cuvette tests were used.

Adsorption studies

The experiments were carried out at T=25°C with an activated sample of clinoptilolite and then with the three types of modified clinoptilolite. The clinoptilolite fraction grain size was 0.5 to 1.2 mm. The goal was to determine the total theoretical exchange capacity (TEC) of the zeolite towards ammonia ions and to determine the influence of calcium ions on this capacity.

RESULTS AND DISCUSSION

Kinetic study

The rate of ammonium removal process is a very important factor for exchanger application, since low exchange rates often pose serious limitations to the applicability of the process. The rate of reaching the ion exchange equilibrium depends on a number of

technological parameters such as the temperature, size and distribution of aluminosilicate particles, hydrodynamics of the reaction system, concentration and the hydrated radii of exchangeable ions. 100 g of activated clinoptilolite were put in Plexiglas column and saturated with ammonium in a batch system. The amount of adsorbed ammonium ions for three initial concentrations was calculated and the effect of contact time on the ion exchange process was studied. Figure 2 indicates that ammonium removal increased with increasing contact time. The adsorption rate by all sets occurred rapidly at the beginning of the contact and gradually decreased with increasing contact time. The equilibrium in the batch system is reached for 90 min for all concentrations. When using concentration of 100 mg/L all present in the solution ammonium cations are ion-exchanged. When using concentration of 500 mg/L equilibrium is reached without using the full ion-exchange capacity of clinoptilolite. When using concentration of 1000 mg/L the full ion-exchange capacity of clinoptilolite (8 meq/g) is reached.

Effect of initial ammonium and phosphates concentrations

When determining the sorption capacity of a filter material with an agitation experiments the initial concentration of the solution greatly impacts the sorption results. In general, the sorption increases with a higher initial concentration of the species. This phenomenon was seen in the conducted experiments.

Sorption isotherm studies were conducted by adding 1 g of Cl-Na to a 250 ml solution containing various ammonia and calcium ion concentrations in the range of 20 to 550 mg/L. The clinoptilolite sample was in contact with the solutions for 48 h at T=25°C.

The total theoretical capacity for Cl-Na is 8.5 meq NH_4^+/gCl, but decreases to 6 meq NH_4^+/gCl in the presence of calcium ions. A competition between the two kinds of cations (Na^+ and Ca^{2+}) for the available ion-exchange sites in the clinoptilolite structure takes place and the removal of ammonium is influenced negatively. This data lead to the conclusion that using clinoptilolite for ammonium removal in hard and very hard water (high calcium and magnesium concentrations) is restricted. Water hardness can vary a lot depending on the water source (surface or ground waters), and is a point of concern since the concentration of calcium and magnesium cations is often higher than the one of ammonium in wastewaters, then the selectivity row is not valid anymore.

Table 1 summarizes the experimental results obtained at various initial concentrations of ammonium and calcium.

Figure 3 and Table 1 illustrate that the presence of calcium ions in solution decreases the ammonia
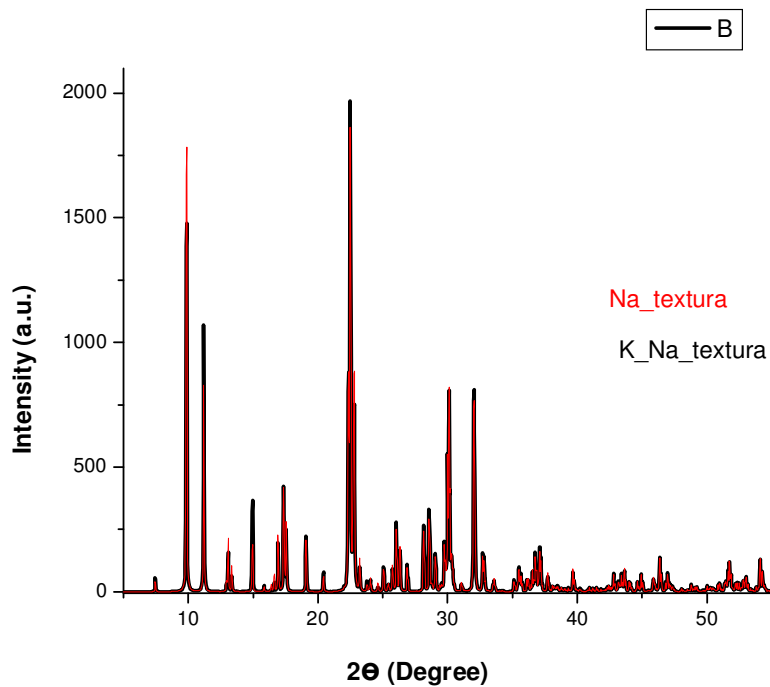
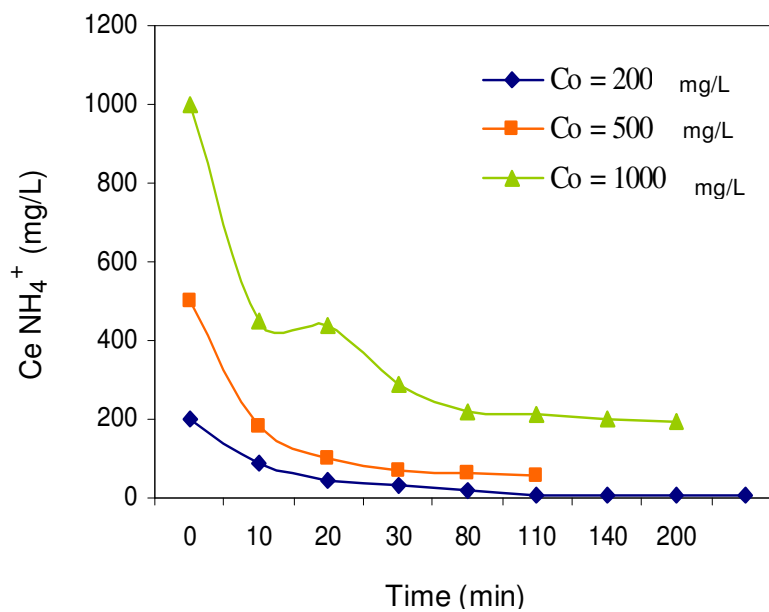**Figure 1.** X-ray diffraction diagram of a sample activated clinoptilolite.

Figure 2. Kinetic study for ammonia ion-exchange process.

Table 1. Ion-exchange capacity of activated clinoptilolite reached as function of $Co\ NH_4^+$.

$Co\ NH_4^+$ (mg/L)	Capacity (meq NH_4^+/gCl) without Ca^{2+}	Capacity (meqNH_4^+/gCl) with Ca^{2+}
100	6	4
200	8	4.5
350	8.5	6
550	8.5	6
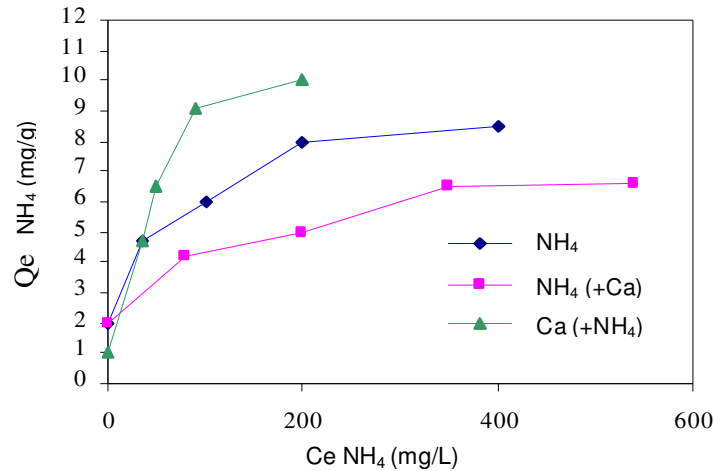
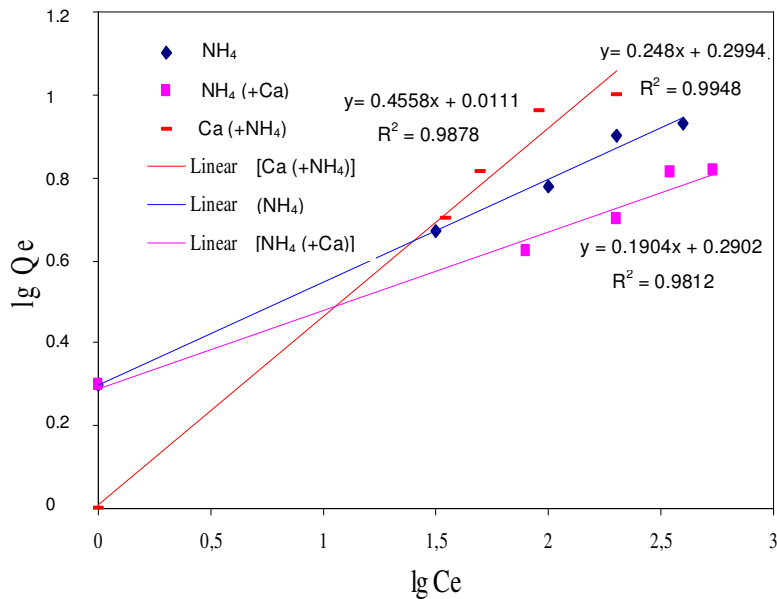**Figure 3.** Ammonium adsorption isotherm for activated clinoptilolite.

Figure 4. Freundlich adsorption isotherm applied to the equilibrium relationship for ammonia and calcium adsorption onto activated clinoptilolite.

adsorption capacity. Calcium adsorption is influenced by the presence of ammonium ions in less degree.

$$Qe = (Co - Ce) \times V/m \qquad (1)$$

Where C_O and Ce are:

For the measurements of calcium, titration with ethelyenediaminetetraacetic acid (EDTA) using a coloured indicator, Eriochrome Black T, at pH = 10, was the most suitable.

Adsorption isotherms are essential for the description of how NH_4^+ concentration will interact with zeolites and

are useful to optimize the use of zeolites as adsorbents. Therefore, empirical equations (Langmuir and Freundlich isotherm model) are important for adsorption data interpretation and prediction. The data obtained in these experiments were fitted to both Fruendlich and Langmuir adsorption isotherms, two most commonly employed models in describing the distribution of ammonium between the solid phase and solution phase. The data fitted better with Freundlich isotherm Figure 4. The Langmuir model assumes only one solute molecule per site, and also assumes a fixed number of sites. The Freundlich model describes a logarithmic relationship between the solid and solution concentrations, and is
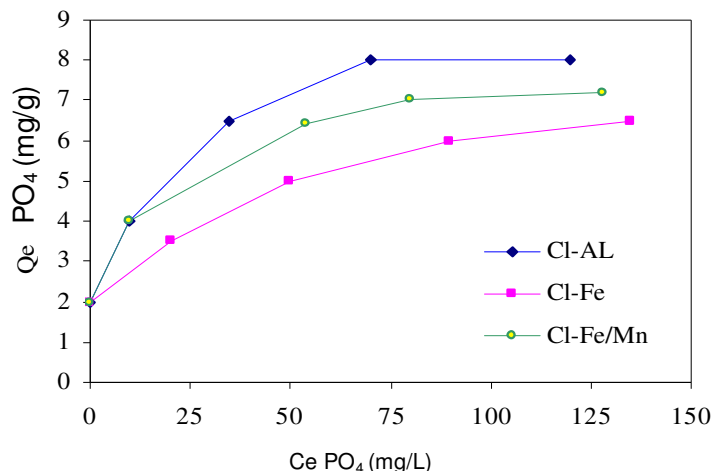
Figure 5. Phosphates adsorption isotherm for modified clinoptilolite 6. Effect of initial pH.

useful in correlating isotherm data obtained over a wide range of concentrations. The Freundlich isotherm relates the uptake of solute onto the exchanger to the solution equilibrium concentration, as shown in Equation (2).

$$Q_e = kC_e^{1/n} \qquad (2)$$

This isotherm can also be presented by the following equation:

$$\log Q_e = \log k + \frac{1}{n} \log C_e \qquad (3)$$

When $\log Q_e$ is plotted against $\log C_e$ the coefficients k and n, which are generally temperature dependent, can be calculated. Knowing all coefficients and using experimental date for C_e, Freundlich theoretical Q_e can be calculated according to Equation (3).

Sorption isotherm studies were conducted by adding 1 g of C-Al, C-Fe and C- Fe/Mn to a 250 ml solution containing various phosphate ion concentrations in the range of 10 to 140 mg/L. The clinoptilolite samples were in contact with the solutions for 48 h. The proposed mechanism of removal of phosphates is the formation of low soluble phosphate salts on the surface of the clinoptilolite sample. Comparison between the adsorption capacities of three modified clinoptilolite samples can be seen on Figure 5. The aluminium modification has the best adsorption capacity in static conditions.

To investigate the pH effect on ammonium removal, a number of equilibrium batch processes were conducted. The experiments were carried out at room temperature and Co NH_4^+ = 50 mg/L. 1 g of activated sample was in contact with 250 ml of solution containing 12.5 mg ammonium. Initial pH values of solutions were adjusted by addition of 1 M HCl and 1 M NaOH solutions. The

results are shown on Figure 6. The obtained results indicate that ammonium exchange increases with increasing the pH up to pH = 7. At pH > 7.5, ammonium exchange shows a rapid decrease. It is assumed that NH_4^+ is converted into NH_3 specimen in alkaline media and is removed from the solution as ammonia. In very acid media (pH =1 to 3), the exchange of ammonium ions is considerably reduced compared to their exchange in slightly acid, neutral and slightly alkaline media (pH = 6 to 7.5). According to reaction (1):

$$MA(s) + x\ H_2O(l) \leftrightarrow HA(s) + (x{-}1)\ H_2O(l) + M^{z+}(l) + OH{-}(l) \qquad (1)$$
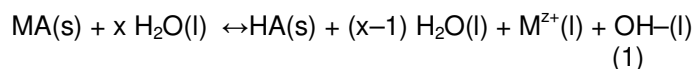
where M^{z+} is the exchangeable cation and z is the charge number of cations in the aluminosilicate structure A, with the decrease of the solution pH, the equilibrium is shifted to the right, that is, the concentration of exchangeable ions in solution increases. Thus, the conditions of ion exchange are more favourable in a more acid medium, however a stronger attraction of H^+ ions to exchangeable sites and competition between H^+ and NH_4^+ is observed. For this reason, the experiments were performed in a stable pH range, optimal to study the binding of ammonium ions.

When the initial pH of the solution increases from 2.5 to 10 the removal of phosphates ions increases till pH=6 and then decreases. The decrease in the phosphate ion uptake, occurring beyond pH=6 (Figure 7), implies probably a competition between phosphate and hydroxyl ions for the sorption on the surface of the sorbents. The experiments were carried out at room temperature and Co PO_4^{3-} = 10 mg/L. 1 g of each of the modified samples was in contact with 250 ml solution containing 2.5 mg phosphates.

The increase of pH value from 6 to 10 implies a decrease in the development of positive charges in the
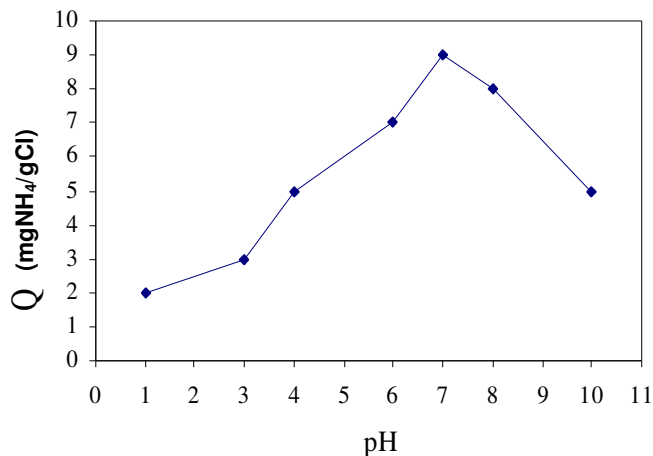
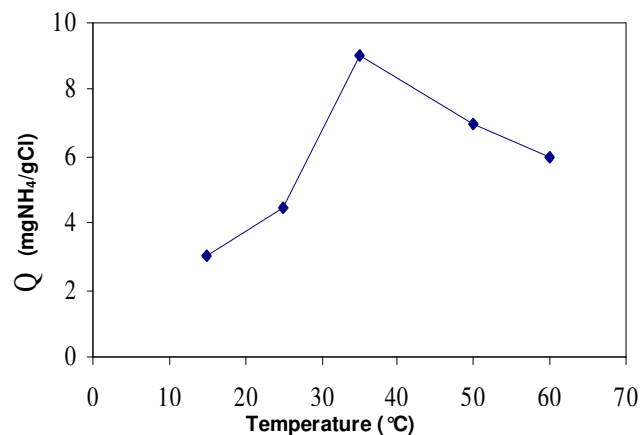**Figure 6.** Removal of ammonia as a function of pH.

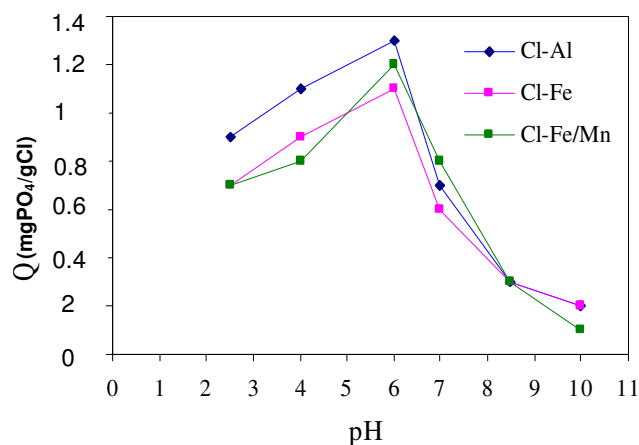**Figure 8.** Removal of ammonia as a function of temperature.

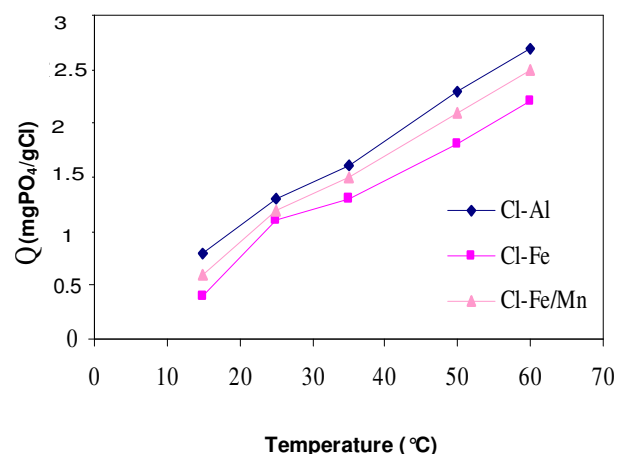**Figure 7.** Removal of phosphates as a function of pH.

Figure 9. Removal of phosphates as a function of temperature.

particles surface, which means a lower electrostatic interaction between the adsorbent and the adsorbate. This decrease is more signficant for Cl-Fe particles as adsorbent. The large variations observed for Cl-Al as compared with the Cl-Fe supports the assumption that the interaction between adsorbent and adsorbate are mainly electrostatic for Cl-Fe/PO_4 systems and are both electrostatic and hydrogen-bonding for Cl-Al/PO_4 systems.

Effect of temperature

The experiments with activated clinoptilolite sample were conducted at pH=7 in the range of values of temperature between 15 and 60°C. Figure 8 shows that the removal efficiency of ammonia increases till 35°C and above this value the ion-exchange process decreases. A decrease in the removal efficiency of NH_4^+ ion with the rise in

temperature was due to the increasing tendency to desorb from the interface to the solution. This result also indicated that the adsorption process of NH_4^+ onto natural zeolite was exothermic in nature.

The experiments with modified clinoptilolite samples were conducted at pH=6. The removal of phosphates increases with increasing temperature (Figure 9). The results indicate that surface adsorption of phosphates is an endothermic process.

Conclusion

1. The presence of calcium ions decreases the ammonia adsorption capacity. Calcium adsorption is influenced by the presence of ammonium ions in less degree.
2. The aluminium modification has the best adsorption capacity in static conditions.
3. The optimal studied parameters for ammonium ion-exchange is pH = 7 and temperature of 35°C.

4. The optimal pH for phosphates adsorption is 6.

5. Surface adsorption of phosphates is an endothermic process and is favoured by higher values of the temperature.

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