SURFACE MODIFICATION OF ANALCIME FOR REMOVAL OF NITRITE AND NITRATE FROM AQUEOUS SOLUTIONS

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Abstract

The capacity of natural zeolites to absorb anionic pollutants from water is limited. This limitation can be overcome by modifying the surface of the minerals with organic cations. In this research, natural zeolite, Analcime was used for removing the nitrate and nitrite impurities from aqueous solutions. The surface of the zeolite was modified by tetramethylammonium and tetraethylammonium ions to increase the capacity of the samples to absorb the anions. The modified zeolite showed higher affinity for NO_2^- and NO_3^- compared to the natural sample.

Introduction

Nitrogen is essential for all living things, as it is a component of proteins. In addition to fertilizers, nitrogen occurs in the soil in organic forms from decaying plants and animal residues. In the soil, bacteria convert various forms of nitrogen containing compounds into nitrate. This is desirable as the majority of the nitrogen used by plants is absorbed in the nitrate form. However, nitrate is highly leachable and readily moves with water through the soil profile. If there is excessive rainfall or over-irrigation, nitrate will be leached below the plant's root zone and nitrate in drinking water can be hazardous to health, especially for infants and pregnant women. The primary health hazard from water with nitrate occurs when nitrate transformed into nitrite in digestive system. The nitrite oxidizes iron in the hemoglobin of the red blood cells to form methemogloblin, which lacks the oxygen-carrying ability of hemoglobin. This creates the conditions known as methemoglobinemia (blue baby syndrome), in which blood lacks the ability to carry sufficient oxygen to organs causing the veins and skin to appear blue. Under such situation, it is obvious that nitrate must be removed from drinking water. It can be removed by three methods: distillation, reverse osmosis, and ion exchange. Considering both initial and operating costs, the distillation and reverse osmosis methods are relatively expensive, and the remaining anions in these methods may vary between 5-10 percent depending on the initial quality of the water, the system design and water temperature. On the other hand, the availability and low cost of natural zeolites make these minerals excellent candidate for environmental remediation. However, these minerals in their natural forms are not very efficient for removing anions from aqueous solutions. A simple surface modification of zeolites using organic cations, greatly improves the absorption capacity of the minerals for some anions [1].

Keywords: Analcime; Zeolite modification; Nitrite; Nitrate

It is believed that the attitude is attributed to the absorption of cationic surfactants onto the zeolite surface [2,3]. Studies of contaminants by modified

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zeolites indicated that the modified zeolites not only have the ability to absorb nonionic organic compound such as benzene, toluene and xylene [4], but also retain inorganic anions chromate, sulfate, and selenate [5-9].

Experimental Section

Natural zeolite was collected from Torfeh area, Kerman region in Iran. The sample was characterized by methods explained elsewhere [10,11]. Wet chemical method, as well as X-ray diffraction and thermal methods of analysis were used. Surface modified zeolites; $(Me)_4$-Ze and $(Et)_4$-Ze were respectively prepared by treatment of the sample with tetramethyl ammonium hydroxide and tetraethyl ammonium iodide. 250 ml of each individual cation solution was added to a suspension which was prepared by adding 50 g of zeolite to 100 ml of deionized water. The mixture was rotated at 25°C for 24 h. The solution was then filtered and the modified zeolite was dried at 50°C. The replacement of cations in zeolite by organic cations was qualitatively confirmed by taking FT-IR spectra of the modified zeolites. The amount of absorbed organic cations was calculated through measurement of out-coming cations by atomic absorption method. To investigate the rate of absorption of NO_2^- and NO_3^-, 5 g of natural or modified zeolite was transferred into a 100 ml glass bottle and 25 ml of solution containing 5 meq/l of anions was added to the bottle. The bottle was sealed and rotated in an oven at one of the constant temperatures of 25, 35, or 45°C. After known period of time, the mixtures was filtered and the concentration of the anions was measured in the filtrates as well as in the original solution by UV/Visible spectrometry at wavelengths of 354.4 and 301.6 nm respectively for NO_2^- and NO_3^-. The experiment was also carried out for the solutions with initial concentration of 2, 4, 6, 8, and 10 meq/l for both natural and modified zeolites at different temperatures.

Results and Discussion

From the characterization experiments (chemical analysis, XRD and thermal methods), it was concluded that the sample was Analcime with a unit cell formula of $Mg_{0.04}K_{0.09}Ca_{0.22}Na_{1.74}Al_{1.66}Si_{3.19}O_{10}.(H_2O)_{1.77}$. IR spectrums of the modified zeolites confirmed that some of the organic cations were absorbed on the surface of zeolite, since characteristic peaks of C-H, N-C, and C-C bonds were clearly observed. Quantitative measurement of the organic cations was carried out by analysis of the out-coming cations in the equilibrated solutions. The total amounts of Na and Ca released from zeolite were respectively 0.108 and 0.106 meq/g for $(Me)_4$-Ze and $(Et)_4$-Ze, whereas the amounts of K and Mg were negligible (Table 1). This amount is suggested to be replaced by organic cations. Derivative thermo-gravimetry curves (DTG) of the modified samples taken from 25 to 700°C showed a weight loss of 8.45% and 9.06%, respectively for $(Me)_4$-Ze and $(ET)_4$-Ze, whereas the weight loss of natural zeolite at the same conditions was 7.70%. It is believed that the difference is attributed to the organic cations absorbed by zeolite. The amounts of tetramethylammonium and tetraethylammonium were calculated from the difference. The values were respectively 0.101 and 0.105 meq/g (Table 2). Absorption of NO_2^- and NO_3^- in natural and modified zeolites was measured against time at 25°C in solutions with initial concentration of 5 meq/l. The equilibrium was established after 16 h for both anions (Figs. 1 and 2). Absorption of NO_2^- and NO_3^- in natural and modified zeolites was also studied at different concentrations of anions and different temperatures (Figs. 3-8). Following conclusions may be withdrawn from the experiments:

A: Modification of zeolite with organic cations increased the absorption capacity of the zeolite. This is due to the fact that the charge balancing cations present on the zeolite surface were replaced by quaternary amines with higher affinity towards anions.

B: Absorption capacity of $(Me)_4$-Ze for both anions was greater than that of $(Et)_4$-Ze. Tetramethyl ammonium is a smaller organic cation and provides higher charge density which causes more affinity towards anions.

C: As NO_2^- and NO_3^- concentrations increased, absorption of anions increased. Absorption of anions by modified zeolites is attributed to the anion exchange, a process which is controlled by diffusion of the anions from the bulk of the solution to the surface of the zeolite, a phenomenon which depends on the concentration of the species.

D: No significant relation between absorption behavior of zeolite and exchange temperature was observed. In natural zeolite and $(Et)_4$-Ze ,the highest absorption capacity was observed at 25°C, where $(Me)_4$-Ze showed higher absorption at 35°C. Similar observation was made for NO_3^-. The highest absorption capacities for NO_3^- in natural zeolite, $(Me)_4$-Ze,and $(Et)_4$-Ze were respectively observed at 45, 25, and 35°C. It may be concluded that modification of natural zeolites by organic cations will sharply increase their affinity towards anions. More research can be carried out for other harmful anions and other natural zeolites which are abundant in many countries.

Table 1. Replacement of Na and Ca by organic cations

Zeolite	**Na (meq/g)**	**Ca (meq/g)**	**(Na+Ca) replaced by organic cations (meq/g)**

Natural	3.660	1.05	–
$(Me)_4$-Ze	3.579	1.023	0.108
$(Et)_4$-Ze	3.561	1.023	0.106

Natural	7.70	–	
$(Me)_4$-Ze	8.45	0.75	$0.75/74^{*}$x10=0.101
$(Et)_4$-Ze	9.06	1.36	$1.36/130^{**}$ x10=0.105

*Molecular weight of tetramethylammonium

**Molecular weight of tetraethylammonium

Table 2. Weight loss of the samples upon heating

Zeolite	Weight loss (%)	Difference (%)	meq/gof organic cations

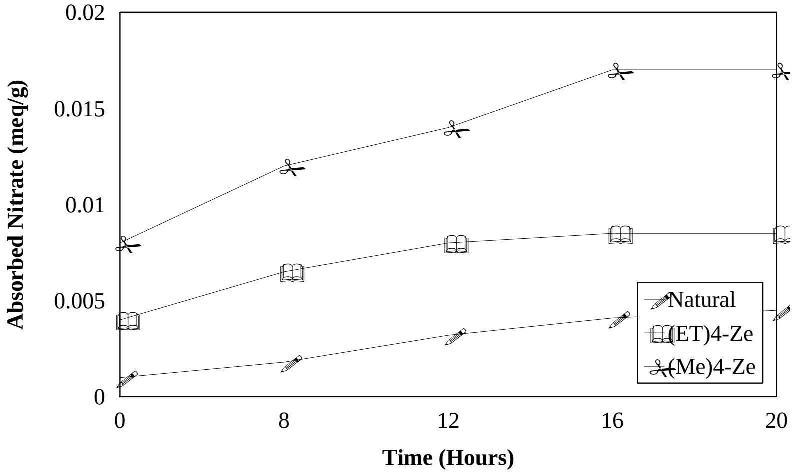

Figure 1. Absorption of nitrate on natural Analcime at different times.

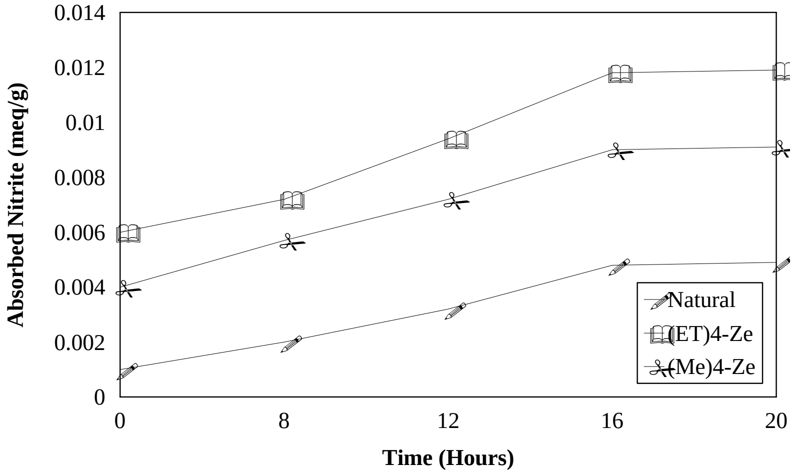

Figure 2. Absorption of nitrite on natural Analcime at different times.

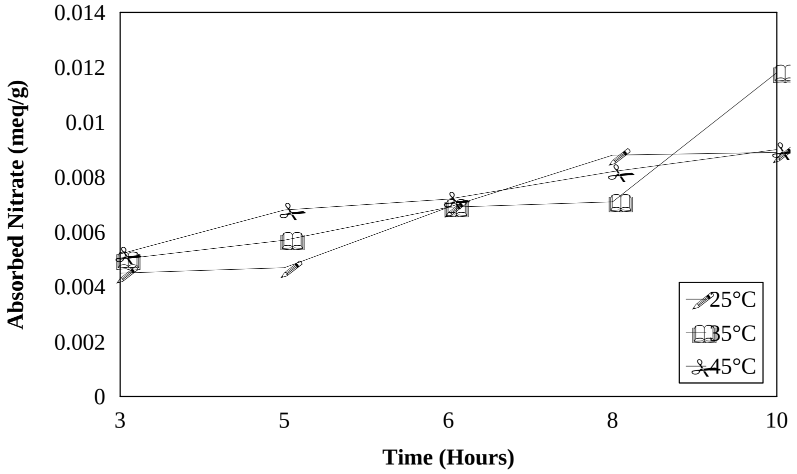

Figure 3. Absorption of nitrate on natural Analcime at different temperatures.

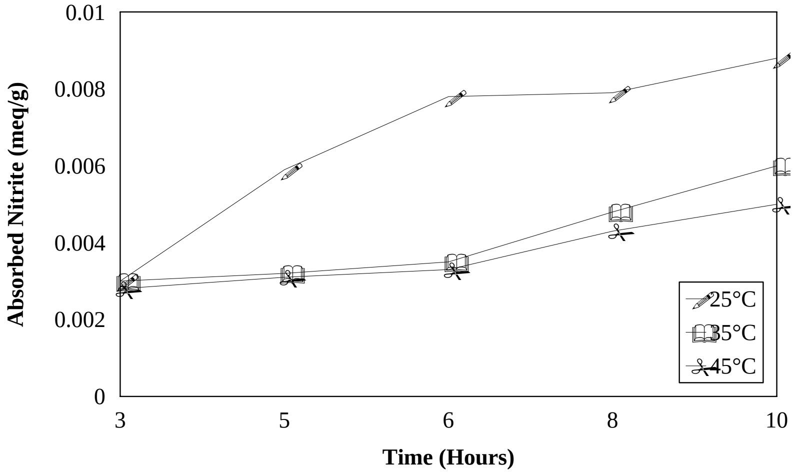

Figure 4. Absorption of nitrite on natural Analcime at different temperatures.

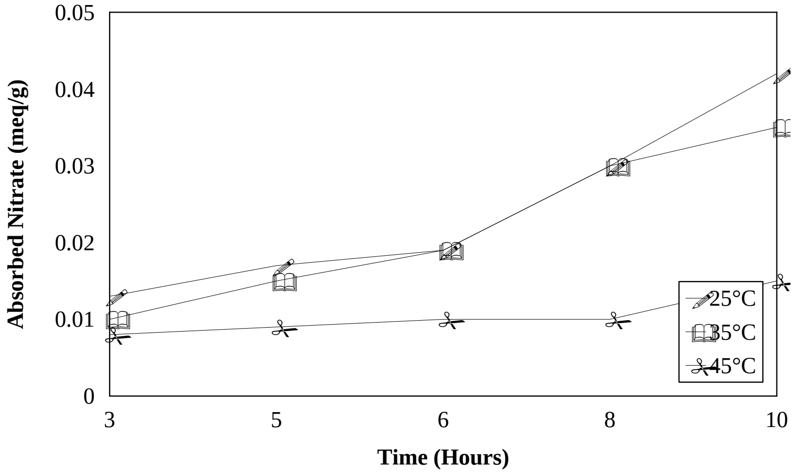

Figure 5. Absorption of nitrate in $(Me)_4$-Ze at different temperatures.

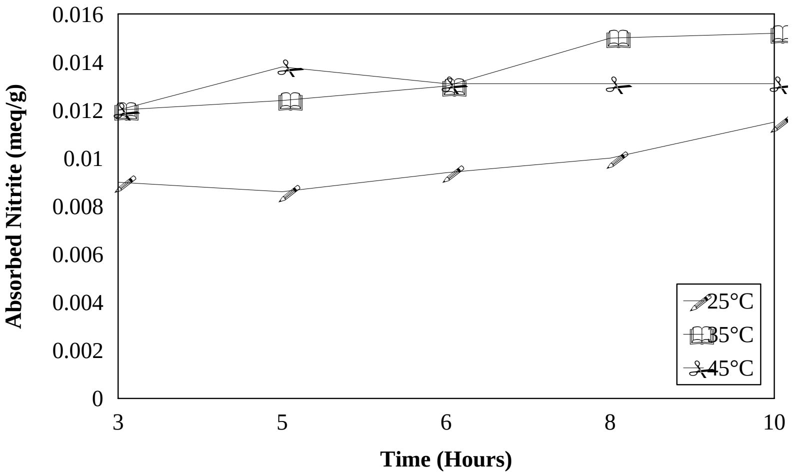

Figure 6. Absorption of nitrite in $(Me)_4$-Ze at different temperatures.

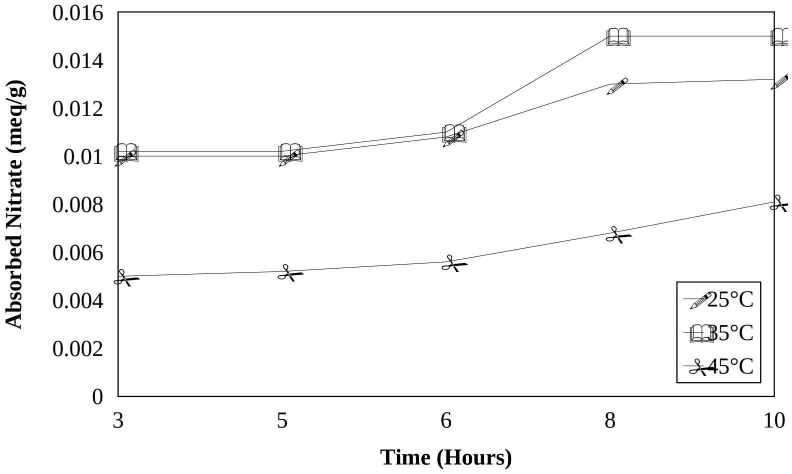

Figure 7. Absorption of nitrate in $(ET)_4$-Ze at different temperatures.

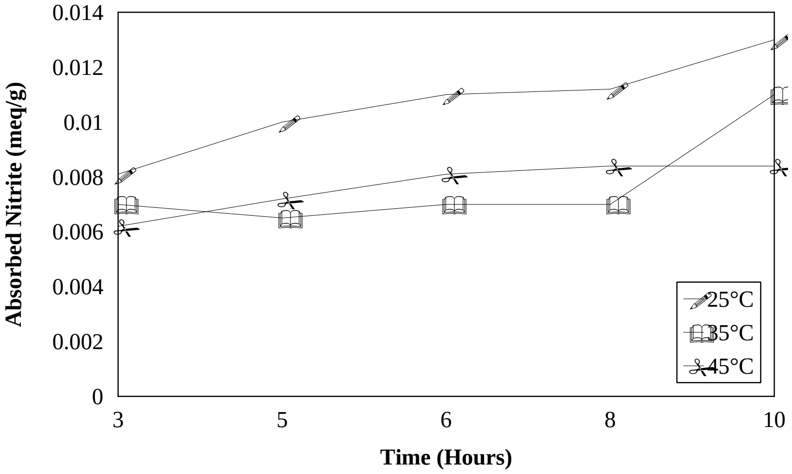

Figure 8. Absorption of nitrite in $(ET)_4$-Ze at different temperatures.

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