

KINETICS AND THERMODYNAMIC FOR SORPTION OF ARSENATE BY LANTHANUM-EXCHANGED ZEOLITE

Md Jelas Haron*, Saiful Adli Masdan, Mohd Zobir Hussein, Zulkarnain Zainal and Anuar Kassim

Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

*Corresponding author email: mdjelas@fsas.upm.edu.my

Keywords :La-exchanged zeolite, arsenate sorption, thermodynamic and kinetics

Abstract

Zeolites are crystalline, hydrated aluminosilicate containing exchangeable alkaline and alkaline earth cations in their structural frameworks. Since zeolites have permanent negative charges on their surfaces, they have no affinity for anions. However recent studies have shown that modification of zeolites with certain surfactants or metal cations yield sorbents with a strong affinity for many anions. In this paper, modification of zeolites (zeolite A, X and ZSM5) were performed by exchange of naturally occurring cations with lanthanum ion that forms low solubility arsenate salt. The exchanged zeolites were used to sorb arsenate from aqueous solution. Among parameters investigated were effect of pH, arsenate initial concentrations, contact time and temperature. The maximum exchanged capacity of La(III) ion was obtained when using solution with initial pH of 4. Zeolite X gives the highest La(III) exchanged capacity compared to other zeolites. The results showed that As(V) sorption by La-zeolites occurred at about pH 6.5 and increased as pH increased and reaching maximum at equilibrium pH about 7.8. On the other hand, almost no arsenate sorption occurred on unexchanged zeolites. This indicates that La(III) ion on the exchanged zeolites is taking part on the As(V) sorption via surface precipitation. The results also showed that the sorption capacities increased with increasing initial As(V) concentrations. The sorption followed Langmuir model with maximum sorption capacities of 0.41, 0.21 and 0.19 mmol/g at 25°C for La exchanged zeolite X (La-ZX), La exchanged zeolite ZSM5 (La-ZSM) and La exchanged zeolite A (La-ZA), respectively. The amounts of sorption of As(V) by La exchanged zeolite increased as temperature increased from 25 to 70°C indicating that the process is endothermic. The free energy changes (ΔG°) for the sorption at 25°C were -10.25, -9.65 and -8.49 kJ/mol for La-ZX, La-ZSM and La-ZA, respectively. The negative values of ΔG° meant that the sorption of As(V) ions on La-exchanged zeolite was spontaneous, perhaps because the La(III) had high affinity towards the arsenic ion as indicated by a low K_{sp} value of of lanthanum arsenate. A slightly positive entropy change for sorption of As(V) ion on La-exchanged zeolite could be due to fixation of the ions on the La(III) exchange sites that was randomly distributed on the sorbents. The kinetics study showed that the As(V) sorption followed first order kinetic model. The first-order kinetic constants for the sorption are 2.77×10^{-3} , 2.25×10^{-3} and $1.60 \times 10^{-3} \text{ min}^{-1}$ for La-ZX, La-ZSM and La-ZA, respectively.

Abstrak

Zeolit adalah kristal aluminosilikat terhidrat yang mengandungi kation logam alkali dan alkali bumi yang boleh ditukarganti dalam struktur bingkainya. Oleh kerana strukturnya mempunyai cas negatif kekal, ia tidak mempunyai afiniti terhadap anion. Walau bagaimana pun kajian terkini mendapati pengubahsuaian dengan surfaktan atau ion logam tertentu boleh menjadikan zeolit sebagai penyerap dan mempunyai afiniti yang kuat terhadap anion. Kertas ini melaporkan penukaran kation asal zeolit (A, X and ZSM5) dengan ion logam lanthanum yang berupaya membentuk garam arsenat yang mempunyai nilai keterlarutan rendah. Zeolit yang mengandungi kation lanthanum telah digunakan untuk menyerap arsenat dari larutan akueus. Diantara parameter yang dikaji termasuklah kesan pH, kepekatan awal arsenat, masa sentuh dan suhu. Muatan pertukaran maksimum La(III) ke dalam zeolit berlaku pada pH 4. Zeolit X mempunyai muatan pertukaran La(III) paling tinggi berbanding zeolite lain. Keputusan kajian menunjukkan erapan As(V) oleh La-zeolit berlaku pada pH 6.5 dan meningkat dengan penigkatan pH, dan mencapai maksimum pada pH 7.8. Sebaliknya zeolit asal tanpa pertukaran lanthanum hampir tidak menunjukkan sebarang erapan terhadap arsenat. Ini menunjukkan La(III) pada zeolit mengambil bahagian didalam erapan arsenat berkemungkinan melalui pemendakan permukaan.

Keputusan juga menunjukkan muatan erapan arsenat meningkat dengan peningkatan kepekatan awal ion arsenat. Erapan As(V) mengikuti model Langmuir dengan muatan erapan maksimum 0.41, 0.21 dan 0.19 mmol/g pada 25°C masing-masing bagi zeolit X tertukar La (La-ZX), zeolite ZSM5 tertukar La (La-ZSM) dan zeolite A tertukar La (La-ZA). Amaun erapan As(V) meningkat dengan peningkatan suhu daripada 25 ke 70°C menunjukkan proses ini adalah eksotermik. Perubahan tenaga bebas (ΔG°) pada 25°C adalah -10.25, -9.65 dan -8.49 kJ/mol masing-masing untuk La-ZX, La-ZSM dan La-ZA. Nilai ΔG° negatif menunjukkan proses erapan adalah spontan, mungkin disebabkan oleh afiniti yang tinggi ion lanthanum terhadap ion arsenik seperti yang ditunjukkan oleh nilai K_{sp} lanthanum arsenat yang rendah. Nilai perubahan entropi yang positif pula menguatkan lagi anggapan berlaku tindak balas antara ion As(V) dengan ion lanthanum yang bertaburan secara rawak pada zeolit. Kajian kinetik menunjukkan erapan As(V) mematuhi model kinetik tertib pertama. Pemalar kinetik tertib pertama adalah 2.77×10^{-3} , 2.25×10^{-3} dan $1.60 \times 10^{-3} \text{ min}^{-1}$ masing-masing untuk La-ZX, La-ZSM and La-ZA.

Introduction

Although arsenic is known as a highly toxic element, the compounds are still widely used in many applications. Among others they are used for the productions of ceramics, semiconductors, pesticides and fertilizers. The arsenic also enters the environment through other anthropogenic activities such as petroleum refineries, fossil fuel power plants and non-ferrous smelting. Recently most international drinking water standards were lowered to 0.01 mg/l. The international standard for effluent was set to 1.0 mg/l. Consequently there is growing interest in the study on removal of arsenic ion from aqueous systems.

Conventional precipitation methods for arsenic removals have not been successful to meet drinking and effluent standards for As due to limitation of solubility of the resultant product. On the other hand, adsorption appears to be one of the promising methods for removal of arsenic from water. Among others, the removal of As(V) by adsorption methods have been studied using spodic [1], aquifer material [2], oxides of antimony and manganese [3], iron hydroxide [4] iron coated catalyst [5] and ion exchanger [6].

Zeolites are crystalline, hydrated aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations normally of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium, and barium, as well as water molecules in their structural frameworks. Structurally, they are complex, porous, crystalline inorganic polymers, enclosing interconnected cavities in which the metal ions and water molecules are contained. They are based on an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygen ions [7]. Zeolites may be represented by an empirical formula of $\text{M}_{2/n}\text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$. In this oxide formula, x is generally equal to 2 or greater since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra, n is the cation valence which neutralize the negative charge on the aluminosilicate framework and y represents the water contained in the voids of the zeolite [8].

Zeolites have excellent catalytic as well as separation properties. Several properties of zeolite minerals have been studied, including adsorption and ion exchange. These were important applications of zeolites for removal of heavy metals by both processes. Among others, the advantages of ion exchange over the chemical precipitation method for heavy metal removal are high selectivity, can be recovered and produce less sludge. The availability of natural zeolites provides a low cost ion exchanger [9]. Table 1 shows a few examples of zeolite composition [10].

The Si/Al ratio of a zeolite indicates its cation content; the fewer aluminium atoms there are, the fewer the exchangeable cations will be present. The highly siliceous zeolites such as zeolite ZSM 5 can have a Si/Al ratio that lies between 20 and 1.5 where else zeolite A and X have Si/Al ratio around 1. The zeolites with high Si/Al ratios are stable in the presence of concentrated acids [11].

Table 1: Zeolite Compositions [10]

Zeolite	Typical formula
Natural	
Mordenite	$\text{Na}_8[\text{AlO}_2]_8(\text{SiO}_2)_{40} \cdot 24\text{H}_2\text{O}$
Faujasite	$(\text{Ca}, \text{Mg}, \text{Na}_2, \text{K}_2)_{4.5}[\text{AlO}_2]_{59}(\text{SiO}_2)_{27} \cdot 27\text{H}_2\text{O}$
Clinoptilolite	$\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}] \cdot 24\text{H}_2\text{O}$
Synthetic	
Zeolite A	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$
Zeolite X	$\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264\text{H}_2\text{O}$
Zeolite ZSM-5	$(\text{Na}, \text{TPA})_3[(\text{AlO}_2)_3(\text{SiO}_2)_{93}] \cdot 16\text{H}_2\text{O}$

Since zeolites have a permanent negative charge on their surface, they have no affinity for anions. However recent studies have shown that modification of zeolites with certain surfactants or metal cations yield sorbents with a strong affinity for many anions [12]. In order to sorb anions, the modified surface must either possess positively charged exchange sites, or there should be replacement of weakly held counter ions of the surfactant by more strongly held counter ions. Cationic-surfactant-modified zeolites were shown to remove chromate from aqueous solutions [12, 13]. Some cationic exchanged forms of zeolites showed high uptake of iodide and molybdate from solution [14]. Since As(V) presence in water as arsenate anion in wide pH range, the removal of As(V) by zeolites can be enhanced after loading it with various metal ions such as Al(III) [15] and Pb and Cu [16]. Previous reports have shown that rare earth compounds including lanthanum [17] were effective for removal of As(V) from aqueous solutions. In this paper, modification of zeolites A, zeolite X and zeolite ZSM5 were performed by exchange of their naturally occurring cations with lanthanum ion. The exchanged zeolites were used to sorb arsenate from aqueous solution. Parameters investigated include effect of pH, arsenate initial concentration, contact time and temperature. The lanthanum exchanged zeolite has been reportedly used as a catalysts [18].

Experimental

Aluminium sulphate hexahydrate, sodium hydroxide, sulphuric acid, hydrochloric acid and sodium dodecyl sulphate were purchased from BDH. Propylamine, lanthanum chloride heptahydrate, sodium arsenate were purchased from Fluka while silicic acid and tetrapropylammonium bromide were purchased from Aldrich. These chemicals were 99.9% pure.

Zeolites used in this study were zeolite X (Fluka) and zeolite A (BDH) and used without further treatment. Zeolite ZSM5 was synthesised as follows [19]: 2 grams of silicic acid, 1 g of tetrapropylammonium bromide (TPABr) as templating agent and 0.5 g of sodium hydroxide were mixed in 5 mL of distilled water followed by addition of 1 mL of n-propylamine and mixed well. Another solution containing 0.25 g of aluminium sulphate and a few drops of concentrated sulphuric acid was also prepared. The former solution was added to the latter and the resulting solution was thoroughly mixed, and aged in a hydrothermal bomb at 160°C for 5 days. The resulting zeolite mixture was calcined at 500°C for 2 hours.

Preparation of La(III)-exchanged on Zeolites

About 5.0 g zeolite was added to a 100 mL 0.10 M lanthanum chloride heptahydrate (Fluka) solutions at pH 5 (HCl) and stirred for 12 hours at ambient temperature. The zeolite was separated from the solution by centrifugation. The pH of the final solution was measured and the amount of lanthanum ion in the supernatant was determined by Inductively Couple Plasma-Atomic Emission Spectrometer (ICP-AES) (Perkin Elmer P1000) using recommended procedure by the manufacturer.

Sorption of Arsenic Ion on Zeolites and La-exchanged Zeolites

A series of NaH_2AsO_4 (Aldrich) solutions (25 ml) with concentration ranges from 25-125 mM were prepared. The pH of the solution was adjusted by 0.1M hydrochloric acid and about 0.1 g of zeolite sorbent was added. The mixture was then stirred at ambient temperature. At a specific contact time, the adsorbent was separated from the solution by centrifugation. The pH of the final solution was measured and the arsenate ion was quantified by ICP-AES. Parameters that can affect the sorption capacities such as pH, concentration of arsenate ions, adsorbent dosage and temperature were studied. Zeolite A, zeolite X, zeolite ZSM5 and La-exchanged zeolite X (La-ZX), La exchanged-zeolite ZSM5 (La-ZSM) and La-exchanged zeolite A (La-ZA) were used as sorbents.

Results and Discussion

La(III) Metal Ions Uptake by Zeolite

La exchange capacity in zeolite increased by increasing the initial pH value [20]. In the present study, the highest exchange capacity of La(III) was obtained when using solutions with initial pH of 4, which changed to give a final pH value of 5-6. The results are similar with previous studies of metal sorption by natural zeolite, which revealed that the sorption capacity is low at pH below 4.0 [21, 22]. Moreover, low pH values are undesirable for zeolite sorption because this would affect its physical and chemical structure [23]. Zeolite X gives the highest La exchanged capacity compared to other zeolite as shown in Table 2. This was expected since zeolite X has the biggest pore diameter [19]. The La exchange of the zeolite is carried out in acidic solution in order to avoid the hydrolysis and precipitation of lanthanum hydroxides. However, under this condition, the sodium ions in the zeolite will be exchanged not only for La(III), but also for hydronium ions from the solution [24].

Table 2 Exchanged capacities of zeolite for La

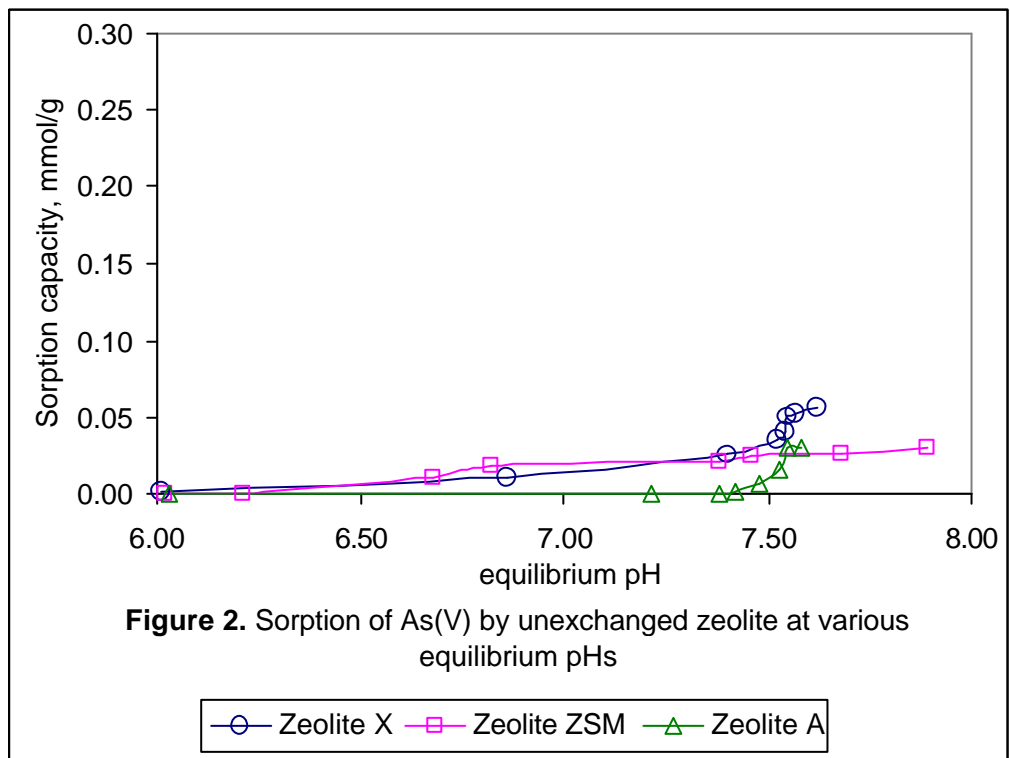
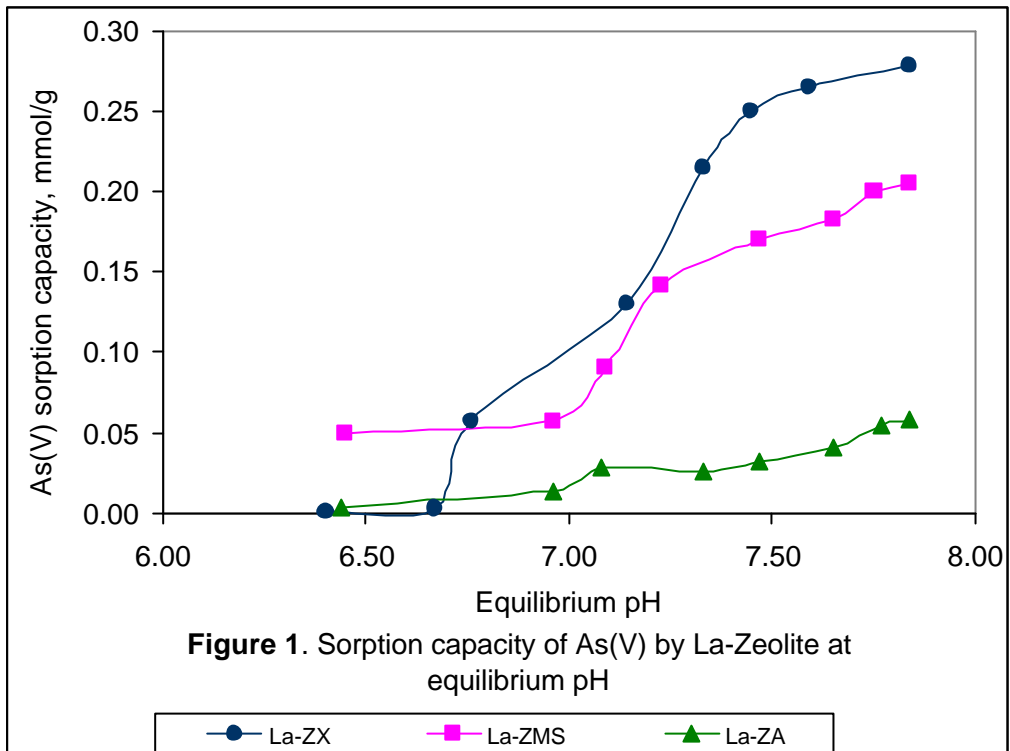
Zeolite	Pore diameter ^[19] Nm	La exchanged capacity mmol/g
Zeolite X	1.20	1.10
Zeolite ZSM5	0.55	0.80
Zeolite A	0.42	0.58

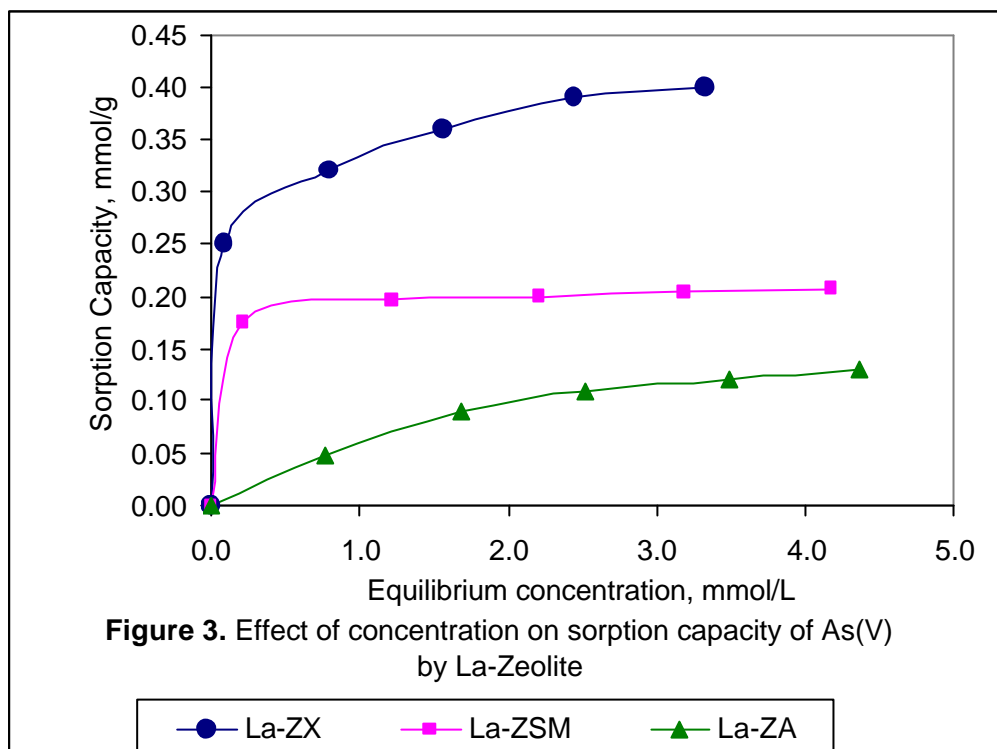
Sorption of Arsenate Ion by Zeolites

The experiments conducted by Bonnin [25] showed that natural zeolites were unable to adsorb significant amount of As(V) from aqueous solution. Modification of the zeolite by exchanged with ferrous ion increased the As(V) sorption by 92% in the order of 25 mg/g. In the present study, sorption of arsenate ion was carried out using original and La exchanged zeolite A, X and ZSM5. Figure 1 shows the capacities at equilibrium pH for the sorption of arsenate ion on La-ZA, La-ZX, La-ZSM. The results show that the As(V) sorption occurred at about pH 6.5. The sorption increased as pH increases and reaching maximum at about pH 7.8. At higher pH, La will be precipitated as La(OH)₃. On the other hand, almost no arsenate sorption occurred on unexchanged zeolites as shown in Figure 2. This confirmed that La(III) ion on the zeolites was taking part on the As(V) sorption. Since the K_{sp} of lanthanum arsenate is reasonably low, $3.55 \times 10^{-22} \text{ M}^2$, the As(V) removal by the La-exchanged zeolites most likely occurred via surface precipitation. The As(V) retention is highest on the La-ZX. This could be due to highest La exchanged capacity of zeolite X compared to the other zeolites as shown in Table 2.

Effect of As(V) Concentrations on Sorption

The sorption of arsenate ion on La-exchanged zeolites was conducted with various initial concentrations (1 mM to 5 mM) at initial pH 5 (equilibrium pH 7.5). The results show that the sorption capacities increased with increasing initial concentration (Figure 3). In order to establish the maximum As(V) sorption capacity, the Langmuir equation of the following form was applied to the sorption equilibria at different concentrations:





$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (1)$$

where C_e is the concentration of metal solution at equilibrium (mmol/L), q_e the amount of As(V) sorbed at equilibrium (mmol/g), q_m the maximum sorption capacity and b is constant related to binding energy of sorption system. The linearity of the plots (Fig. 4) shows that the sorption follows the Langmuir model with maximum capacities of 0.41, 0.21 and 0.19 mmol/g for La-ZX, La-ZSM and La-ZA, respectively (Table 3). It appears that there is a strong correlation ($R^2=0.88$) between As(V) sorption capacity to exchange capacity of La in zeolite. However there is no correlation found between binding constants and capacities.

Table 3. Maximum sorption capacities of La-zeolites for As(V)

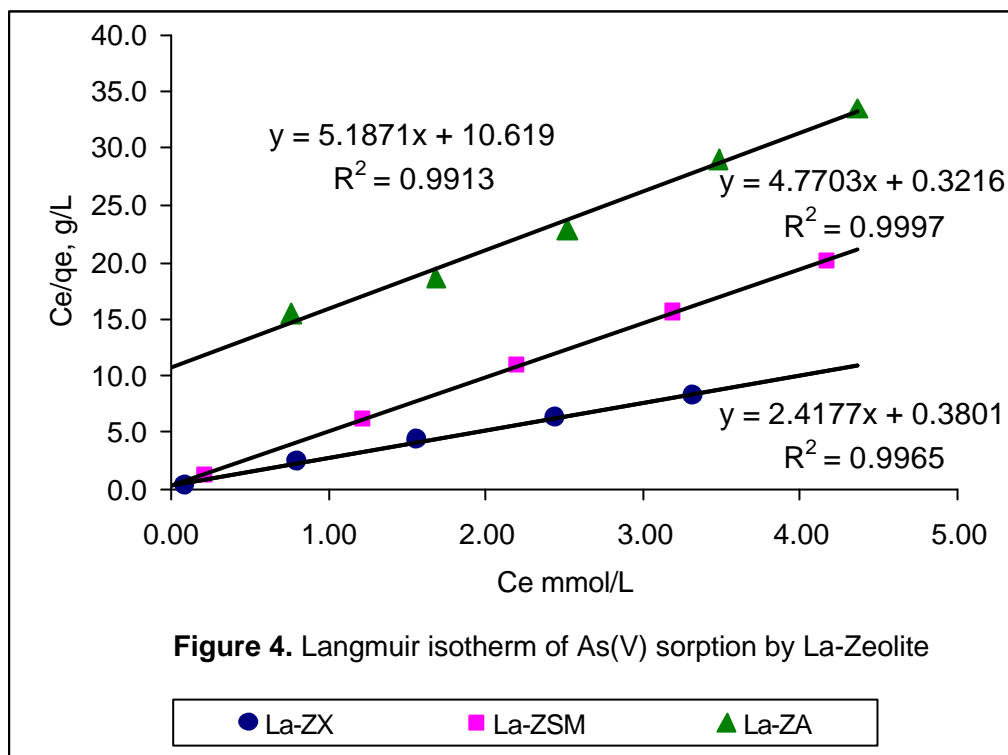
Zeolite	La exchanged capacity mmol/g	As(V) maximum sorption (q_m) mmol/g	Langmuir binding energy constant, (b) L/mmol
La-ZX	1.10	0.41	6.36
La-ZSM	0.80	0.21	14.82
La-ZA	0.58	0.19	0.49

Thermodynamic Parameters

The amount of sorption of As(V) by La-exchanged zeolites increased as temperature increases from 25 to 70 °C. The following relationships has been used to evaluate the thermodynamic parameters of the standard Gibbs free energy ΔG° , enthalpy ΔH° and entropy ΔS° :

$$\Delta G^\circ = -RT \ln K_d \quad (2)$$

and

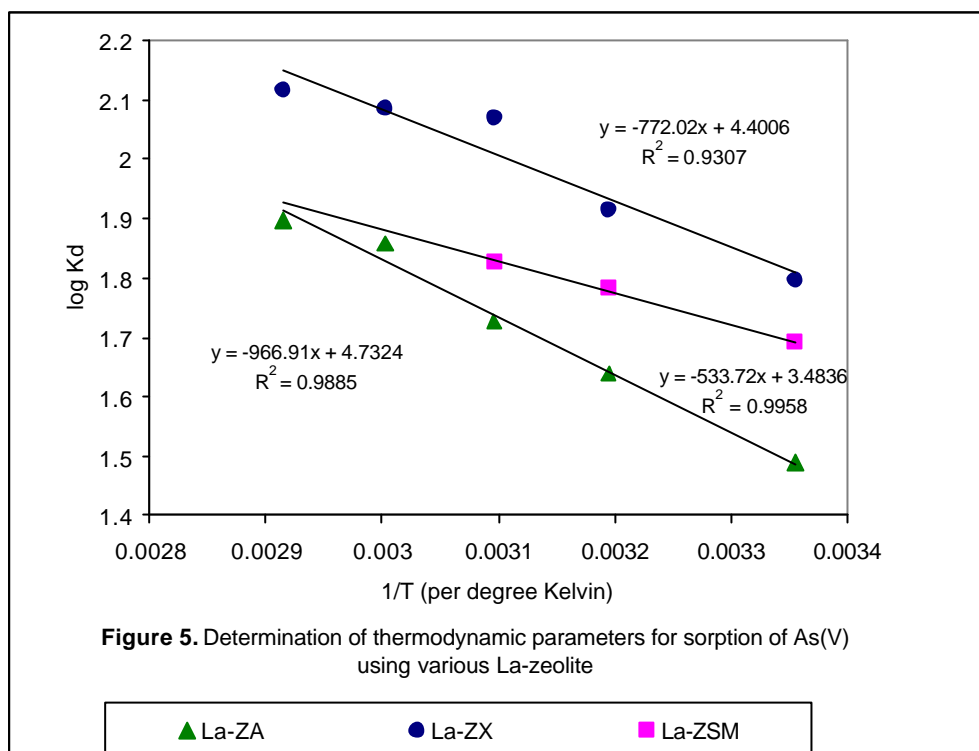


$$\log K_d = -\left(\frac{\Delta H^\circ}{2.303R}\right)\frac{1}{T} + \frac{\Delta S^\circ}{2.303R} \quad (3)$$

where K_d is the equilibrium partition constant calculated as the ratio between sorption capacity and equilibrium concentration. The change in free energy (ΔG°) for As(V) sorption were calculated using equation (2) and calculated K_d values and were found to be -10.25 , -9.65 and -8.49 kJ/mol for La-ZX, La-ZSM and La-ZA, respectively at 25°C . The negative values of ΔG° means that the sorption of As(V) ions on La-exchanged zeolite is spontaneous, perhaps because the La have high affinity towards the arsenic ion due to low K_{sp} value of 3.55×10^{-22} [26] (for comparison, K_{sp} AgCl is 1.77×10^{-10} M^2). From equation (3) a plot of $\log K_d$ versus $1/T$ (Fig. 5) would give ΔH° and ΔS° which are given in Table 4. The positive values of ΔH° indicate the endothermic nature of sorption process which is compared favorably with that reported using lanthanum oxide [27]. A slightly positive entropy change for sorption of As(V) ion on La-exchanged zeolite is due to fixation of the ions on the exchange sites of the randomly distributed La ions on the sorbents.

Table 4. Thermodynamic parameters for the adsorption of As(V) by La-zeolite

Adsorbent	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° J/molK
LaZX	-10.25	14.78	0.085
LaZMS	-9.65	10.21	0.067
LaZA	-8.49	18.51	0.091



Sorption Kinetics of As(V) by La-zeolite

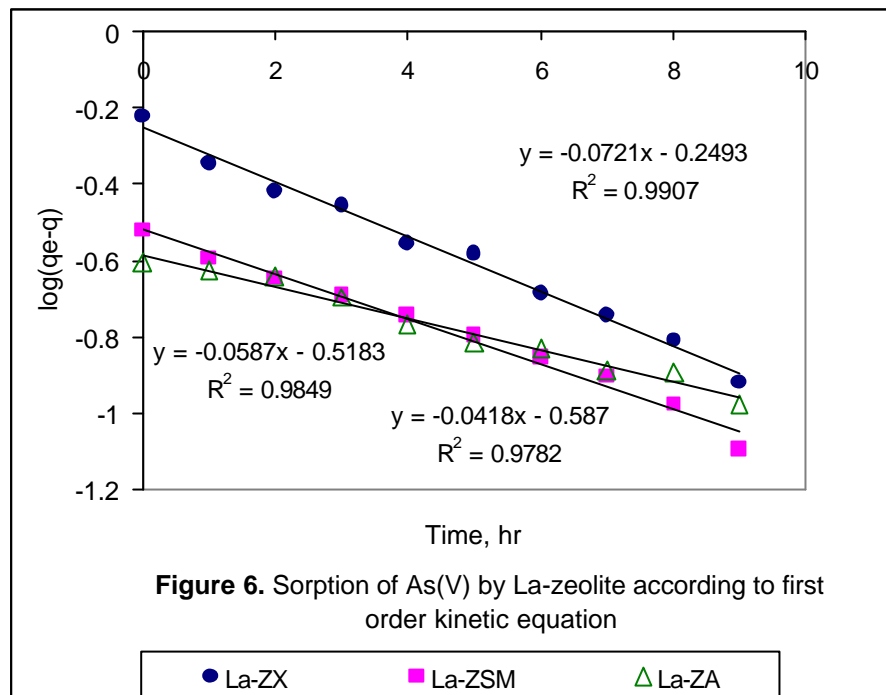
The kinetics of sorption of As(V) by modified zeolite was studied in batch experiments. The pseudo-first-order rate constants for sorption of arsenic ions are determined using the following equation

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (5)$$

where q_t refers to the amount of As(V) sorption at any time t . A straight line plot of $\log(q_e - q_t)$ versus t (Fig. 6) indicates the applicability of the first order kinetics for As(V) sorption. The sorption is rapid at the beginning with $t_{1/2}$ of about 3, 4 and 5 hours for La-ZX, La-ZSM and La-ZA, respectively. The pseudo-first-order kinetic constants k_1 for As(V) sorption for the respective zeolites were 2.77×10^{-3} , 2.25×10^{-3} and $1.60 \times 10^{-3} \text{ min}^{-1}$.

Conclusion

The maximum exchanged capacity of La(III) ion was obtained when using solutions with initial pH of 4. At this initial pH, zeolite X giving the highest La(III) exchanged capacity compared to zeolite ZSM5 and zeolite A. The results showed that the As(V) sorption by La-zeolites occurred at about pH 6.5 and increased as pH increased and reaching maximum at about pH 7.8. Almost no arsenate sorption occurred on unexchanged zeolites which indicated that La(III) ion on the exchanged zeolites was taking part on the As(V) sorption probably via surface precipitation. The results also show that the sorption capacities increased with increasing initial As(V) concentrations. The sorption followed Langmuir model with maximum sorption capacities of 0.41, 0.21 and 0.19 mmol/g at 25°C for La-ZX, La-ZSM and La-ZA, respectively. The amounts of sorption of As(V) by La-zeolite increased as temperature increased from 25 to 70°C indicating that the process was endothermic. The free energy change (ΔG°) for the sorption at 25°C were -10.25, -9.65 and -8.49 kJ/mol for La-ZX, La-ZSM and La-ZA, respectively. The negative values of ΔG° shows that the sorption of As(V) ions on La-exchanged zeolite is spontaneous, perhaps because the La(III) have high affinity towards the arsenic ion as indicated by a low K_{sp} value of the lanthanum arsenate. A slightly positive entropy change for sorption of As(V) ion on La-exchanged zeolite could be due to fixation of the ions on the La(III) exchange sites that randomly distributed on the sorbents. The kinetics study showed that the As(V) sorption followed first order kinetic model. The first-order rate constants for the sorption were 2.77×10^{-3} , 2.25×10^{-3} and $1.60 \times 10^{-3} \text{ min}^{-1}$ for La-ZX, La-ZSM and La-ZA, respectively.



Acknowledgements

The authors thank to Ministry of Science, Technology and Innovation for SciFund and Fundamental Research Grants.

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