ADSORPTIVE REMOVAL OF As(V) FROM AQUEOUS SOLUTION USING NATURAL MORDENITE AND MODIFIED FORMS AS MEDIA

Pratap Chutia, Shigeru Kato, Toshinori Kojima and Shigeo Satokawa*

Department of Materials and Life Science, Faculty of Science and Technology,
Seikei University, Tokyo (JAPAN)

ABSTRACT

Natural mordenite (NM) produced in Japan and its modified forms were investigated with respect to their sorption efficiency for arsenate ions (As(V)) from water. Two modified natural mordenite examined were aluminum treated natural mordenite (Al-NM) and acid treated natural mordenite (AT-NM). The adsorption experiments were performed by batch equilibrium technique. Effects of equilibrium time, initial arsenic concentration (in the 5-100 mgL^{-1} range) and pHs (in the range 3-12) were investigated. The Al-NM was superior to NM and AT-NM. This could be the fact that concentration of terminal Al-OH groups took the key role in ion-exchange taking place during adsorption. The concentration of this aluminol group in Al-NM is higher than the other two due the externally loaded Al-sites. Moreover, surface area of NM increased remarkably on Al^{3+}-loading which enhances the adsorption process. The obtained results indicated that maximum As(V) uptake of 52.06, 67.04 and 74.91 % were observed at 24, 36, 48 h by NM, Al-NM and AT-NM respectively. After the equilibrium time, no adsorption observed due to saturation of adsorbent active sites. With the increase of initial As(V) concentration, metal uptake decreases for all the adsorbents up to a certain value after which it again became saturated. The maximum uptake was recorded at pH near respective pH$_{PZC}$ of the adsorbents. The arsenic removal by zeolite followed the first order kinetics indicating the adsorption is dependent on the concentration of metal only. The experimental data were fitted with Freundlich isotherm model.

Key Words : Natural mordenite, Zeolite modification, Arsenate, Point of zero charge, Ion-exchange, Adsorption, Isotherm models

INTRODUCTION

Naturally occurring hydrated aluminosilicate zeolites belong to the class of minerals known as tactosilicates[1,2]. Natural zeolites found in volcanogenic sedimentary rocks have been and are being used increasingly in various applications such as industry, agriculture, environmental protection and even in medicine. Although, it could not be found out the occurrence of these minerals all over the World, some countries e.g. Cuba, USA, Russia, Japan, Italy, South Africa, Hungary and Bulgaria have important reserves and production potentials. In the year 2001, it was reported that the total consumption of zeolites

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* Author for correspondence

was 3.5 million tons of which 18% came from their natural resources and rest from synthetics. About fifty different naturally occurring zeolites are identified, but most well known are analcime, chabazaite, clinoptilolite, erionite, ferrierite, laumonite, mordenite and phillipsite[3-5].

Arsenic is naturally occurring element in environment. Arsenic in ground water is largely the results of minerals dissolving naturally from weathered rocks and soils. Arsenic has many industrial applications as well as also used extensively in the production of agricultural pesticides[3,5]. Runoff and the leaching of arsenic from waste generated from these uses has resulted in increased levels of various forms of soluble arsenic in water. Using untreated water contaminated by arsenic causes numerous diseases of the skin and internal organs[5-9]. Although various techniques exist, adsorption is generally considered to be promising method for arsenic removal due to easy separation of adsorbent from aqueous media after treatment[10]. If low-cost and easily available natural zeolites are used for arsenic adsorption, it will be more cost effective than other available adsorbents used. The use of ion-exchange properties of zeolites has received much attention over the past decade in water and industrial waste treatment[8,11]. The mechanism of adsorption by zeolites is ion-exchange. In the three dimensional zeolite framework, there are large channels containing negatively charged sites resulting from Al^{3+} replacement of Si^{4+} in the O_4 tetrahedra linked by sharing oxygen atoms in the rings. The cages-cavities are occupied by cations which are weakly held in the framework to compensate the charge imbalance. The overall negative charge of the anions is balanced by cations that occupy the channels within the structure, and can be replaced with heavy metal ions[1,3].

In the present investigation, the ion-exchange property of the natural zeolites is used to remove arsenic ions from model aqueous solution. The feasibility of use of natural mordenite, Al^{3+}-loaded natural mordenite and acid-activated natural mordenite for removal of As(V) under various environmental conditions were investigated with the use of batch technique. The experimental data were also fitted with Freundlich isotherm model to estimate the various parameters related to adsorption process.

MATERIAL AND METHODS
EXPERIMENTAL
Adsorbents

NM was obtained from Sendai area of Miyagi prefecture, Japan. It was grind, sieved (100 im) and washed. The sample was dried at 200°C for about 24 h. The Al-NM was prepared by suspending 1 g of NM into 500 mL of 7 mmolL^{-1} aluminum sulfate. The mixture was agitated for 24 h. The Al-NM thus obtained was washed thoroughly with de-ionized water and dried. The Al-NM contained 12.5wt% of aluminum loaded by the treatment. The preparation of AT-NM comprised acid washed with 2M HCl with agitation at 70°C for 10 h, keeping them for 24 h in the acid solution, decantation and washing with water until a pH of 5.5 was obtained and the $AgNO_3$ chloride test provide negative result. Finally, the sample was dried at 200°C for 12 h.

Reagents

Reagent grade HCl (Kanto Chemical Co., Inc.) and aluminum sulfate (Wako Pure Chemical Industries) were used to modify/ activate natural mordenite. A stock solution of 1000 mLL^{-1} of As(V) was prepared by dissolving required amount of $Na_2HASO_4.7H_2O$ (Wako Pure Chemical Industries, Ltd., Japan) in de-ionized water and was used to prepare the adsorbate solutions by appropriate dilution for different experiments performed. The stock solution prepared had a pH 9.09 and did not change considerably with dilution.

Adsorption experiments

A preweighed sample of the adsorbents NM, Al-NM and AT-NM and a measured volume of As(V) solution were taken in a conical flask and the mixture was agitated in a rotary shaker for a definite period. The mixture was separated by filtration and filtrate was preserved for As(V) concentration measurement.

The adsorption experiments were conducted by taking 1 g of adsorbents in 100 mL of 5 mlL^{-1} As(V) solution (pH slightly lower than stock solution pH of 9.09) at room temperature ($22 \pm 2^{\circ}$C) and interaction time of 24, 48 and 36 h (equilibrium time) for the adsorbents NM, Al-NM and AT-NM respectively. For observing the effect of pH, the same was varied from 3-12 and for the kinetic measurements, time is varied from 10 min to 72 h at appropriate intervals by using adsorbent amount of 1 g. To investigate the effect of initial As(V) concentration and to obtain the different isotherms, the concentration was varied from 5 to 100 mlL^{-1} while keeping the adsorbent load constant at 1 g.

Instrumentation

The adsorbents were characterized by X-ray diffraction (XRD, Rigaku Miniflex with CuKá filtered radiation; 30 kV, 15 mA), Fourier transform infrared spectroscopy (Jasco 460 plus spectrophotometer, range 400-4000 cm^{-1}) and Surface area analyzer (Gemini, Micrometrics). The concentration of all the solutions were measured by using a Inductively Coupled Plasma-atomic emission Spectroscopy, (Model ICPS-7500; Sequential Plasma Spectrometer; Shimadzu Corporation, Japan). A digital pH meter of Horiba Ltd, Japan (Model D-51) was used for pH measurement.

THEORETICAL BASIS

(a) % of As(V) adsorption

$$\frac{Ci - Cf}{Ci} \times 100$$

where Ci and Cf are the concentrations (mg L^{-1}) of arsenic in initial and final solutions respectively, V is the volume of the reacting solutions (L), M is the weight (g) of the adsorbents.

(b) Pseudo-first order kinetics

$$\log (q_E - q_T) = \frac{K_1}{2.303} t$$

where K_1 (h^{-1}) is the rate constant q_T (mg g^{-1}) is the amount adsorbed at time t (h) and q_E (mg g^{-1}) denotes the amount adsorbed at equilibrium. The values of K_1 can be obtained from the slope of the plot of log($q_E - q_T$) against time, t.

(c) Freundlich isotherm model

$$InQ = InK_E = 1/n\ InCe \qquad \text{Non-linear}$$
$$Q = K_F Ce \qquad\qquad \text{Linear}$$

This isotherm is usually used in special cases for heterogeneous surface energy where it is characterized by the heterogeneity factor 1/n. The other parameter Q is the equilibrium value of arsenic adsorbed per unit weight of natural zeolite powder (mg g^{-1}), Ce is the liquid-phase sorbate concentration at equilibrium (mg L^{-1}) and K_F is the Freundlich constant. K_F and n are calculated from the intercepts and slopes of the Freundlich plot logQ against logCe.

RESULTS AND DISCUSSION

Crystal structure analyses, performed by X-ray diffraction, reveal that the NM obtained was in well-crystalline form (**Fig. 1**). The XRD pattern of Al-NM showed that the crystal structure of the parent NM remain intact after aluminum loading. The crystal structure of the zeolite was destabilized after acid treatment and the intensity of the observed bands reduced significantly compared to the other two adsorbents. The surface area (**Table. 1**) of NM is 171 m^{2}g^{-1} which is increased in Al-NM up to 309 m^{2}g^{-1}. AT-NM bears a surface area of 181 m^{2}g^{-1} which is marginally higher than the parent NM due to the fact that acid activation has not much affect on the same. The IR bands observed in the NM and other two modified zeolites are summarized and assigned[12, 13] in **Table. 2**. All

the adsorbents show similar IR bands indicating structural stability and similarity amongst them. It is worth to mention that the intensities of the bands are lower for AT-NM compared to other two due to its poor crystalline nature. The other physicochemical properties of the three adsorbents are listed in the **Table. 1**. The Si/ Al atomic ration for Al-NM is lower compared to the other two adsorbents due to externally loaded-Al^{3+} into zeolite surface.

Adsorption behaviours of the NM, Al-NM and AT-NM are illustrated in **Fig. 2**. The experiments were performed with 1g of each adsorbent taking into interaction with 100 mL

Table 1: Studied natural zeolite types and their physicochemical properties

Adsorbents	NM	Al-NM	AT-NM
Si/Al (atomic)	5.87	4.56	5.75
pH in water	6.49	6.20	5.29
pH_{PZC}	4.20	4.00	3.40
Surface area / $m^2 g^{-1}$	171	309	181

Table 2: IR peak positions and assignments for adsorbents NM, Al-NM and AT-NM

Adsorbents	Peak position (cm^{-1})						
	A	B	C	D	E	F	G
NM	3616	3420	1644	1225	1057	784	540, 449
Al-NM	3612	3446	1639	1224	1051	788	545, 448
AT-NM	3625	3424	1637	1227	1067	789	546, 449

A: O-H stretching vibration of terminal Si-OH; **B:** O-H stretching vibration of extrazeolitic Z-OH (also designated as Si(OH)Al); **C:** bending mode of OH; **D :** and **E:** External and internal vibration of framework TO_4 tetrahedra (T=Si, Al); **F:** -OTO- linkage; **G:** T-O bending mode.
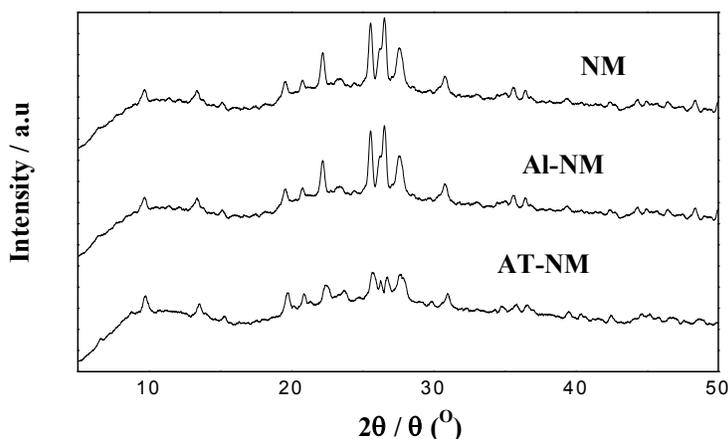

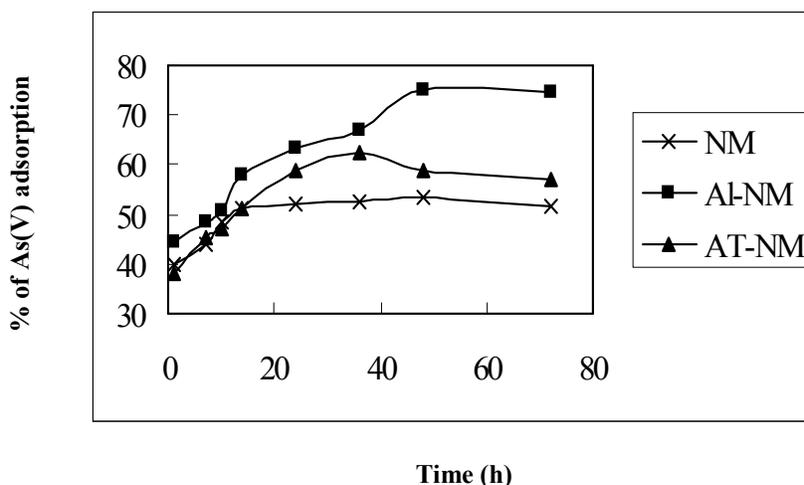**Fig. 1 :** XRD Pattern of NM, Al-NM and AT-NM

Time (h)

Fig. 2 : Influence of contact time on As(V) adsorption by different adsorbents
(conditions : Adsorbent amount : 1g; Initial As(V) concentration : 5 mg L^{-1}(100 mL);
Reaction temperature : r.t.

of 5mLL^{-1} As(V) solution at room temperature at 1, 5, 10, 14, 24, 36, 48 and 72 h to obtain equilibrium time. The equilibrium time is of course depends on the number of active sites in adsorbents and will very from adsorbents to adsorbents. In the present study, NM equilibrates at around 24h while Al-NM and AT-NM show equilibrium time near around 48 and 36 h respectively. Allowing the further contact of AT-NM with As(V) solution after equilibrium, concentration of arsenic adsorption starts to decrease. In this regard, the possibility of donation or removal of protons by the Bronsted sites in zeolites during interaction with As(V) molecules should be considered due to which additional amount of As(V) may form[14]. The experimental data infer that Al-NM sample has increased affinity towards arsenate. This could be explained on the basis of Si/Al contents in the adsorbents. The Al-NM with low Si/Al ratio (4.56) giving rise to high concentration of terminal aluminol sites (-Al-OH) when in contact with water[6,15] and accelerate the ion-exchange process taking place during adsorption. A hypothetical ligand exchange reaction is presented in Equation 1. Moreover,

it could be due to the fact that in Al-loading natural mordenite, the surface area increased remarkably which enhances the adsorption process[15, 16].

$$-Al_r-PH + {}^-O\cdot AsO)OH)_2 \equiv Al_r - {}^-O\cdot AsO(OH)_2 - OH^-$$
Eq. 1
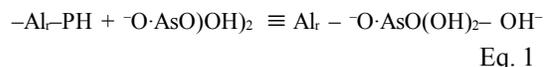
Adsorption of As(V) by zeolites is found to be time dependent and follows the first order kinetics to a significant extent, indicating the adsorption of the metal on to zeolites is dependent on the concentration of the reacting metal[17]. Logergren's pseudo-first order plots (**Fig. 3**) have good linearity with the regression coefficient (r^2) 0.9859, 0.9809 and 0.9580 for NM, Al-NM and AT-NM respectively. The respective first order rate constants for NM, Al-NM and AT-NM are 8.8 x 10^{-2}, 3.5 x 10^{-2} and 1.8 x 10^{-2} h^{-1} respectively. Although NM has lowest arsenic adsorption performance, it possesses largest first order rate constant compared to others. The equilibrium time of the three adsorbents lie in the order NM < AT-NM < Al-NM and hence their first order rate constant follows the reverse order i.e. NM > AT-NM > Al-NM.
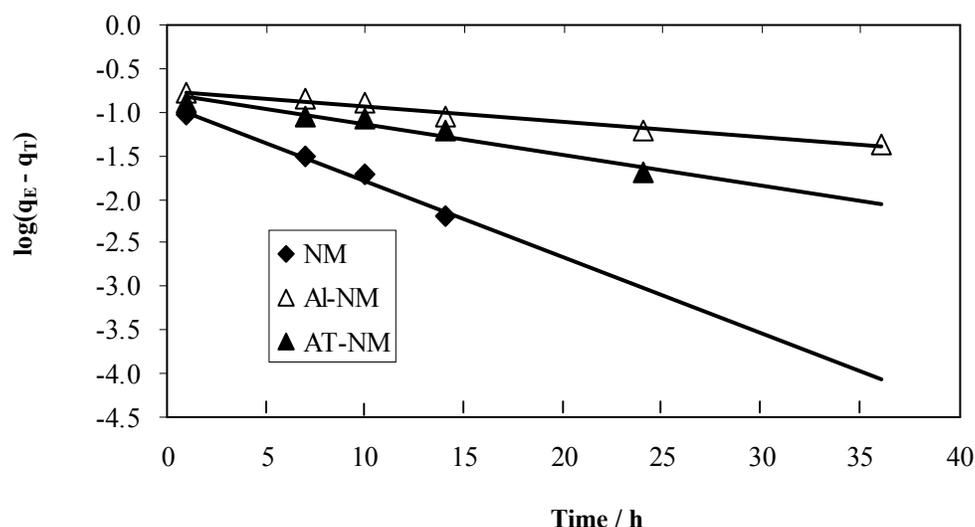
The efficiency of NM, Al-NM and AT-

Fig. 3 : Pseudo-first-order kinetic model of As(V) sorption by NM, Al-NM and AT-NM at r.t
(conditions: Adsorbent amount: 1g; Initial As(V) concentration: 5 mg L^{-1} (100 mL

NM decrease with increase of initial As(V) solution concentrations (**Fig. 4**). This result indicates that energetically less favorable sites become involved with increasing metal concentration in the aqueous solution[1,18]. Due to saturation of active sites by arsenic species, the decrease of arsenic adsorption continues up to a certain value of initial As(V) concentration. If the concentration increased further, no effect is observed on adsorption efficiency of the adsorbents.
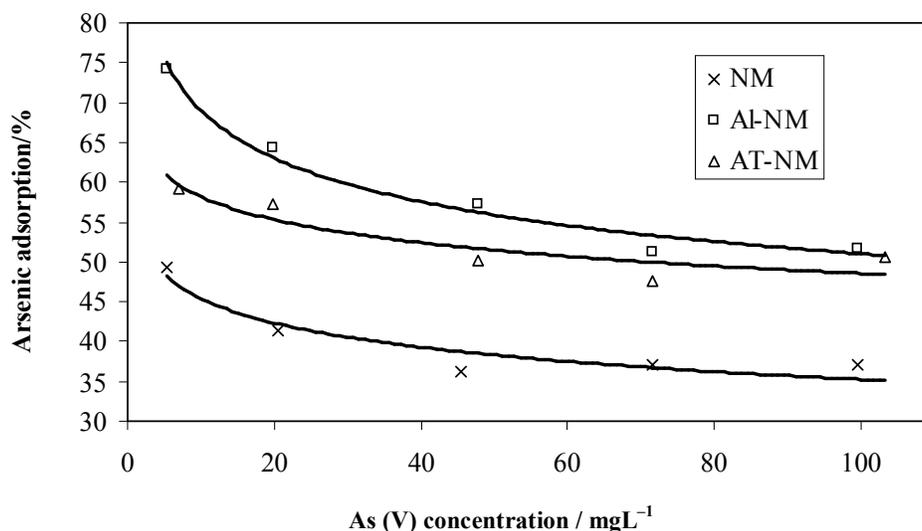

Fig. 4 : Adsorption of As(V) ion as a function of initial concentration. Adsorbent mass: 1 g; Volume of solution: 0.1L and Contact time: 24, 48 and 36 for NM, Al-NM and AT-NM respectively.

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The Freundlich isotherm plots for the initial As(V) concentration of 5, 20, 50, 70 and 100 mgL^{-1} are presented in **Fig. 5**. The plots have a regression coefficient (r) 0.9961 (NM), 0.9982 (Al-NM) and 0.9944 (AT-NM) indicating a near-perfect linear relationship between logQ and logCe. Their respective n values 1.20, 1.40 and 1.18 are within the range between 1 and 10 showing beneficial adsorptions[19]. The numerical value of $0 < 1/n < 1$ (in our case 0.8307 (for NM); 0.7092 (for Al-NM) and 0.8462 (for AT-NM)) indicates an
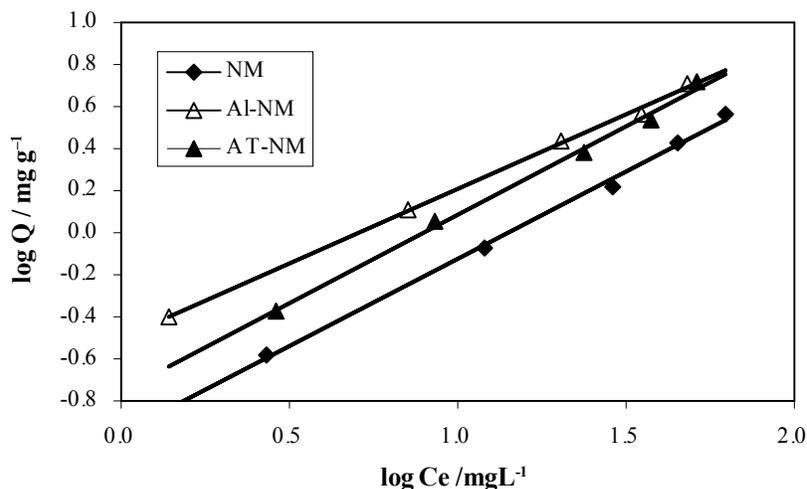

Fig. 5 : Freundlich adsorption isotherms for As(V) adsorption by NM, Al-NM and AT-NM at r.t(conditions: Adsorbent amount: 1 g; Initial Arsenic concentration: 100 mL 5-100 mg L^{-1}; Contact time: 24, 48 and 36 for NM, Al-NM and AT-NM respectively.)

adsorption process that only slightly suppressed at lower equilibrium arsenic concentrations[1]. These values further attributed to a heterogeneous structure of the adsorbent surface without any interaction between adsorbed atoms, molecules or ions[20]. The Freundlich adsorption capacity (K$_F$) values are in the order 0.32 (Al-NM) > 0.17 (AT-NM) > 0.11 (NM).

The dependence of arsenic removal efficiency for all the zeolites were evaluated by changing the pH of the initial solution from ~3 - ~12 using NaOH or HNO$_3$ solution. Each of the adsorbent adsorbs highest arsenate near pH$_{PZC}$ which could be due to the fact that adsorption of multivalent cations occurs effectively at pH just lower than pH$_{PZC}$[12]. pH$_{PZC}$ could be defined as a pH value of solution above which adsorbent surface is negatively charged (AlO$^-$) due to interaction between terminal aluminol sites (-Al–OH) and OH$^-$.

CONCLUSION

Natural mordenite and modified forms are capable of removing arsenic from aqueous solution. Al^{3+}-loading and acid activation enhance the adsorption capacity compared to untreated zeolite due to their increased terminal aluminol site concentration and surface area. The uptake of As(V) on the adsorbents is influenced by contact time, initial arsenic concentration and pH of solution. The adsorption process follows the first order kinetic significantly indicating adsorption process is dependent on the reacting metal. Good linear fits obtained with the Freundlich isotherm points to the nonspecific and energetically nonuniform nature of the adsorption sites.

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