

Isomorphous Substitution of P(V) in Natural Clinoptilolite: Evaluation of the Product for Removal of NO_3^- , NO_2^- and F^- from Aqueous Solutions

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ABSTRACT: Nitrate is an anion of major importance particularly in biological areas. Excessive amounts in water supplies indicate pollution from sewage or agricultural effluents. The effects of excessive quantities of nitrate in water are well known. In this research structural modification of natural clinoptilolite by isomorphous substitution was performed. Isomorphously substituted zeolite was prepared under melting conditions from natural clinoptilolite. It was characterized by XRD, XRF, DTG and SEM techniques. The characterization process revealed that product is different from AlPo. Ion exchange property of the modified product was studied for NO_3^- , NO_2^- and F^- ion. The uptake of F^- was higher than those of NO_3^- and NO_2^- . Anion exchange isotherms were constructed for NO_3^- and discussed. The ion exchange chromatography and neutron activation technique were used to study the extent of the exchange.

KEY WORDS: Nitrate removal, Isomorphous substitution, Clinoptilolite, Anion exchanger.

INTRODUCTION

Nitrate is a wide spread contaminant of ground and surface waters worldwide [1, 2]. Together with phosphate they cause high algal growth followed by decay, this leading to deoxygenation of water with the resulting death of fish and other aquatic animals. Nitrate is a potential human health threat especially to infants, causing the condition known as methemoglobinemia, also called "blue baby syndrome". Chronic consumption of high levels of nitrate may also cause other health problems, for example some cancers and teratogenic effects; data are inconclusive, but cause for concern [3, 4].

Interest in inorganic ion exchangers has increased greatly during recent years due to their potential use as selective and temperature stable exchangers. Especially the natural zeolites as molecular sieves with aluminosilicate are more interested, they are very cheap and available.

Zeolites are crystalline aluminosilicates constituted by corner-sharing $[\text{TO}_4]$ tetrahedral, where T represents a silicon or an aluminum atom. The chemical composition of zeolite can be described by the general formula: $\text{X}^{n+}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y]_x \cdot \text{H}_2\text{O}$. Introduction of a trivalent

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Table 1: XRD pattern of clinoptilolite, New product and AlPo.

Clinoptilolite		New product		AlPo	
d value Angstrom	Relative Intensity (%)	d value Angstrom	Relative Intensity (%)	d value Angstrom	Relative Intensity (%)
9.02373	97.3	5.65454	100.0	4.37	100.0
7.97175	57.2	5.19745	13.4	4.13	100.0
6.81162	20.1	4.15169	16.1	3.86	75
5.14793	37.7	4.05871	45.3	2.55	50
4.66430	23.3	3.86425	57.1	2.33	50
3.97488	100.0	3.08199	14.8	2.11	50
3.91266	47.2	2.91725	82.3		
3.42780	41.0	2.39251	13.4		
3.39695	24.7				
2.98031	44.5				
2.80091	31.4				

Al(III) atom in a $[TO_4]$ unit (substituting the tetravalent Si(IV) atom), induces a net negative charge to zeolitic framework which is compensated by the presence of charge balancing extra framework cations ($X^{n+}_{x/n}$), [5].

Clinoptilolite with the ideal formula of $(Na,K)_6Si_{30}Al_6O_{72}.nH_2O$ is the most common natural zeolite found mainly in sedimentary rocks of volcanic origin [6]. Early attempts to modify zeolites [5, 6] by the isomorphic substitution of framework were of limited success. More recent work initiated by *Flanigen* and *co-worker* has resulted in the synthesis of zeolite aluminophosphates (AlPos) and silicoaluminophosphates (SAPos) [7,8]. However these materials have near neutral frameworks and no recorded anion exchange properties.

Phosphorous was inserted into zeolite [9], to create anion exchange properties, by changing the overall framework charge from negative to positive. A group of zeolite was modified [10] by isomorphic substitution of phosphorous with aluminum into their tetrahedral structure and considered the reason for its in adsorption of some anions in aqueous solutions.

EXPRIMENTAL

The sample was collected from Semnan region in north-east of Iran. The sample was ground and the fractions between 45-75 μm were selected. Characterization of zeolite was performed by different techniques including differential thermogravimetry (DTG), X-ray powder diffraction (XRD) and X-ray fluorescence (XRF).

A weighed amount of the sample was mixed thoroughly with excess amount of ammonium dihydrogen phosphate 1:10 (wt/wt) in a pyrex beaker. The melting conditions (220 °C) were held for 24 hours. The melt mixture was poured into a beaker containing deionized water and thoroughly stirred to dissolve untreated phosphate. The product was filtered, washed with sufficient amount of deionized water and dried at 110 °C. Then was stored in a desiccator over saturated sodium chloride solution in order to retain constant water content. Ion exchange property of the modified sample was studied for NO_3^- , NO_2^- and F^- by placing of 1.000 g of phosphorated zeolite in contact with 50 ml of 1 N solution of each anion. The mixture was rotated in a plastic vial for one week at room temperature. The amount of uptake of anion was determined every 12 hours.

The exchange isotherm of the sample loaded with fluoride for NO_3^- was constructed at three different temperatures of 25, 55 and 75 °C. 0.5000 g of the phosphated zeolite loaded with F^- was shaken with 20 mL of solution containing varying amounts of anions (F^- and NO_3^-) in a polyethylene vessel. The total normality of solution was 0.1 N. After six days the mixture was centrifuged and the sample was dried. The amount of NO_3^- was determined by ion chromatography technique.

RESULTS AND DISCUSSION

XRD data of clinoptilolite, with those of new product and AlPo are shown in table 1. In XRD pattern of product

Table 2: XRF pattern of clinoptilolite and new Product.

Compound	% W Clinoptilolite	% W New product
SiO ₂	60.68 ± 2.19	58.99 ± 2.24
Al ₂ O ₃	15.90 ± 1.14	8.62 ± 1.11
Na ₂ O	2.05 ± 0.23	0.05 ± 0.02
K ₂ O	3.78 ± 0.27	0.02 ± 0.01
CaO	1.50 ± 0.18	-----
MgO	0.30 ± 0.05	0.11 ± 0.03
Fe ₂ O ₃	0.95 ± 0.09	0.99 ± 0.07
P ₂ O ₅	0.04 ± 0.01	23.53 ± 1.43
H ₂ O	13.65 ± 1.21	8.32 ± 1.10

Table 3: Anion exchange capacity of new product for the studied anions.

Anion	AEC (meq. g ⁻¹)
Fluoride	2.81
Nitrate	0.95
Nitrite	0.90

only one phase was observed. No similarity between XRD pattern of the prepared sample with those of clinoptilolite and AlPO₄ was observed showing that the new crystalline phase was formed by isomorphous substitution of clinoptilolite. The chemical compositions of clinoptilolite and new product are represented in table 2.

Phosphorus is mostly exchanged with aluminum rather than silicon. The amount of Al is reduced from 4.20 % to 2.28 % and that of Si from 28.23 % to 27.53 %. At mean while, 5.14 % of P is introduced to the structure. As we have predicted schematically in Fig. 1, introduction of P changes the net Charge from negative to positive.

The water content of modified sample, calculated from DTG curves is reduced from 13.61 % to 8.32 %. This is related to the lower cation content of the modified sample. The kinetic of adsorption of NO₃⁻, NO₂⁻ and F⁻ by modified zeolite is represented in Fig. 2.

Anion exchange capacities (AEC) of the sample for different anions are shown in table 3. Because of higher capacity of the sample for fluoride the exchange isotherms were constructed using fluoride loaded samples.

Isotherms were naturally constructed in order study the equilibrium aspects of the exchange, a measure of the preference that sample displays for NO₃⁻ ion over F⁻ ion. They were constructed by plotting at equilibrium the equivalent fraction of the incoming ion present within the

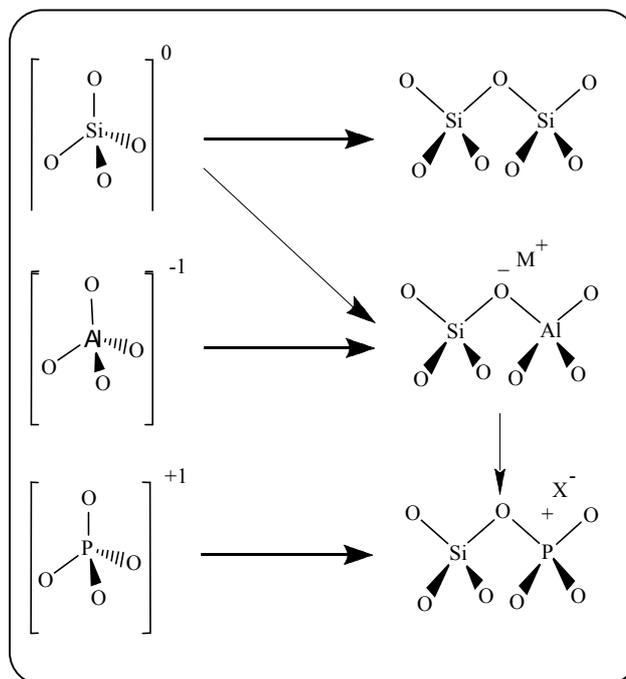
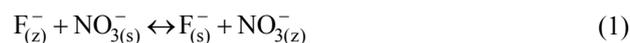


Fig. 1: Suggested isomorphous substitution mechanism.

solution phase (A_s) against the equivalent fraction of the same ion in solid sample (A_z) equation (1).



The temperature was kept constant; in addition, both the zeolite and the solution phase were kept isonormal. The isotherms are shown in Fig. 3 for phosphated zeolites initially converted to the fluoride form. According to the classification made by Barrer [11], The curves at 25 °C and 55 °C are isotherms of the first kind and represent relatively simple systems in which the exchanger is either selective for incoming ion (NO₃⁻) or unselective for ingoing ion (F⁻). The curve at 75 °C is isotherm of the third kind. Isotherms describing such exchange reactions exhibit hysteresis where the forward and reverse exchange paths don't coincide.

CONCLUSIONS

Isomorphous substitution of P(V) in clinoptilolite affects the framework element of clinoptilolite and changes its negative net charge to positive. The exchange capacity of the product for studied anion is high. It is a promising material for removal of the anion from liquid wastes.

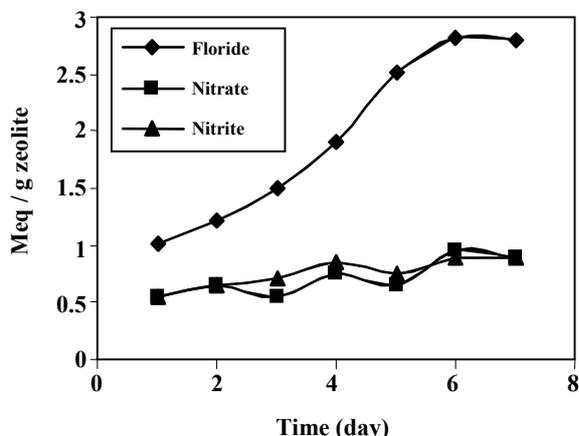


Fig. 2: Uptake of anions by modified clinoptilolite.

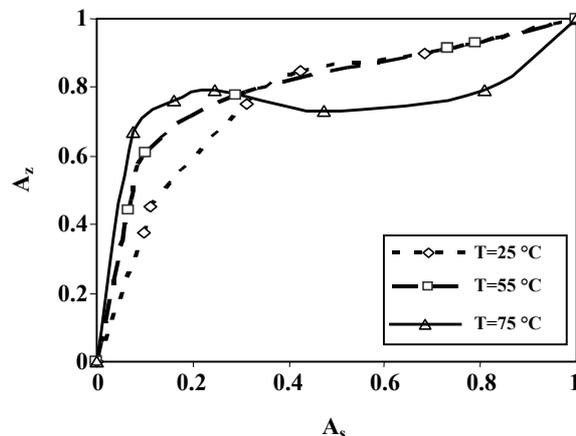


Fig. 3: $F \leftrightarrow NO_3^-$ isotherm on new product at 25, 55 and 75 °C.

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REFERENCES

- [1] Hallberg, G.R., "Nitrate in Ground Water in the United States", In Follet, R.F. (Ed.), "Nitrogen Management and Ground Water Protection", Elsevier, Amsterdam, p. 35, (1989).
- [2] Puckett, L.J., Identifying the Major Sources of Nutrient Water Pollution, *Environmental Science & Technology*, **408A**, (1995).
- [3] Bruning Fann, C.S., Kaneene, J.B., The Effects of Nitrate, Nitrite, and N-Nitroso Compounds on Human Health: A Review., *Vet Human Toxicology*, **35**, 521, (1993).
- [4] Kross, B.C., Hallberg, G.R., Bruner, D.R., Cherryholmes, K. and Johnson, J.K., The Nitrate Contamination of Private Well Water in Iowa, *Am. J. Public Health*, **83**, 270, (1993).
- [5] Dyer, A. and White, K.J., Cation Diffusion in the Natural Zeolite Clinoptilolite, *Thermochimica Acta*, **340-341**, 341 (1999).
- [6] Doula, M.K., Synthesis of a Clinoptilolite-Fe System with High Cu Sorption Capacity, *Chemosphere*, **67**, 731, (2007).
- [7] Flanigen, E. M. and Grose, R. W., Phosphorus Substitution in Zeolite Frameworks, *Adv. Chem. Ser.*, NO. **101 76**, 101, (1971).
- [8] Flanigen, E.M., Lok, B.M., Patton, R.L. and Wilson, S.T., Aluminophosphate Molecular Sieves and the Periodic Table, *Pure & App. Chem.*, **58** (10), 1351, (1986).
- [9] Dyer, A. S., Malik, A. and Araya A., "Recent Developments in Ion Exchange", Elsevier Applied Science, London, New York, p. 134, (1987).
- [10] Cerjan Stefanovic, S., Kastelan Macam, M. and Filipan, T., Ion Exchange Characterization of Modified Zeolite, *Wat. Sci. Tech.*, **26** (9), 2269 (1992).
- [11] Van Bekkum, H., Flanigen, E.M., Jacobs, P.A. and Jancen, J.C., Studies in Surface Science and Catalysis in: "Introduction to Zeolite Science and Practice", Elsevier, Amsterdam, 2nd Ed., **137** (8), 353, (2001).