

ADSORPTION OF ARSENATE ION BY Fe, Pb AND Ag-EXCHANGED FORMS OF CLINOPTILOLITE*

H. FAGHIHIAN**

Department of Chemistry, University of Isfahan, I. R. of Iran
Email: h.faghih@sci.ui.ac.ir

Abstract – Experiments were set up to estimate the effectiveness of clinoptilolite for the removal of arsenate from aqueous solutions. The removal of arsenate by the exchanged forms was analyzed in the light of the Langmuir model of adsorption. A kinetic study of adsorption was carried out at different intervals of time, and the K_{ad} values were calculated by using Lagergren's equation. Adsorption of arsenate proceeds through the formation of arsenate precipitates.

Keywords – Arsenate, clinoptilolite, waste treatment

1. INTRODUCTION

The use of arsenic in agriculture, industry and domestic applications has increased the concentration of arsenic in the environment. Arsenic is currently removed from contaminated water by flotation, precipitation, adsorption and ion exchange methods [1]. Different types of adsorbents have been studied for the removal of arsenate from aqueous media [2-4]. However, comparatively few published papers deal with the application of zeolites for arsenic elimination [1, 5-7]. Recently, we reported the adsorption of iodide and molybdate by zeolites [8, 9]. The present research deals with the applicability of clinoptilolite for arsenate removal from liquid wastes.

2. EXPERIMENTAL

a) Reagents

Natural zeolite used in this work was obtained from deposits of Absard in Damavand, Iran. The minerals have already been characterized and are known to be clinoptilolite [8]. The chemicals used were reagent grade and the solutions were prepared by deionised water. A stock solution of arsenate was prepared by dissolving $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$. The pH of the solution was adjusted by 10mM solutions of HCl or NaOH.

*Received by the editor June 13, 2003 and in final revised form December 27, 2004

**Corresponding author

b) Procedures

The modification of zeolites was performed by treating zeolite with 0.1M solutions of appropriate salts of Fe, Pb and Ag. The amount of cations impregnated into zeolite was calculated by the measurement of the cations either in the liquid or in the solid phase by atomic absorption spectroscopy. Adsorption isotherms were obtained at 25, 35 and 45 °C. A series of 10.0, 20.0, 30.0, 40.0, 50.0 and 60.0 mmol.L⁻¹ arsenate solutions were prepared. 0.1 g zeolite and 40 mL of arsenate solution were placed in a 50-mL centrifuge tube. The tubes were shaken for 24 h, a period shown sufficient for attaining sorption equilibrium. The amount of adsorbed arsenate was determined from the difference between the anion concentration in the solution before and after equilibration. The removal of arsenate by the exchanged forms was analyzed by the Langmuir model of adsorption. The following rearranged Langmuir equation was used to calculate the Langmuir constant; $C_e/q_e = 1/Q^{\circ} b + C_e/Q^{\circ}$

The plot of C_e versus C_e/q_e at different temperatures gives a straight line, showing applicability of Langmuir isotherms. A kinetic study of adsorption of arsenate was carried out at different intervals of time. The adsorption of arsenate was almost completed after 3 hours. The adsorption constant was calculated by using Lagergren's equation; $\log(q_e - q) = \log q_e - (K_{ad}/2.300)t$. The value of K_{ad} was calculated from the slope of the respective linear plots of $\log(q_e - q)$ versus time.

The measurement of arsenate was carried out with a Perkin Elmer Atomic Absorption Spectrometer equipped with a hydride generator MHS 20 at 193.7 nm.

3. RESULTS AND DISCUSSION

Based on chemical analysis data, the theoretical cation exchange capacity (CEC) of the zeolite was calculated as 2.21 meq.g⁻¹. The maximum exchange level was 1.31, 0.47 and 0.41 meq.g⁻¹ respectively for Ag, Pb and Fe forms, and less than 100% of the theoretical exchange capacity. The failure to attain a 100% exchange appears the most striking feature of this set of experiments, because these cations react with arsenate to form entrapped arsenate precipitates. Initial measurements showed that the uptake of arsenate by untreated clinoptilolite was negligible. It is believed that the presence of Pb, Fe and Ag promotes anions precipitation on the surface and in the cavity of zeolite. The driving force to overcome the charge repulsions between arsenate and framework is likely the small solubility products of arsenate precipitates. Adsorption of arsenate showed to be concentration dependent. The amount of zeolite was held constant, while the initial concentration of the anion varied from 1.0 to 60 mmol.L⁻¹, (Fig.1 for Ag-clinoptilolite). The adsorption was analyzed by the rearranged Langmuir model of adsorption to calculate the Langmuir constant. The plot of C_e vs C_e/q_e at different temperatures gives a straight line showing the applicability of the Langmuir isotherm. The values of Q° and b are shown in Table 1. The kinetic of adsorption was studied at 25 °C. All samples reached equilibrium after about 3 hours. The K_{ad} values were measured using Lagergren's equation and were 0.2533, 0.1865 and 0.1543 respectively for Pb, Ag and Fe-exchanged forms, Fig. 2. As expected, the highest adsorption rate was observed for Pb-exchanged forms due to the lower k_{sp} of lead arsenate.

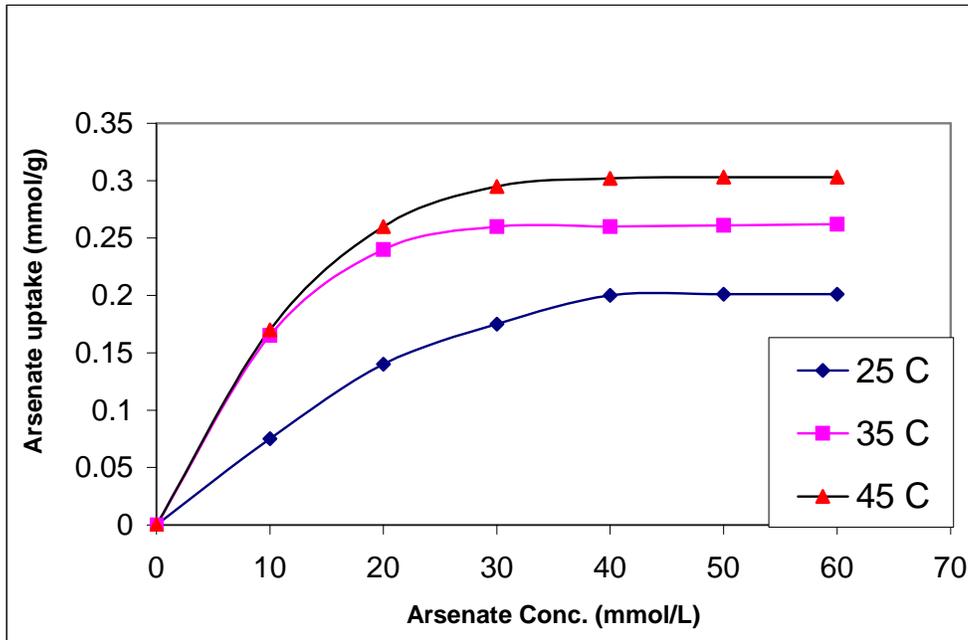


Fig 1. Arsenate uptake by Ag-clinoptilolite

Table 1. Langmuir constants for arsenate adsorption by exchanged forms

Exchanged form	temperature (°C)	Q (mmol/g)	b(1/mmol)
Ag-Clinoptilolite	25	0.0310	0.2441
Ag-Clinoptilolite	35	0.0347	0.1205
Ag-Clinoptilolite	45	0.0420	0.0702

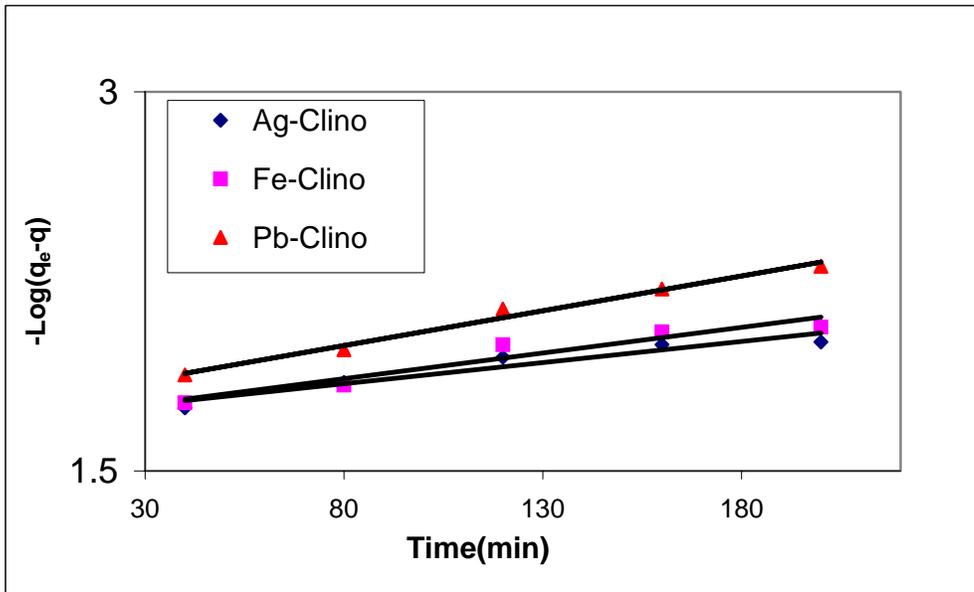


Fig 2. Lagergren's plot for arsenate adsorption

The effect of the silver content on the uptake of arsenate was studied. Arsenate adsorption increased as the silver content of the zeolite increased. The uptake of arsenate by an Ag-exchanged form is much higher than the other adsorbents used for this purpose [1, 2, 9].

Figure 3 shows the effect of pH on the removal of arsenate. In all samples, the maximal uptake was observed around a pH range of 7.0-9.5. The stability and dominance of arsenate species depends directly on the pH of the solution. Although AsO_4^{3-} is the predominant species between pH 12-14 [7], the adsorption becomes insignificant at about pH 13. It is likely that the high concentration of OH^- ion promotes hydroxide precipitation, a process which competes with arsenate adsorption in high pH. In the Fe-exchanged form, two mechanisms are operating for the removal of arsenate, viz. precipitation and complex formation. The removal of arsenate by complex formation takes place in the pH range between 3 and 6 due to the presence of H_2AsO_4^- species. The arsenate adsorption in acidic media is insignificant because of the presence of H_3AsO_4 as the predominant species.

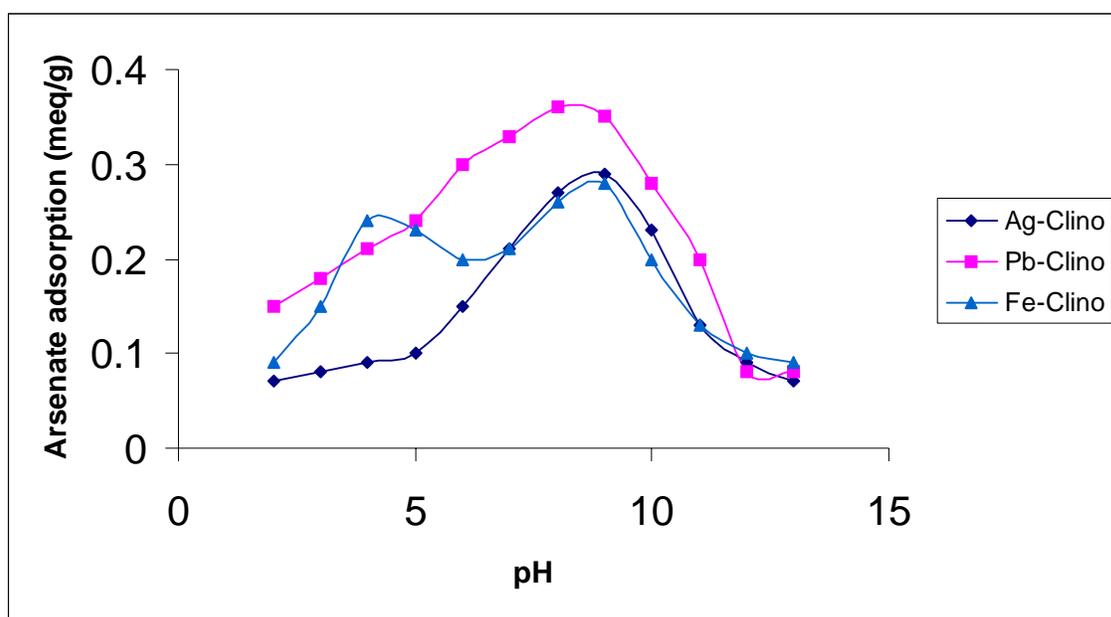


Fig. 3. Effect of pH on arsenate removal

4. CONCLUSIONS

Major treatment methods to remove arsenic include coagulation-precipitation with lime, alum, and ferric sulfate, which produce a wet bulky sludge and often require final filtration for secondary treatment. In this method, low-cost natural zeolites that are abundantly present, but a currently useless resource in many parts of the world are used. The preparation of the exchanged forms of zeolites is quite easy and the adsorbent can be used in a column or fixed bed. High adsorption capacity of modified zeolite promotes the application of clinoptilolite as a potential adsorbent for arsenate.

REFERENCES

1. Xu, Y., Ohki, A. & Maeda, S. (1998). Adsorption of arsenic (V) by use of aluminium- loaded Shirasu-zeolites. *Chemistry Letters*, 1015-1016.
2. Lin, T. F. & Wu, J. K. (2001). Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics. *Water Research*, 35(8), 2049-2957.
3. Li, Z. H. & Bowman, R. S. (2001). Retention of inorganic oxyanions by organo- kaolinite. *Water Research*, 35(16), 3771-3776.
4. Halter, W. E. & Pfeifer, H. R. (2001). Arsenic (V) adsorption onto alpha-Al₂O₃ between 25 and 70 °C. *Applied Geochemistry*, 16(7-8), 793-802.
5. Elizalde-Gonzales, M. P., Muittusch, J., Wennrich, R. & Morgenstern, P. (2001). Uptake of arsenite and arsenate by clinoptilolite-rich tuffs. *Microporous and Mesoporous Materials*, 46, 277-286.
6. Elizalde-Gonzales, M. P., Muittusch, J. & Wennrich, R. (2001). Application of natural zeolites for preconcentration of arsenite species in water samples. *J. Environ Monit*, 3, 22-26.
7. Elizalde-Gonzales, M. P., Muittusch, J., Einicke, W. D. & Wennrich, R. (2001). Sorption on natural solids for arsenic removal. *Chemical Engineering Journal*, 81, 187-195.
8. Faghihian, H., Maragheh, M. G. & Malikpour, A. (2002). Adsorption of radioactive iodide by natural zeolites. *J. of Radioanal. and Nucl. Chem.*, 254(3), 545-550.
9. Faghihian, H. Malekpour, A. & Maragheh, M. G. (2002). Adsorption of molybdate ion by natrolite and clinoptilolite-rich tuffs. *Int. J. of Environmental and pollution* 18(2), 181-185.