



Adsorption of As(V) on surfactant-modified natural zeolites

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ABSTRACT

Natural mordenite (NM), natural clinoptilolite (NC), HDTMA-modified natural mordenite (SMNM) and HDTMA-modified natural clinoptilolite (SMNC) have been proposed for the removal of As(V) from aqueous solution (HDTMA = hexadecyltrimethylammonium bromide). Influence of time on arsenic sorption efficiency of different sorbents reveals that NM, NC, SMNM and SMNC require about 20, 10, 110 and 20 h, respectively to reach at state of equilibrium. Pseudo-first-order model was applied to evaluate the As(V) sorption kinetics on SMNM and SMNC within the reaction time of 0.5 h. The pseudo-first-order rate constants, k are 1.06 and 0.52 h⁻¹ for 1 and 0.5 g of SMNM, respectively. The observed k values 1.28 and 0.70 h⁻¹ for 1 and 0.5 g of SMNC, respectively are slightly high compared to SMNM. Surfactant surface coverage plays an important role and a significant increase in arsenate sorption capacity could be achieved as the HDTMA loading level on zeolite exceeds monolayer coverage. At a surfactant partial bilayer coverage, As(V) sorption capacity of 97.33 and 45.33 mmol kg⁻¹ derived from Langmuir isotherm for SMNM and SMNC, respectively are significantly high compared to 17.33 and 9.33 mmol kg⁻¹ corresponding to NM and NC. The As(V) uptake was also quantitatively evaluated using the Freundlich and Dubinin–Kaganer–Radushkevich (DKR) isotherm models. Both SMNM and SMNC removed arsenic effectively over the initial pH range 6–10. Desorption performance of SMNM and SMNC were 66.41% and 70.04%, respectively on 0.1 M NaOH regeneration solution.

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1. Introduction

Arsenic in ground water is largely due to the minerals dissolving naturally from weathered rocks and soils. Furthermore, it has many industrial applications and is also used extensively in the production of agricultural pesticides [1,2]. Runoff from these uses and the leaching of arsenic from generated wastes has resulted in increased levels of various forms of soluble arsenic in water. Use of arsenic contaminated water may cause numerous diseases of the skin and internal organs [1–5]. Consequently, extensive research to develop cost-effective methods for arsenic removal has been carried out recently using different sorbents [6–9]. Adsorption technique is generally considered to be promising method amongst the different existing technologies due to easy separation of sorbent from aqueous media after treatment [10].

Naturally occurring zeolites are hydrated aluminosilicate materials with high cation exchange capacities [11–15]. Sorption of arsenic on natural zeolites has been studied extensively in recent years due to their low cost and availability in nature [16–30]. In contrast, arsenic sorption by surfactant-modified natural zeolites

has gained much less attention. Sullivan et al. [24] used surfactant-modified zeolites to remove arsenic from soil-washing leachate for the first time. After this, very little work on this field has been carried out by different workers using either surfactant-modified natural zeolites or clay minerals as sorption media [9,13,31–34].

Sorption of surfactant molecules on zeolites is limited to sites of external exchange only [28,35,36]. This is of course due to zeolite channel diameter which is expected to sufficiently large for exchangeable cations but too small for the surfactant cations [28]. A general model of sorption of ionic surfactant on the zeolite surface is summarized in Fig. 1. Surfactant molecules form a monolayer or ‘hemimicelle’ at the solid–aqueous interface via strong Coulombic interaction at surfactant concentration (C) at or below its critical micelle concentration (CMC). Just as surfactant molecules in solution form ‘micelle’ above the CMC, surfactant exposed to a negatively charged zeolite surface will form a bilayer or ‘admicelle’ and charge on the zeolite surface is reversed from negative to positive [9,15,28,35,36]. The positively charge head groups are balanced by anionic counterions (A^-) which make surfactant-modified natural zeolites a potential sorptive media to sorb anionic contaminants such as arsenate oxyanions via ion exchange mechanism [15,28].

Natural zeolites occurring in different regions of the World exhibit different cation exchange capacity depending mainly on the Al content. The objective of the present study is to modify

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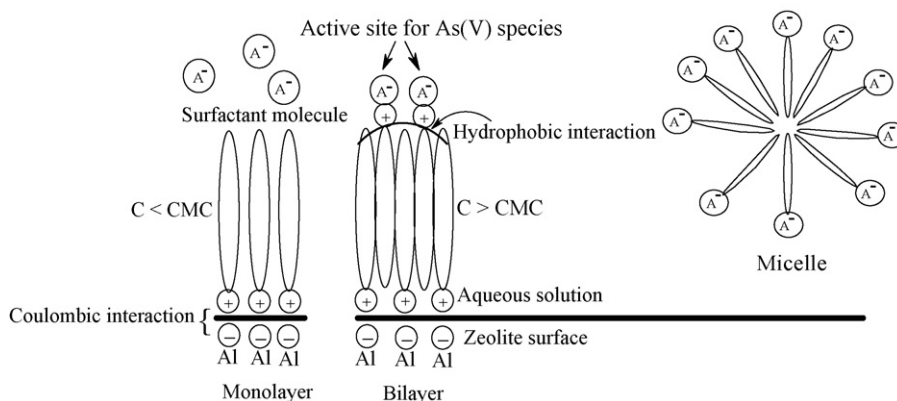


Fig. 1. A model of modification of zeolite surface by surfactant and sorption of As(V) species.

natural mordenite (NM) and natural clinoptilolite (NC) collected from Miyagi and Akita prefecture, Japan, respectively by sorption of cationic surfactant hexadecyltrimethylammonium (HDTMA) bromide in order to create more anion sorption sites. The arsenate (As(V)) sorption performance from aqueous solution by HDTMA-modified natural mordenite (SMNM) and HDTMA-modified natural clinoptilolite (SMNC) were compared with the untreated zeolites NM and NC. The kinetics, sorption isotherms and pH effect on the removal were also studied using batch equilibrium techniques.

2. Experimental

2.1. Materials

Reagent grade hexadecyltrimethylammonium bromide, tetramethylammonium bromide were supplied by Wako Pure Chemical Industries, Ltd., Japan. A stock solution of 1000 mg dm^{-3} of As(V) was prepared by dissolving 4.17 g of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd., Japan) in de-ionized water and was used to prepare the sorbate solutions of concentrations $0.2, 0.5, 1, 5, 10, 20, 35, 50, 75, 100, 150, 200$ and 250 mg dm^{-3} by appropriate dilution for different experiments performed. Essentially, the concentration of arsenic species is always given as the concentration of elemental arsenic.

2.2. Sorbents and modification

NM and NC were obtained from Miyagi and Akita prefecture of Japan, respectively. Zeolites were ground, sieved ($100 \mu\text{m}$) and washed. The samples were heated at 200°C for about 24 h. Once the zeolite's surface has been activated by the heat treatment, the organic modification with HDTMA was performed by adopting previous techniques [11,27] so that the zeolite's external cation exchange capacity is exceeded and HDTMA molecules form a bilayer surfactant configuration at approximately twice the external cation exchange capacity. 100 cm^3 of HDTMA solution with concentration of 0.03 mol dm^{-3} was placed in flask and 10 g of zeolite added. The resulting suspensions were shaken at room temperature (RT) for 24 h, a time sufficient to reach sorption equilibrium. Finally, solid was separated by filtration and washed with distilled water repeatedly in order to remove superficially held HDTMA molecules. The surfactant-modified zeolite was dried at 50°C in an oven for 12 h.

The SiO_2 and Al_2O_3 contents in SMNM and SMNC were determined by LiBO_2 flux-fusion technique using ICP-AES. For this, 0.1 g of power sample was mixed with 0.4 g of LiBO_2 . This mixture was then fused in Pt-crucible at 1050°C for 10–12 min. $10 \mu\text{L}$ of

0.172 mM aqueous LiBr solution was added to the mixture before fusion, as an anti-wetting agent to prevent the fused cooled mass from sticking to the crucible. Cooled mass was dissolved in 50 mL of 10% HNO_3 acid solution and shaken in a sonicator bath for 45 min. After complete dissolution of the mass, the solution was filtered. The final analyte solution for ICP-AES was prepared by pipetting a 5 mL aliquot of the filtered solution and diluting it with 35 mL of 10% HNO_3 .

2.3. Sorption experiments

The sorption experiments were conducted by taking 1 g of sorbents in 100 cm^3 of $\sim 5 \text{ mg dm}^{-3}$ As(V) solution and kept on a shaker at RT ($23 \pm 2^\circ\text{C}$). An initial screening study was performed to examine performance of all the sorbents at a fixed total As concentration, pH (pH maintained $< \text{pH}_{\text{PZC}}$) and liquid:solid ratio for a period of up to 120 h at RT. Subsequent detailed studies were carried out to examine the influence of pH (range 1.9–13.9) and initial As concentration (range $5\text{--}250 \text{ mg dm}^{-3}$). A fixed reaction period of 20, 10, 110 and 20 h for NM, NC, SMNM and SMNC, respectively were employed, since the screening study indicated that a state of equilibrium were achieved within these reaction period. In addition, kinetics of sorption within 0.5 h reaction period at 5 min intervals using 1 and 0.5 g sorbents was also evaluated for As(V) sorption on SMNM and SMNC. After completion of reaction, solid–liquid separation was achieved by filtration. The amount of sorbed As(V), q (mg g^{-1}) and the sorption efficiency, ε (%) were calculated using equations adopted from literature [19].

The point of zero charge (pH_{PZC}) was estimated by using batch equilibrium techniques. For this, 0.1 g of each sorbent was treated with 50 mL 0.1 M NaNO_3 solution which was used as an inert electrolyte. The initial pH values ($\text{pH}_{\text{initial}}$) were adjusted in the range ~ 2 to ~ 12 by adding minimum amounts of 0.01 M NaOH or 0.01 M HNO_3 . The suspensions were allowed to equilibrate for 24 h in a rotary shaker fixed at 200 rpm at RM. After completion of the equilibration time, the admixtures were filtered and final pH values (pH_{final}) of the filtrates were measured again.

2.4. Desorption of As(V) from surfactant-modified zeolites

100 mL As(V) solution of 5 mg dm^{-3} concentration was equilibrated with 1 g of SMNM and SMNC in order to determine sorbed As(V) amount. In desorption tests, SMNM and SMNC (0.5 g each) saturated with As(V) were added to 100 mL of 0.1 M NaOH or 0.1 M HCl regeneration solutions which were then shaken in a rotary shaker fixed at 200 rpm for 24 h at RT. The solids were filtered off and filtrates were analyzed in order to find out desorbed As(V). The

desorption efficiency was calculated as the difference between the amount of As(V) sorbed and that of desorbed.

2.5. Instrumentation

X-ray diffraction (XRD) patterns of all the sorbents were recorded using Rigaku Miniflex with Cu K α filtered radiation (30 kV, 15 mA). Crystallinity was obtained by comparing the intensities of the modified zeolites with those of parent zeolites which were considered to be 100% crystallinity. BET surface area was determined from nitrogen adsorption with the Gemini, Micromeritics analyzer at 77 K. Before operation, the samples were degassed at 200 °C for 3 h under -0.1 MPa to remove any contaminants that may be present at the surface. The initial and final concentrations of arsenic solutions as well as Si and Al contents were measured using an inductively coupled plasma-atomic emission spectroscopy (Model ICPS-7500; Sequential Plasma Spectrometer; Shimadzu Corporation, Japan) with an arsenic detection limits <0.001 mg dm $^{-3}$. The instrument model has both axial and radial viewing modes and equipped with an autosampler and nebulizer. Pure de-ionized water as a sample solution for wavelength calibration was used to avoid errors due to very close wavelength between Ar gas and impure water. Calibration standards were prepared using standard solutions certified by the supplier. Samples were acidified with concentrated HNO $_3$ and filtered with a millipore 0.45 μ m pore size membrane filter before analysis. A digital pH meter of Horiba Ltd., Japan (Model D-51) was used for pH measurement. Total cation exchange capacity (CEC) and external cation exchange capacity (ECEC) were determined by adopting literature techniques [15,35]. Small surfactant molecule tetramethylammonium (TMA) bromide was used to determine the ECEC. Amounts of surfactant sorbed on to zeolites upon modification have been calculated from the organic carbon content (Atomic High Sensitive NC analyzer; Sumigraph NC-22A, Sumika Chemical Analysis Service (SCAS), Japan). The sorbed surfactant concentration was calculated as the difference between initial surfactant concentration and the surfactant concentration in the supernatant after the modification process.

2.6. Quality assurance

In order to ascertain reliability, accuracy and reproducibility of the assembled data, the batch equilibrium tests carried out for the As(V) removal were replicated twice and experimental blanks were run in parallel. All the glasswares were presoaked before use in a 5% HNO $_3$ for about 24 h followed by washing with de-ionized water and drying in oven. Sample blanks were analyzed for correction of background effect on instrument response. Average values of the replicated measurements were reported in all experiments. Linear regression analyses were applied to the data sets used to fit different sorption and kinetic models with correlation coefficient representing the applicability of models.

3. Results and discussion

3.1. Sorbents physicochemical properties

Sorbents physicochemical properties and their chemical composition are presented in Table 1. The resulting Si/Al ratios in SMNM and SMNC determined by ICP-AES are essentially same with the corresponding untreated zeolites which imply that the framework Al atoms are not dealuminate in to solution upon modification with surfactant and could still generate the native cationic ion exchange sites ($-Al-O(C^+)-Si-$; C^+ = cations), which also constituted adsorption centers for the surfactant sorption. XRD analyses of all the zeolites were carried out in order to confirm the crystal structure

Table 1

Studied sorbents along with their physicochemical properties and chemical composition

Sorbents	NM	SMNM	NC	SMNC
pH in water	6.5	6.7	7.9	7.0
pH _{pzc}	4.2	6.4	5.2	6.5
Surface area (m 2 g $^{-1}$)	20.1	8.9	21.9	7.3
CEC (mmol kg $^{-1}$)	1043	–	949	–
ECEC (mmol kg $^{-1}$)	147	–	113	–
SiO $_2$ (wt.%)	72.1 ^a	71.9 ^b	69.4 ^c	69.4 ^b
Al $_2$ O $_3$ (wt.%)	12.9 ^a	12.8 ^b	11.0 ^c	10.9 ^b
Fe $_2$ O $_3$ (wt.%)	1.5 ^a	–	0.8 ^c	–
MgO (wt.%)	–	–	0.7 ^c	–
CaO (wt.%)	2.6 ^a	–	1.4 ^c	–
Na $_2$ O (wt.%)	1.8 ^a	–	3.3 ^c	–
K $_2$ O (wt.%)	2.1 ^a	–	3.2 ^c	–
H $_2$ O (wt.%)	6.2 ^a	–	8.1 ^c	–
Others (wt.%)	0.8 ^a	–	2.1 ^c	–

^a Information supplied by Shin Tohoku Chemical Industry Co., Ltd., Japan.

^b Measured by ICP-AES.

^c Information supplied by Sun Zeolite Industry Co., Ltd., Japan.

and identity. XRD pattern reveals that NM and SMNM contain about 90.47% mordenite, 6.64% clinoptilolite and 2.99% quartz (Fig. 2A). Mineralogical analyses of NC and SMNC from X-ray patterns show a composition of 77.90% clinoptilolite, 9.07% quartz, 6.43% feldspar and 6.60% mordenite (Fig. 2B). The d_{hkl} indexes along with intensity of X-ray peaks corresponding to some typical crystallographic planes of all the zeolites are presented in Table 2. The structural parameters of surfactant-modified zeolites are very close to that of corresponding parent zeolites which indicate that the crystalline nature of the zeolite sorbents remained intact after required chemical treatment with HDTMA molecules and heating treatment for drying. A change in the relative intensities of the (222) and (-422) peaks in SMNM and SMNC, respectively reveals that cation exchange reaction took place in natural zeolites. In order to evaluate surfactant configuration on the modified zeolites, CEC and ECEC of NM and NC are also determined (Table 1). The CEC of NM and

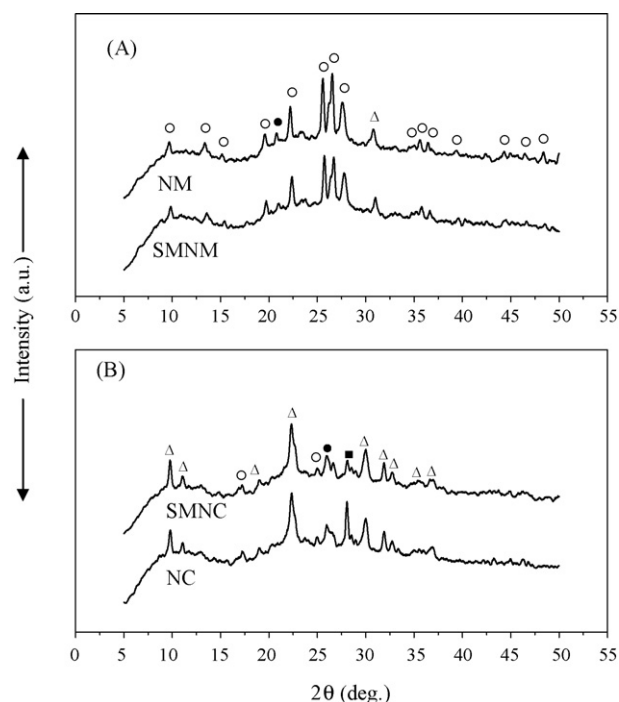


Fig. 2. XRD patterns of (A) NM and SMNM; (B) NC and SMNC (Δ = clinoptilolite, \circ = mordenite, \bullet = quartz, \blacksquare = feldspar).

Table 2
Typical X-ray peaks of natural zeolites and surfactant-modified natural zeolites

hkl	2θ	NM		SMNM		hkl	2θ	NC		SMNC	
		d (Å)	I/I ₀ (%)	d (Å)	I/I ₀ (%)			d (Å)	I/I ₀ (%)	d (Å)	I/I ₀ (%)
200	9.85	8.97	100	8.95	87	020	9.78	9.03	100	9.01	107
111	13.55	6.53	100	6.52	91	200	11.06	7.99	100	7.98	86
330	19.69	4.50	100	4.48	79	111	17.21	5.15	100	5.13	100
150	22.37	3.97	100	3.97	85	-131	18.99	4.67	100	4.67	87
202	25.71	3.46	100	3.45	91	131	22.31	3.98	100	3.98	81
222	26.69	3.34	100	3.32	78	420	24.96	3.56	100	3.54	91
511	27.76	3.21	100	3.21	92	-511	25.93	3.43	100	3.43	71
062	35.26	2.54	100	2.54	106	-422	28.06	3.18	100	3.18	56
352	35.76	2.51	100	2.50	96	151	30.00	2.98	100	2.97	81
641	36.58	2.45	100	2.43	100	530	31.88	2.80	100	2.80	94
931	48.56	1.87	100	1.86	88	-261	32.71	2.73	100	2.73	86

$I/I_0 = (\text{intensity (final)}/\text{intensity (initial)}) \times 100$.

NC are 1043 and 949 mmol kg⁻¹, respectively while their corresponding ECEC are 147 and 113 mmol kg⁻¹. The ECEC for NC is in agreement with those reported by previous workers [14,26]. The cation exchange capacity is dependent on the Al content in the zeolite framework. The high Al content in NM compared to that of NC (Table 1) could be the cause of showing high CEC and ECEC. The sorbed amounts of HDTMA in SMNM and SMNC are 270 and 214 mmol kg⁻¹, respectively which are almost twice as much as their corresponding measured ECEC. These results indicate that sorbed HDTMA molecules formed a partial bilayer surface configuration and reserved the surface charge to positive as illustrated in Fig. 1 which is responsible for sorption of As(V) from water [9,15,24]. ECEC of NM is high than NC which is consistent with observed high HDTMA concentration on SMNM than SMNC. BET surface area of the modified zeolites are almost half in magnitude compared to that of corresponding untreated zeolites (Table 1) indicating zeolite surface coverage with bulk HDTMA molecules. The quite low surface area in untreated and modified zeolites suggests that dominating mechanism of sorption is different than physical sorption.

The pH value of sorbent solution where the net surface charge is zero is defined as pH_{PZC}. A plot (figure omitted for sake of brevity) of pH values of filtered solution after equilibrium (pH_{final}) as a function of initial pH values (pH_{initial}) provides pH_{PZC} of sorbents by the common plateau of constant pH to the ordinate at around 4.2, 5.2, 6.4, and 6.5 for NM, NC, SMNM and SMNC, respectively (Table 1). The pH_{PZC} of sorbents depend on various factors like nature of crystallinity, Si/Al ratio, impurity contents, temperature and sorbability of the electrolytes and degree of H⁺ and OH⁻ ions sorption, etc. and therefore it may vary from sorbent to sorbent [37]. pH_{PZC} will have great impact in As(V) sorption by untreated zeolites because multivalent cation sorption occurred effectively at a pH below pH_{PZC}. In contrary, it may be less important in case of surfactant-modified zeolites because ion exchange took place with Br⁻ ions significantly. Moreover, literature survey reveals no report on pH_{PZC} determination of surfactant-modified zeolites. For sake of convenience, sorptions were carried out at pH < pH_{PZC} unless otherwise stated for all the sorbents.

3.2. Effect of time on different sorbents and sorption kinetics

Influence of time on arsenic sorption efficiency of different sorbents is summarized in Fig. 3. The reaction mixture of sorbent and sorbate of concentration ~5 mg dm⁻³ was stirred for 120 h. SMNM and SMNC are very effective for removal of arsenate. The amounts of solute sorbed at equilibrium are 0.48 mg g⁻¹ (92% efficiency) and 0.46 mg g⁻¹ (86% efficiency) for SMNM and SMNC, respectively. The reaction was completed at 110 and 20 h for SMNM and SMNC, respectively. Arsenate sorption on SMNM

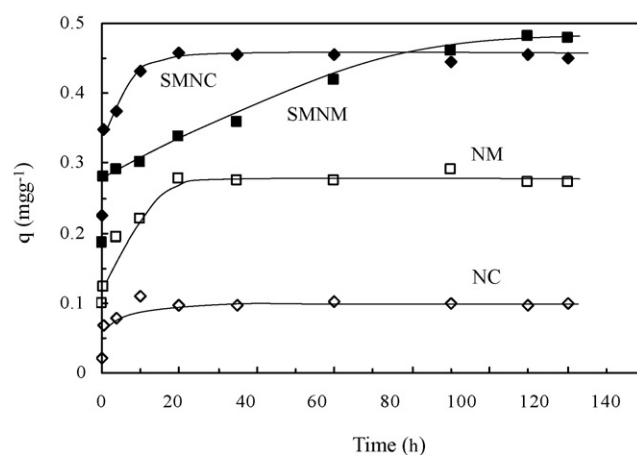
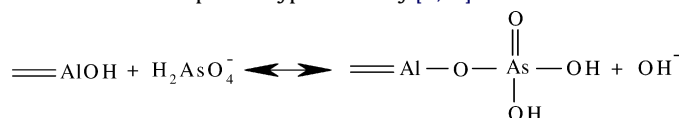


Fig. 3. Amount of As(V) sorbed per unit mass (q) of sorbents NM, NC, SMNM and SMNC at 296 K at different time intervals.

and SMNC depends on amount of sorption sites available which in turn depend on HDTMA surface coverage and ECEC. The difference between total amount of HDTMA sorbed onto zeolite's surface and the experimentally obtained ECEC of the zeolite is the amount of sorption sites available. The sorption site of 123 mmol kg⁻¹ available on SMNM is significantly high compared to that of SMNC (101 mmol kg⁻¹) which is consistent with the high arsenic sorption efficiency obtained for SMNM. Contrast to the modified zeolites, the untreated NM (52% efficiency) and NC (20% efficiency) are not effective for the purpose. Li et al. [9] reported that with 0% surfactant surface coverage, natural clinoptilolite (from St. Cloud Mine in Winston, NM) has no affinity for As(V). In contrast, Elizalde-Gonzalez [4] reported 70% input arsenic removal by natural clinoptilolite (from Hungary and Mexico). A comparably high arsenate sorption affinity of NM (Al₂O₃ = 12.9%) than NC (Al₂O₃ = 11.0%) could be due to high Al content which is an important factor for arsenic sorption [2,38]. When zeolite is in contact with water, terminal aluminol hydroxyl groups will develop at the edges of the zeolite particles. A higher concentration of terminal aluminol species (=AlOH) in high alumina NM leads to a greater capacity for a ligand exchange reaction which could be depicted hypothetically [2,19] as follows:



The reaction stoichiometry will depend on the predominant protonation state of the surface aluminol group and the arsenate oxyanion. The better performance of NM in removing arsenate in

comparison to NC may be also due to the almost twofold higher content of iron (Table 1), which leads to the formation of insoluble arsenic compounds, such as FeAsO_4 [4].

The time courses of SMNM and SMNC as presented in Fig. 3 reveal that the uptake of As(V) is rapid within the first 0.5 h and it continues to increase up to 110 (for SMNM) and 20 h (for SMNC), when state of equilibriums are reached. A plot of arsenic uptake versus square root of time for the whole range of contact time (figure omitted for sake of brevity) gives raise two straight lines with different slopes indicating that two types of mechanisms are operating in the As(V) removal [39]. The initial arsenic uptake rate by both SMNM and SMNC is high as a large number of sorption sites are available for sorption. In the initial bare surface, the sticking probability is large and consequently sorption proceeds with a high rate. As the active sites are gradually filled up by the sorbent species, sorption process became slow and the kinetics became more dependent on the rate at which the sorption is transported from the bulk phase to the actual sorption sites [40]. After external surface loading is completed, the intraparticle diffusion takes place. However, the intraparticle diffusion is not the rate-controlling step because the straight lines are not passing through the origin [39].

Pseudo-first-order model is applied to evaluate the As(V) sorption kinetics on SMNM and SMNC within the reaction time of 0.5 h. Arsenic uptake was measured in every 5 min intervals using 1 and 0.5 g of sorbents with sorbate concentration fixed at $\sim 5 \text{ mg dm}^{-3}$. For short period, sorption of arsenic on to zeolite surface follows the pseudo-first-order kinetics indicating that the zeolite concentration remains effectively constant during the course of the reaction, and only As(V) concentration changes appreciably with time. Also, literature survey reveals that pseudo-first-order kinetic model fits well over the initial stage of the sorption process [39,41]. The first-order rate equation can be expressed as $\log(C_f/C_i) = -kt$; where C_i and C_f denote initial As(V) concentration (mg dm^{-3}) and concentration at time, t (h), respectively and k is the rate constant in h^{-1} [10]. The plot of $\log(C_f/C_i)$ versus time, t gives a good linear fit (Fig. 4) with regression coefficient (R^2) values 0.9930 and 0.9858 for SMNM and SMNC, respectively using 1 g sorbent. Their respective R^2 values are 0.9407 and 0.9967 for 0.5 g of sorbent. The pseudo-first-order rate constants (k) computed from slopes of the plots are 1.06 and 0.52 h^{-1} for 1 and 0.5 g of SMNM, respectively. The observed k values 1.28 and 0.70 h^{-1} for 1 and 0.5 g of SMNC, respectively are slightly high compared to SMNM. Thus, the sorption rate is found to accelerate with an increase in the sorbent amount. This result indicates that sorption rate also appears to be related to the amount of sorption sites which in turn increase as a function of amount of modified zeolites added. Within 30 min reaction period, sorption of As(V) on SMNC proceeds with a high rate despite its low efficiency

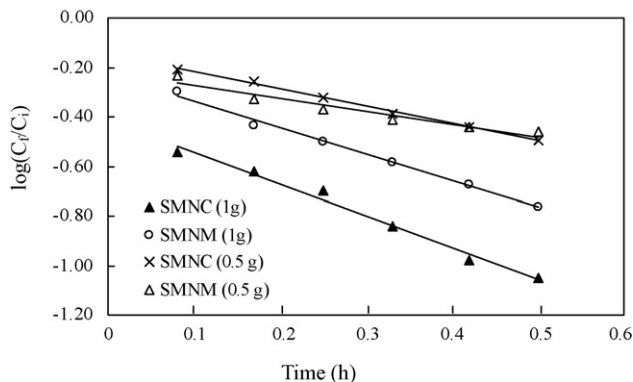


Fig. 4. Short period kinetic study at As(V) initial concentration $\sim 5 \text{ mg dm}^{-3}$ and $\text{pH} < \text{pH}_{\text{PZC}}$.

than SMNM at equilibrium. The potentiality of such rapid kinetics is that it will facilitate smaller reactor volumes ensuring efficiency and economy [10].

3.3. Case study

The concentration of arsenic in fresh water varies from less than 0.05 to more than $5000 \text{ } \mu\text{g dm}^{-3}$ depending on the source of arsenic, mobility and the local geographical environment [8,16]. Moreover, U.S. EPA reduced arsenic concentration in public drinking water from 50 ppb (0.05 mg dm^{-3}) to 10 ppb (0.01 mg dm^{-3}) starting from January 2006 [6]. Therefore, it is very important to investigate the applicability of the developed sorbents at an initial arsenic concentration in ppb levels so that they can bring the arsenic concentration below 10 ppb or not. Also, sorbents having good efficacy at high concentrations may fail to remove arsenic at low concentrations levels. The sorbents reported in literature [2,8,31] were effective in removing arsenic from an initial concentration up to 100 mg dm^{-3} . But, it was not investigated whether these will be equally active to remove arsenic having concentration in ppb levels. In the present investigation, surfactant-modified zeolites are used to investigate the effectiveness using initial concentrations of 0.2, 0.5, 1, 5 and 10 mg dm^{-3} maintaining initial pH approx. at 6. Both the sorbents show increasing sorption efficiency with decrease in initial arsenic concentration (figure omitted for brevity). With initial arsenic concentrations of 10 and 5 mg dm^{-3} , the concentrations are decreased to 1.15 and 0.44 mg dm^{-3} , respectively by SMNM which are still above WHO's earlier guideline value of 0.05 mg dm^{-3} . An initial arsenic concentration of 1 mg dm^{-3} is reduced to 0.033 mg dm^{-3} which is below 0.05 mg dm^{-3} . While using an initial concentration of 0.5 mg dm^{-3} , arsenic concentration is reduced to $0.0025 \text{ mg dm}^{-3}$ which is below target level of 0.01 mg dm^{-3} . The arsenic concentration is further decreased below detection limit of 0.001 mg dm^{-3} using an initial concentration of 0.2 mg dm^{-3} . While using SMNC as sorbent, arsenic concentration is decreased to 0.017 mg dm^{-3} while using an initial concentration of 0.2 mg dm^{-3} . The SMNC is not efficient to reduce the arsenic concentration even below WHO's earlier guideline value of 0.05 mg dm^{-3} while using concentrations of 0.5, 1, 5 and 10 mg dm^{-3} . This study is focused on highly concentrated model solutions of arsenic. Waste waters usually contain many interfering contaminants that may also influence the removal efficiency.

At lower concentration, i.e. 0.2 mg dm^{-3} in the present research, all arsenic ions present in the solution would interact with

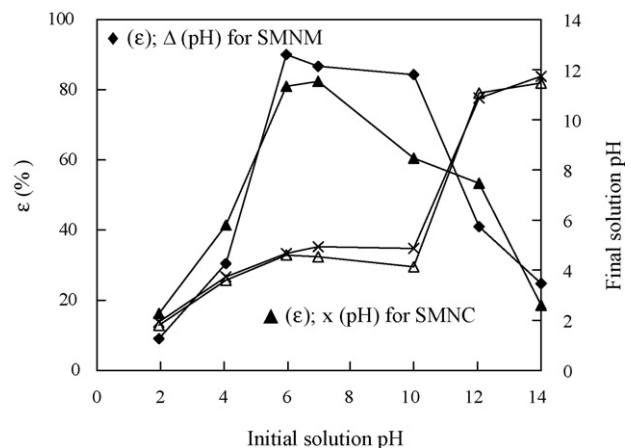
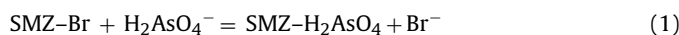


Fig. 5. The dependence of As(V) removal efficiency (ϵ) and final solution pH of surfactant-modified sorbents upon initial solution pH.

the binding sites and thus facilitated a sorption even below detection limit. At higher concentrations, more As(V) species will be left unadsorbed in solution due to the saturation of binding sites.

3.4. Effect of pH on As(V) sorption

The results of experiments carried out in order to evaluate the efficiency of SMNM and SMNC sorbents in removing As(V) over a range of pH 1.9–13.9 are shown in Fig. 5. Both the sorbents removed arsenic effectively over the initial pH range 6–10. The predominant forms of arsenate in this pH range are H_2AsO_4^- and HAsO_4^{2-} [2]. The surface anion exchange between these two arsenate forms and counterion bromide of surfactant-modified zeolites (SMZ) can be presented conceptually by Eqs. (1) and (2) which were well verified and discussed by previous workers [9,24]. It is evident from the figure that both of these forms can be effectively sorbed by SMNM and SMNC. Compared to the previous works related to As(V) sorption by surfactant-modified zeolites, where optimum pH range were reported to be 7.2–7.5 [9] and 7.4 [25], the sorption for As(V) by investigated surfactant-modified zeolites is of a wide optimum pH range, which should be of significant importance for practical operation. At initial pH <2, As(V) in solution exist in neutral form H_3AsO_4 [2], no ion exchange took place with bromide and observed As(V) sorption is only for physical sorption. Therefore, As(V) sorption efficiency is remarkably low at pH ~2.



The change of final pH as a function of initial pH (1.9–13.9) is also presented in Fig. 5. Both the sorbents follow the same trend of pH change indicating homogeneous nature of the surfaces in respect of existing ions. In the pH range 6–10, the pH of solution shifted towards acidic region. This may be due to the fact that zeolite surface could still generate protonated AlOH_2^+ groups [38] in solution even after modification with HDTMA. The drop of final pH is due to OH^- consumption via deprotonation of surface AlOH_2^+ groups giving back terminal aluminol group, $=\text{AlOH}$ (Eq. (3)):



3.5. Sorption isotherms

At the temperature 296 K and As(V) concentration 5, 20, 35, 50, 75, 100, 150, 200 and 250 mg dm^{-3} , the q versus C_e isotherms for As(V) surfactant-modified zeolite interactions for a fixed sorbent amount 1 $\text{g}/100 \text{ cm}^3$ are presented in Fig. 6 where q is the amount of sorbed As(V) per gram of sorbent (mg g^{-1}), C_e is the equilib-

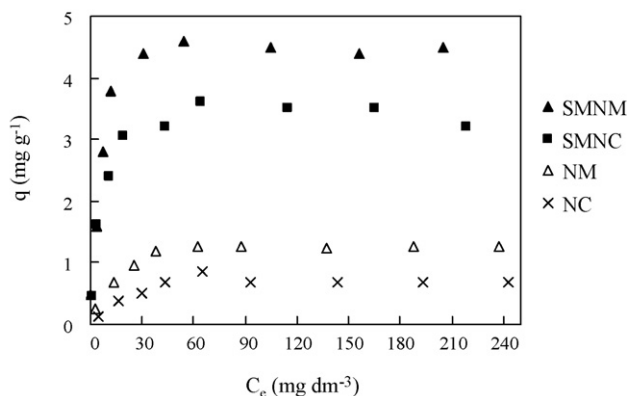


Fig. 6. Plot of q vs. C_e for As(V) sorbed on NM, NC, SMNM and SMNC.

rium concentration (mg dm^{-3}). The initial pH of the solutions was adjusted approx. at 6 which is below the respective pH_{PZC} (Table 1) of SMNM and SMNC.

The Langmuir linear sorption isotherm model is applied in order to quantitative evaluation of sorption performance [8,11,12]. The Langmuir isotherm plots with good regression coefficient (R^2) values for all the sorbents (Table 3) indicate a near-perfect linear relationship between C_e/q and C_e . The Langmuir monolayer sorption capacity (Q_m) is quite large particularly for modified zeolites with values 97.33 and 45.33 mmol kg^{-1} for SMNM and SMNC, respectively. These Q_m values are remarkably high than 7.2 mmol kg^{-1} determined using a HDTMA-modified zeolite [9], but still much less than 430 mmol kg^{-1} determined on octadecylammonium zeolite [13]. These could be due to different experimental conditions such as liquid to solid ratio, initial concentration, etc. used during sorption process. Also, ECEC and surfactant surface coverage are two major factors which play key role during sorption process [9]. The corresponding Langmuir coefficient, b values for SMNM and SMNC are 188.68 $\text{dm}^3 \text{g}^{-1}$ and 152.43 $\text{dm}^3 \text{g}^{-1}$. The Q_m and b values are in accordance with the efficiency (ϵ) trend $\text{SMNM} > \text{SMNC} > \text{NM} > \text{NC}$. Due to large values of Langmuir monolayer sorption capacity, both SMNM and SMNC can retain a large amount of As(V) from aqueous solution helping in the separation of the arsenic ions from solution. Similarly, large b values indicate the stability of As(V)–zeolite sorption complex, which may be the cause of existence of chemical binding forces between arsenate oxyanions and surface of the zeolite sorbents.

Linear form of Freundlich isotherm model is also applied in present sets of data [8,11,12]. Freundlich plots give raise R^2 values near about 0.99 for all the sorbents (Table 3) indicating linear relationship between $\log q$ and $\log C_e$. Freundlich exponent $1/n$ provides information about surface heterogeneity and surface affinity for the solute (Table 3). $1/n$ values computed from slopes of the plots are 0.5543 for SMNM and 0.5045 for SMNC which indicate a favourable sorption of As(V). Since the degree of favourableness increases as $1/n$ approaches zero, both the surfactant-modified sorbents show a very high affinity for As(V). Free energy change, ΔG of arsenic sorption on zeolite is calculated using the Freundlich constant (K) values (Table 3) of the sorbents [42]. The negative free energy values indicate the feasibility of the process and the spontaneous nature of sorption. The observed trend of K values is $\text{NC} < \text{NM} < \text{SMNM} < \text{SMNC}$ which does not follow the actual efficiency trend. This may be due to the high sorption rate on SMNC compared to SMNM at initial reaction period that also been evident from their rate constant (k) values.

Dubin–Kaganer–Radushkevich (DKR) isotherm is based on the heterogeneous surface of the sorbent [8,12]. From DKR plots of $\ln q$ versus ϵ^2 , different parameters were evaluated for all the sorbents

Table 3
Isotherm parameters for the removal of As(V) by NM, NC, SMNM and SMNC at 296 K

Isotherm parameters	NM	SMNM	NC	SMNC
Langmuir isotherm				
Q_m (mmol kg^{-1})	17.33	97.33	9.33	45.33
b ($\text{dm}^3 \text{g}^{-1}$)	133.33	188.68	97.56	152.43
R^2	0.9982	0.9989	0.9839	0.9948
Freundlich isotherm				
K (mg g^{-1})	1.02	1.24	1.00	1.59
$1/n$	0.8177	0.5543	0.9250	0.5045
$-\Delta G$ (kJ mol^{-1})	17.05	17.53	17.00	18.14
R^2	0.9824	0.9655	0.9925	0.9191
DKR isotherm				
β ($\text{mol}^2 \text{J}^{-2}$)	-4.9×10^{-9}	-4.6×10^{-9}	-7.3×10^{-9}	-4.4×10^{-9}
E (kJ mol^{-1})	10.1	10.4	8.3	10.7
R^2	0.9916	0.9754	0.9957	0.9513

and summarized in Table 3. The sorption capacity, Q_m values are unreliably large indicating inconsistency with the present study probably due to the shape of the isotherms and basic principles involved in the mathematical derivation of the model [8]. In contrast, the mean energy of sorption, E values of all the sorbents (Table 3) derived from this isotherm are very informative and lie in the range of 8–16 kJ mol⁻¹ characteristics for ion exchange mechanism during As(V) sorption [8,12].

3.6. Desorption of As(V) from surfactant-modified zeolites

The regeneration of sorbents is a key process in water treatment. In the present study, desorption experiments were carried out with the sorbents SMNM and SMNC considering their good performance in sorption experiments. Fig. 5 reveals that both SMNM and SMNC are more effective in acidic pH range which implies that As(V) can be desorbed by alkaline media. For convenience, desorption tests were conducted with 0.1 M NaOH and 0.1 M HCl solutions. Desorption performances of SMNM and SMNC are 66.41% and 70.04%, respectively while using NaOH solution. In HCl solution, desorption performances are reduced to 40.62% and 47.68% by SMNM and SMNC, respectively. This result indicates that desorption phenomenon is the reverse of the sorption process. The arsenic-laden zeolites have passed EPA's Toxicity Characteristic Leaching Procedure test and can be safely disposed of as non-hazardous waste [1].

4. Conclusion

Present study shows that surfactant-modified zeolites are effective sorbent for the removal of As(V) from aqueous solution. Natural zeolites are inexpensive and readily available in nature. Furthermore, surfactant-modified natural zeolites are much less expensive than granular activated carbon or synthetic ion exchange resins due to very low specific gravity of high-porosity zeolites. A case study with the developed surfactant-modified zeolites shows that both SMNM and SMNC reduce As(V) concentration below WHO's earlier guideline values of 50 ppb arsenic in drinking water. The most promising result is that SMNM further reduce the As(V) concentration below WHO's guideline values of 10 ppb. Thus, availability of the sorbents in nature, low cost, fast sorption rate, excellent sorption and desorption efficiency and wide optimum pH range are expected to cut down the operating costs and warrant their use in actual applications. Because of the many factors that can affect arsenic removal efficiency (including arsenic concentration, speciation, pH and co-occurring solutes), any technology should be tested using the actual water to be treated, before implementation of arsenic removal systems at the field scale.

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