



Kinetic and thermodynamic investigations on arsenic adsorption onto dolomitic sorbents

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ABSTRACT

Arsenic and its compounds are toxic pollutants for the environment and all living organisms. At present, there is considerable interest in studying new sorbent materials for the removal of arsenic from aqueous solutions. This work discusses the feasibility of arsenic uptake onto dolomite which is considered to be a potential inexpensive adsorbent. Thermodynamic and kinetic experiments were undertaken to assess the capacity and rate of As uptake onto dolomite. Experimental data were mathematically described using adsorption kinetic models, namely pseudo-first-order and pseudo-second-order models. The arsenic removal was found to be dependent on the dosage of dolomite, adsorbent particle size and the presence of various anions. Thermodynamic results indicate that the adsorption follows an exothermic chemisorption process. The experimental data indicate successful removal of As(V) ion from aqueous solution indicating that dolomite be used as an inexpensive treatment process.

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1. Introduction

In developing countries, high concentrations of toxic pollutants appear frequently in drinking water posing a significant environmental issue, particularly in densely populated cities where the demand for water is very high [1]. Recently, groundwater contamination by arsenic has been recognized as a global problem since it is present to some extent in every continent. It has been reported that arsenic concentrations in drinking water above 100 µg/L can cause vascular disorders, such as dermal pigments, and skin and lung cancer [2]. In light of this, the World Health Organisation (WHO) has set concentration limits for drinking water at 10 ppb As [3].

Arsenic occurs in various mineral forms, of which 60% are arsenates, 20% are sulphides and sulphosalts, 10% are oxides and the remainder are arsenides, native elements and metal alloys [4]. Several toxicological studies have demonstrated that the toxicity of arsenic is dependent on its chemical forms, oxidation state, physical state (gas or solution), rate of absorption into cells, rate of elimination and chemical nature. Arsenic exists in several states of oxidation: As(0) or as ion forms like As(V) arsenate, As(III) arsenite and As(III) arsine. It is generally recognized that the soluble inorganic arsenicals are more toxic than the organic ones, and the inorganic As(III) species are more toxic than the inorganic As(V) [5]. At moderate or high redox potentials, arsenic can be stabilized as a series of pentavalent (arsenate) oxyanions, H_3AsO_4 , H_2AsO_4^- ,

HASO_4^{2-} and AsO_4^{3-} . Thus, to eliminate these toxic metals from water, a potential adsorbent must have the anion exchange properties [6].

Arsenic is continuously released into aquatic environment from natural processes such as volcanic activity and weathering of rocks. It is also introduced as contaminants (industrial pollution), the industrial activities responsible for the environmental dispersion of arsenic are the agricultural use of arsenic as pesticides, herbicides and fertilizers, the discharges from coal fired in thermal power plants, petroleum refining industry and ceramic industries [1].

Various treatment technologies to remove arsenic from drinking water have been designed such as: coagulation; ion exchange; reverse osmosis; liquid–liquid extraction; and adsorption [7,8]. However, in many areas of the world there is still in a necessity for appropriate technologies, which are inexpensive, simple and easily applied to source use.

Dolomite, which represents a potential low cost adsorbent, is a common sedimentary rock-forming mineral that can be found in sedimentary beds several hundred feet thick, it is also found in metamorphic marbles, hydrothermal veins and replacement deposits [9]. Dolomite is both a mineral and a rock. The dolomite group is composed of minerals with an unusual trigonal bar 3 symmetry. The general formula of this group is $\text{AB}(\text{CO}_3)_2$, where A can be either calcium, barium and/or strontium and the B can be either iron, magnesium, zinc and/or manganese. The amount of calcium and magnesium in most specimens is equal, but occasionally one element may have a slightly greater presence than the other. Small amounts of iron and manganese are sometimes also present [10].

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2. Analysis of adsorption experimental data

2.1. Kinetic modelling

The batch experimental data from this study will be applied to selected adsorption kinetic models, namely pseudo-first-order and pseudo-second-order models. The pseudo-first-order (Lagergren first-order) rate equation is as follows:

$$\ln(q_e - q_t) = \ln q_e - K_{1\text{ads}}t \quad (1)$$

where q_e and q_t are the amount of adsorbate adsorbed ($\mu\text{g/g}$) at equilibrium and at time t (min), $K_{1\text{ads}}$ is the adsorption rate constant. The values of $K_{1\text{ads}}$ and q_e can be calculated from the intercept and slope of the plots of $\ln(q_e - q_t)$ versus t .

The pseudo-second-order equation is also based on the sorption capacity of the solid phase and is expressed as:

$$\frac{dq}{dt} = K_{2\text{ads}}(q_e - q_t)^2 \quad (2)$$

where $K_{2\text{ads}}$ is the rate constant of second-order adsorption. For the same boundary conditions the integrated form becomes:

$$\frac{t}{q_t} = \frac{1}{K_{2\text{ads}}q_e^2} + \left(\frac{1}{q_e}\right)t \quad (3)$$

If second-order kinetics is applicable, the plot of t/q against t should give a linear relationship, from which q_e and $K_{2\text{ads}}$ can be determined from the slope and intercept of plot.

2.2. Thermodynamic modelling

To calculate the thermodynamic activation parameters such as enthalpy of activation, ΔH° , entropy of activation, ΔS° , and free energy of activation, ΔG° , the Eyring equation can be applied [11]:

$$\ln\left(\frac{K_{2\text{ads}}}{T}\right) = \left[\ln\left(\frac{k_B}{h_p}\right) + \frac{\Delta S^\circ}{R}\right] - \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right), \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

where k_B is the Boltzmann constant (1.3807×10^{-23} J/K), h_p is the Planck constant (6.6261×10^{-34} Js), R is the ideal gas constant (8.314 J g^{-1} K^{-1}), $K_{2\text{ads}}$ is the pseudo-second-order constant (k_2) for arsenic adsorption.

The activation energy of arsenic adsorption onto the dolomite can be calculated by the relationship:

$$\ln(K_{2\text{ads}}) = \ln(K_0) - \frac{E}{R}\left(\frac{1}{T}\right) \quad (6)$$

where K_0 is the rate constant of adsorption (g/mg min). Plotting the pseudo-second-order constant against the reciprocal temperature gives a reasonably straight line, the gradient of which is $-E/R$.

3. Experimental materials and methods

3.1. Adsorbent characterisation

The dolomite used in this study was mined from a deposit in Co. Fermanagh, Northern Ireland. The typical chemical composition of the dolomite in the deposit was 44% MgCO_3 and 53% CaCO_3 . The dolomite was ground and sieved on a series of test sieves. Fig. 1 shows a SEM image for a dolomite sample, it can be observed that the dolomite structure consists of a crystalline structure with inter-special voids.

3.2. Adsorbate characterisation

A 2000 ppb stock arsenic solution was prepared in 1 L volumetric flask using deionized water. The stock solution was made from



Fig. 1. SEM of surface of dolomite sample at a magnitude of $2000 \text{ mm} \times 25 \text{ mm}$.

sodium arsenic dibasic heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$), Aldrich Chemical Co. Inc, USA. In addition 0.1 g NaHCO_3 was added to buffer pH fluctuations during the experiment. Most groundwaters have some amount of alkalinity present, which tends to be in the order of $250\text{--}600 \text{ mg/L HCO}_3$. The addition of bicarbonate is therefore not seen to compromise the experiment.

A simple picture of arsenic chemical speciation calculated based on their stability constants has been outlined in Fig. 2 [12]. The monovalent anionic species of arsenate were dominant at pH ranging from 2 to 6, while in the case of arsenite were significant at alkaline region of pH 9–12.

3.3. Experimental methods

Preliminary experiments were conducted to evaluate the impact of using dolomite as an adsorbent for As(III). However, the results indicated very low removal ($<10\%$). Therefore, oxidation of the arsenite to arsenate using ozone or chloride may be required before dolomite adsorption; surface modification of the dolomite could also enhance the removal of As(III).

Equilibrium isotherm experiments were conducted to evaluate the effect of pH on using the dolomite as an adsorbent for As(V). The maximum arsenic removal was found to be at pH 2 [13].

Kinetic experiments were undertaken using a standard ratio of $1.0 \pm 0.0005 \text{ g}$ of dolomite which was contacted with 500 ml of arsenic solution for 8 h on hot plate stirrers to adjust the temperature if required (standard temperature 22°C). Magnetic stirrers were used for agitation. The agitation speed was set at 150 rpm . Appropriate dilutions were made to give a range of arsenic concentrations. The pH was adjusted by using (1 mol/dm^3) HCl or (1 mol/dm^3) NaOH. Samples of the aqueous phase were taken at regular intervals which were then filtered through a $0.45 \mu\text{m}$ cellulose nitrate membrane filter (Swinnex-25 Millipore) and prepared for analyses using ICP-AES. The samples were made up to 10 ml to give a 2% nitric acid solution. Duplicate samples were measured and standard error in the readings was less than 3%. Blank samples were also used. The adsorption of As(V) into filter papers was studied and found to be 73 ppb maximum.

4. Results and discussion

4.1. Effect of pH and initial solute concentration

Previous work by our group has indicated that dolomite removal decreases with the increase in pH [13]. Moreover, it was noted that variation in pH affects the surface charge of the adsorbent and the degree of ionisation and speciation of arsenic. This pH dependence of the binding showed that ion exchange and electrostatic interac-

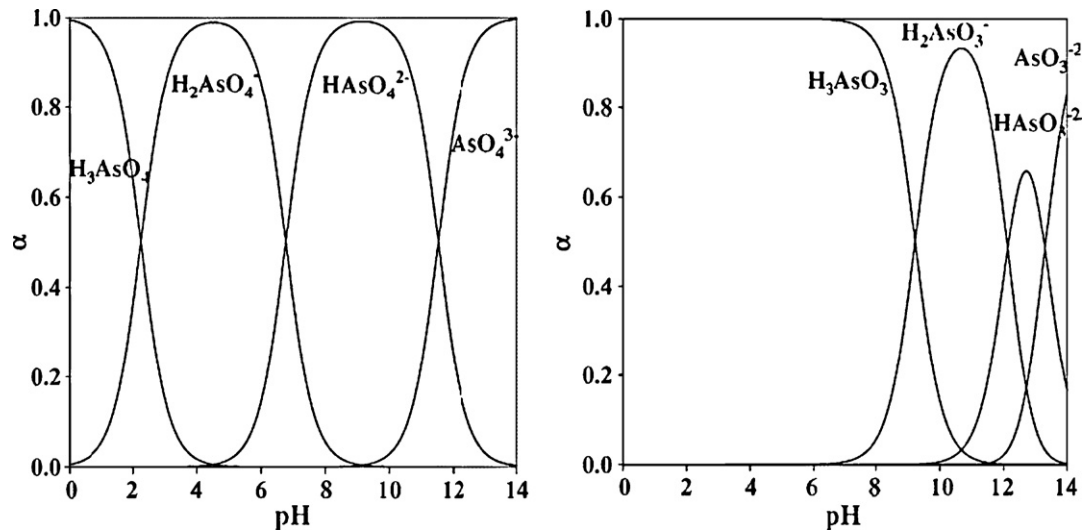


Fig. 2. Distribution of arsenate and arsenite as a function of pH (after Ref. [12]).

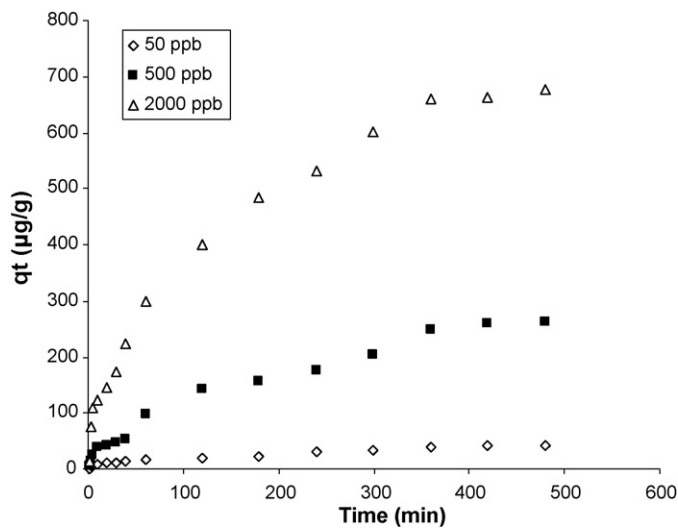


Fig. 3. Adsorption curve of arsenic onto dolomite. Adsorbent ratio: 1 g/L; pH: 2; particle size: 710–2000 µm.

tions are involved in the binding mechanism of As(V) on dolomite. We have proposed that adsorption of As(V) onto dolomite may be due to two effects: firstly, the rough surface of the dolomite gives solid contact resulting in chemisorption of As(V) at low concentration. Secondly, regarding the chemistry of the dolomite, since it is mainly composed of $MgCO_3$ and $CaCO_3$, this may allow the formation arsenic oxide and possibly arsenic carbonate, so precipitation of these compounds may be a further removal mechanism for As(V) [13]. In light of these findings, acidic arsenic solutions (pH 2) were used in this investigation.

The plots of q_t versus t at different initial arsenic concentrations are shown in Fig. 3. Two simplified mathematical analyses: pseudo-

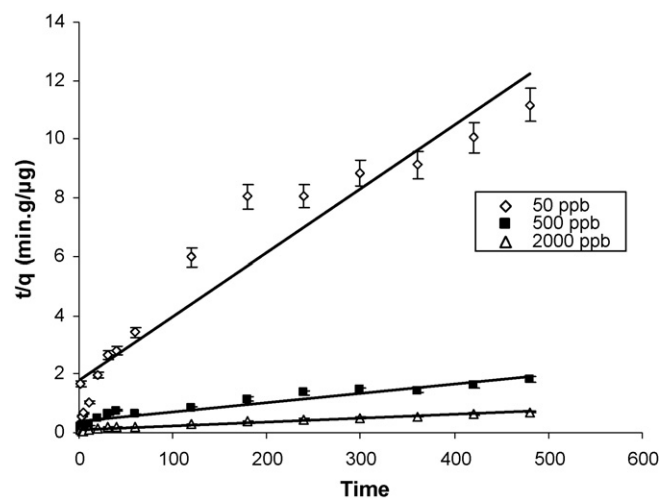


Fig. 4. The linear second-order kinetic sorption data for arsenic in single solute system by dolomite. Adsorbent ratio: 1 g/L; pH: 2; particle size: 710–2000 µm.

first-order and pseudo-second-order kinetic models were used to describe the adsorption data. The data in Fig. 3 indicate that sorption is rapid during the first 60 min and that dynamic equilibrium is attained in approximately 360 min for the three concentrations investigated. Fig. 4 illustrates the applicability of pseudo-second-order kinetics to the adsorption data. The best fit linearization (employing the sum of square errors squared method, SSE) indicates that, although the data appear to follow first-order kinetics during the initial stage of the experiment, near equilibrium the experimental data deviate significantly from the predicted data, especially at low initial concentrations. The pseudo-second-order rate constants, K_{2ads} , were calculated and are listed in Table 1 and show a large variation over the concentration range investigated.

Table 1

Comparison of the first- and second-order reaction rate constants obtained at different initial arsenic concentrations.

Concentration	First-order kinetic model			Second-order kinetic model	
	K_{1ads} (µg/g min)	q_e (µg/g)	R^2	K_{2ads} (µg/g min)	R^2
50 ppb	4.7×10^{-3}	43.13	0.987	2.65×10^{-4}	0.922
500 ppb	6.0×10^{-3}	280.96	0.962	2.67×10^{-5}	0.926
2000 ppb	6.8×10^{-3}	652.04	0.970	1.75×10^{-5}	0.975

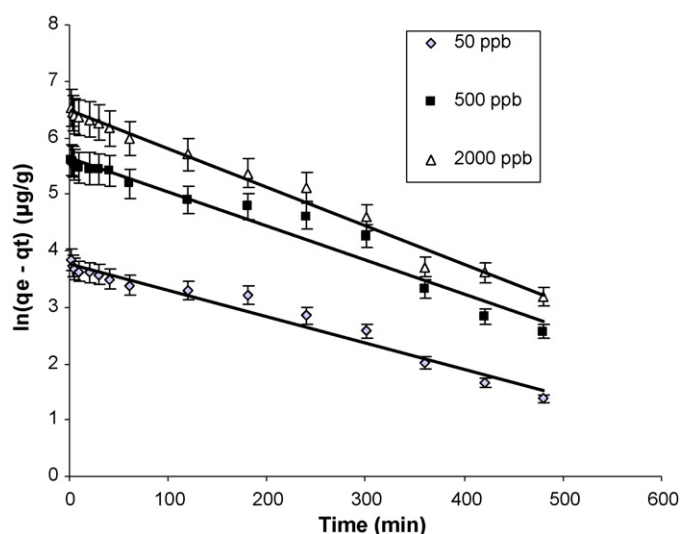


Fig. 5. The linear first-order kinetic sorption data for arsenic in single solute system by dolomite. Adsorbent ratio: 1 g/L; pH: 2; particle size: 710–2000 μm .

The correlation coefficient ranged from $R^2 = 0.922$ – 0.975 , indicating an adequate representation over the course of the experiment.

Fig. 5 illustrates the applicability of pseudo-first-order kinetics to the adsorption data. The best fit linearization (SSE) indicates that, the data closely follow first-order kinetics during the initial stage of the experiment. However, as with the second-order kinetics, near equilibrium the experimental data deviate slightly from the predicted data for each of the concentrations investigated. The pseudo-first-order rate constants, $K_{1\text{ads}}$, were calculated and are listed in Table 1 and show only a slight increase in rate constant with increasing initial concentration ($R^2 = 0.962$ – 0.987).

The liquid phase was also analysed for calcium and magnesium during the course of the kinetic experiment. The relationship between: the arsenic removal from solution onto the surface of the dolomite; and the simultaneous dissolution of calcium and magnesium, is illustrated in Fig. 6. The data indicate an increase in Ca and Mg with As(V) uptake onto the solid, which may imply the formation and precipitation of arsenic oxide and possibly arsenic carbonate on the surface of the dolomite. The graphical relationship in Fig. 6 between both calcium and magnesium versus arsenic removal show the same contour, although the calcium has the higher concentration due to its increased solubility. The Ca/Mg versus Ca relationship shows a good deal of linearity during the early stages of the experiment, however, during the latter stage the system arsenic uptake appears to less dependent on Ca/Mg dissolution. This relationship may indicate a two stage arsenic removal process: (i) an initial stage involving an ion exchange type process which can be described by a pseudo-first-order chemical reaction model, resulting in the formation and precipitation of arsenic oxide on the surface of the dolomite; (ii) in a second process, due to the increase surface coverage of the dolomite by the precipitate, further dissolution of Ca/Mg is limited and the predicted uptake profiles of the reaction models are not achieved, although some As(V) precipita-

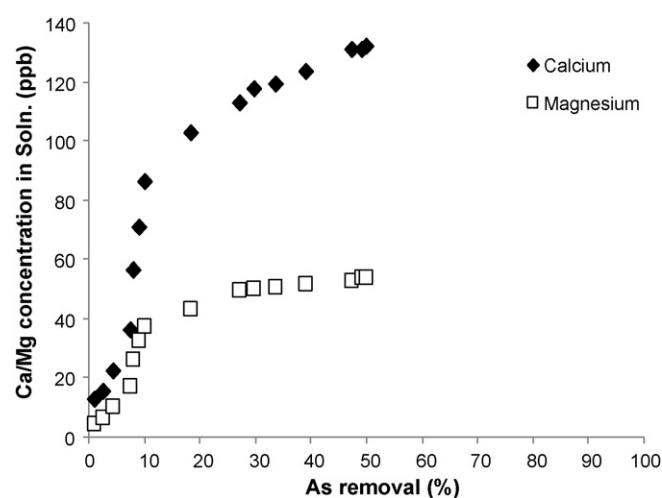


Fig. 6. Ca and Mg relationship with As removal. Adsorbent ratio: 1 g/L; pH: 2; particle size: 710–2000 μm ; initial As concentration: 500 ppb.

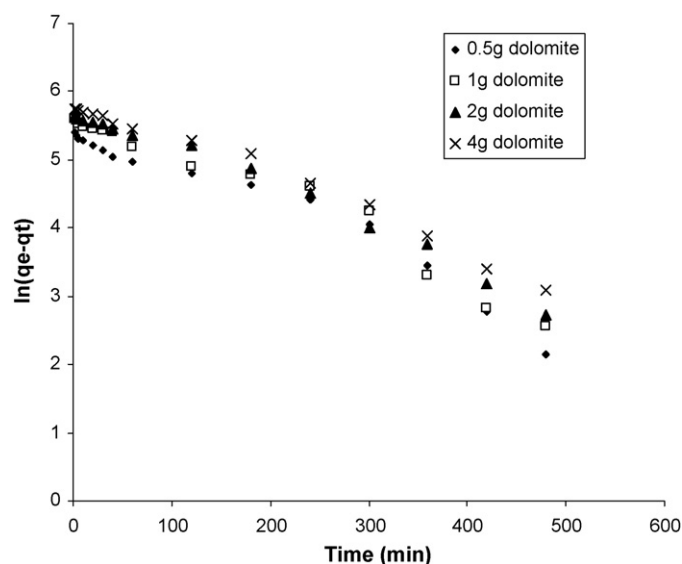


Fig. 7. The linear first-order kinetic sorption data for arsenic in different dolomite dosages. Arsenic concentration: 500 ppb; pH: 2; particle size: 710–2000 μm .

tion still occurs on the surface of the previously precipitated arsenic oxide.

4.2. Effect of adsorbent ratio

Arsenic removal at various mass of adsorbent to volume of solution ratios was studied at 22 °C and at pH 2 by varying the adsorbent amount from 0.5 to 4 g/L at constant volume (500 ml) and initial As(V) concentration. Figs. 7 and 8 illustrate the applicability of the respective pseudo-first-order and pseudo-second-order kinetics to the adsorption data. The kinetic model constants, $K_{1\text{ads}}$ and $K_{2\text{ads}}$,

Table 2

Comparison of the first- and second-order reaction rate constants obtained at different dolomite dosages.

Dolomite dosage	First-order kinetic model			Second-order kinetic model	
	$K_{1\text{ads}}$ ($\mu\text{g/g min}$)	q_e ($\mu\text{g/g}$)	R^2	$K_{2\text{ads}}$ ($\mu\text{g/g min}$)	R^2
0.5 g dolomite	5.8×10^{-3}	225.13	0.949	4.51×10^{-5}	0.942
1 g dolomite	6.0×10^{-3}	280.96	0.962	2.67×10^{-5}	0.926
2 g dolomite	5.8×10^{-3}	303.44	0.984	2.53×10^{-5}	0.898
4 g dolomite	5.4×10^{-3}	303.39	0.984	2.27×10^{-5}	0.901

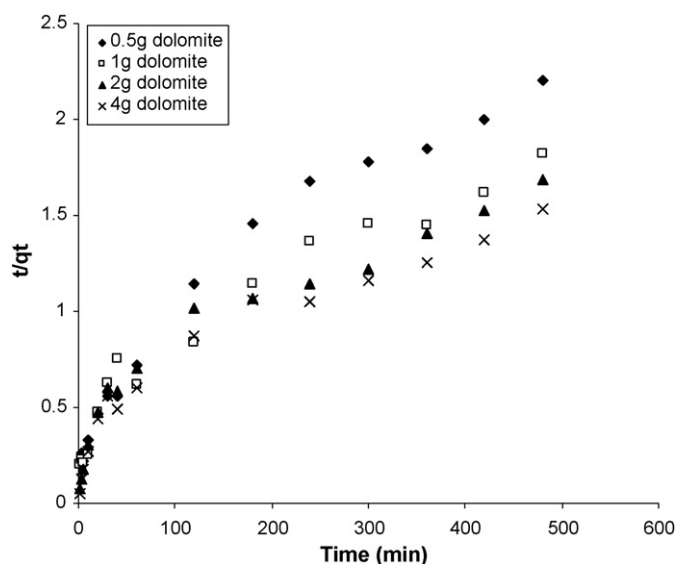


Fig. 8. The linear second-order kinetic sorption data for arsenic in different dolomite dosages. Arsenic concentration: 500 ppb; pH: 2; particle size: 710–2000 μm .

were calculated and are listed in Table 2. It is noted that the percentage of As(V) adsorption increased with time and adsorbent mass:volume ratio. This is obviously due to the increase in the availability of adsorption sites for complexation of As(V) ions. It is also noted that although the percentage removal of As(V) from solution is higher with increasing adsorbent ratio, a lower ratio would maximise As(V) solid phase concentration, q_t (mg g^{-1}) on the surface of the dolomite.

4.3. Effect of adsorbent particle size

Different adsorbent particle size ranges were investigated in order to understand their effect on As(V) removal. The particle size range was varied from 0.1–0.335 mm to 0.710–2.00 mm. The data have been applied to the pseudo-first-order and pseudo-second-order kinetic models with the results shown in Figs. 9 and 10, respectively. The kinetic models constants, $K_{1\text{ads}}$ and $K_{2\text{ads}}$, were calculated (see Table 3) and indicate that the amount of solute adsorbed slightly increases with decrease in particle size of the adsorbent. This is due to an increase in external surface area found with decreasing particle size. Furthermore, the crushing of the large particles to form smaller particles facilitates crack formation, which further increases the surface area available for mass transfer.

4.4. Effect of presence of various salts

The removal of arsenate from solution in the presence of different concentrations of various anions was studied with the pseudo-first-order and pseudo-second-order models applied to the data (Figs. 10 and 11). The removal of As(V) decreased by increasing the sulphate concentration; Su and Puls reported a slight decrease of As(V) removal by zero valence iron in the presence of sulphate [14]. Arsenic removal very slightly increased by increasing the chlo-

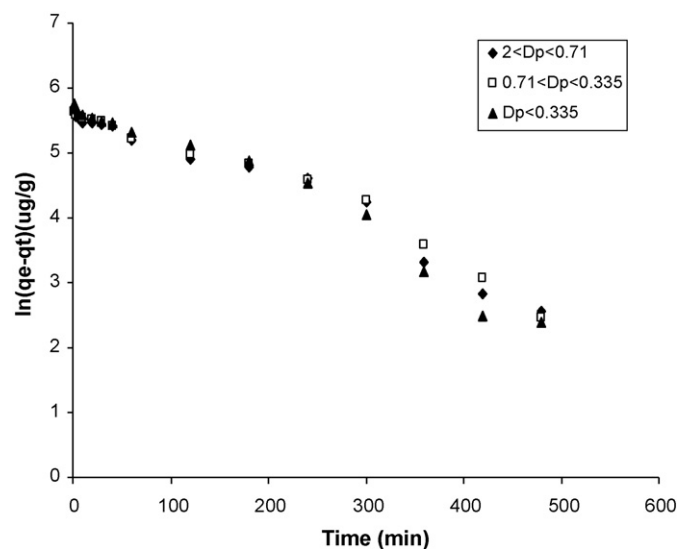


Fig. 9. The linear first-order kinetic sorption data for arsenic adsorption in different dolomite particle sizes. Arsenic concentration: 500 ppb; pH: 2; adsorbent ratio: 1 g/L. Dp: particle size (mm).

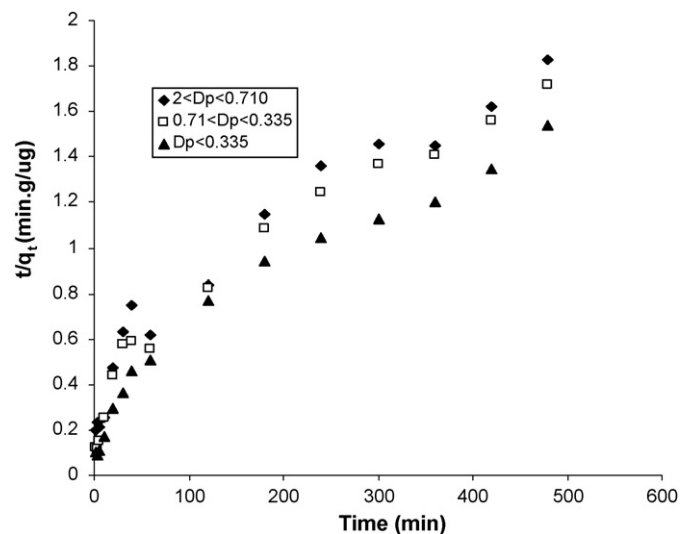


Fig. 10. The linear second-order kinetic sorption data for arsenic adsorption in different dolomite particle sizes. Arsenic concentration: 500 ppb; pH: 2; adsorbent ratio: 1 g/L. Dp: particle size (mm).

ride concentration, this non-effect may be attributed to the fact that Cl^- does not compete with H_2AsO_4 [15], so the chloride can be considered as a non-competing species to arsenate. In the presence of the phosphate the dolomite shows very low efficiency in removing the As(V). This is probably due to AsO_4^{3-} being analogous to PO_4^{3-} and therefore competes for uptake sites on the dolomite surface. Rahman et al. [16] proposed the arsenate uptake in *Spirodela polyrrhiza* L. might occur through the phosphate uptake pathway due to similar chemical behaviour of AsO_4^{3-} and PO_4^{3-} , Maiti et al.

Table 3

Comparison of the first- and second-order reaction rate constants obtained at different dolomite particle sizes.

Particle size (mm)	First-order kinetic model			Second-order kinetic model	
	$K_{1\text{ads}}$ ($\mu\text{g/g min}$)	q_e ($\mu\text{g/g}$)	R^2	$K_{2\text{ads}}$ ($\mu\text{g/g min}$)	R^2
0.700–2.000	6.0×10^{-3}	280.96	0.962	2.67×10^{-5}	0.926
0.355–0.700	5.9×10^{-3}	290.41	0.966	3.22×10^{-5}	0.931
Dp < 0.355	6.9×10^{-3}	321.57	0.965	3.56×10^{-5}	0.942

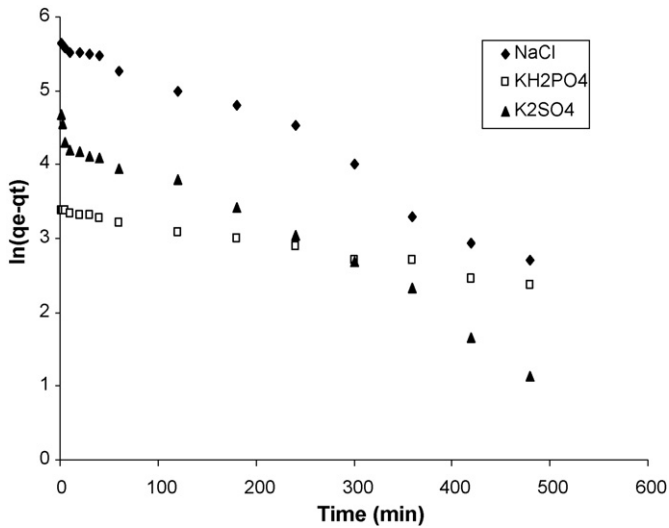


Fig. 11. The linear first-order kinetic sorption data for arsenic in the presence of various anions. Arsenic concentration: 500 ppb; pH: 2; adsorbent ratio: 1 g/L; particle size: 710–2000 μm .

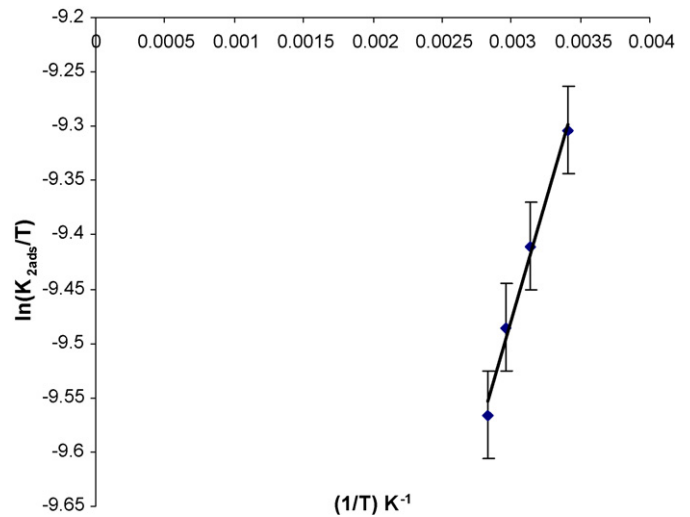


Fig. 13. $\ln(K_{2\text{ads}}/T)$ versus $1/T$ for the diffusion of As(V) onto dolomite.

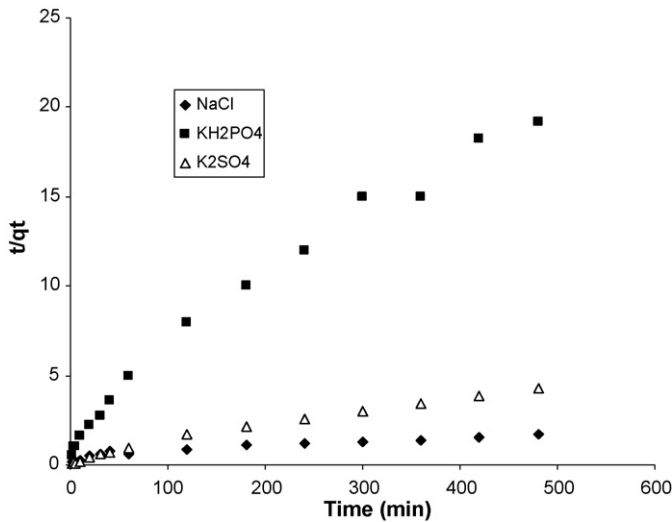


Fig. 12. The linear second-order kinetic sorption data for arsenic in the presence of various anions. Arsenic concentration: 500 ppb; pH: 2; adsorbent ratio: 1 g/L; particle size: 710–2000 μm .

reported a decrease in the adsorption of As(V) and As(III) on treated laterite in the presence of phosphate [20], other researchers also reported a decrease of As(V) removal in the presence of the phosphate [17,18]. Our present findings on the influence of phosphate correlate with these previous investigations (Fig. 12 and Table 4).

4.5. Adsorption thermodynamics

In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will

Table 5

Thermodynamic parameters for the adsorption of As(V) on dolomite.

ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (J/mol K)
T=293	T=318	T=338	T=353		
80.57	87.75	93.50	97.81	-3.67	-287.35

occur spontaneously [19]. In order to investigate these parameters for our present As(V)-dolomite system, adsorption kinetics were undertaken at 20, 45, 65 and 80 $^\circ\text{C}$, from which the equilibrium partition constants, K_c , were evaluated. A plot of $\ln K_c$ as a function of $1/T$ is illustrated Fig. 13. From this linear relationship, ΔH° and ΔS° can be calculated from the slope and intercept, respectively. The values of ΔG° , ΔH° and ΔS° (from Eqs. (4)–(6)) are summarised in Table 5.

The calculated free energies, ΔG° , were positive under the temperature range studied, which indicates that the sorption process was not spontaneous and may be attributed to a chemisorption process. Moreover, the free energy of the process was found to increase with increase in temperature. The negative value of the standard entropy, ΔS° , suggests decreased randomness at the solid/solution interface during the sorption arsenic ions onto dolomite. The change of the standard free energy increases with increase in temperature, which indicates that an increase in the temperature tended to decrease the adsorption capacity. The negative value of ΔH° again indicates the exothermic nature of the adsorption process.

From Eq. (6), the rate parameter of arsenic adsorption, K_0 , was estimated to be 17.78×10^{-3} g/mg min and the activation energy, E , is -1.002 kJ/mol. Low activation energy values (<42 kJ/mol) indicate diffusion control processes and the higher activation energy values (>42 kJ/mol) indicate chemically controlled processes. This is because the temperature dependence of the pore diffusivity is

Table 4

Comparison of the first- and second-order reaction rate constants obtained in the presence of various anions.

Anion	First-order kinetic model			Second-order kinetic model	
	$K_{1\text{ads}}$ ($\mu\text{g/g min}$)	q_e ($\mu\text{g/g}$)	R^2	$K_{2\text{ads}}$ ($\mu\text{g/g min}$)	R^2
NaCl	6.1×10^{-3}	294.33	0.983	2.36×10^{-5}	0.926
K_2SO_4	6.4×10^{-3}	84.44	0.979	2.75×10^{-4}	0.985
KH_2PO_4	2.1×10^{-3}	28.95	0.993	9.24×10^{-4}	0.978

relatively weak. Here, the diffusion process refers to the movement of the solute to an external surface of adsorbent and not diffusivity of the adsorbate along micropore wall surface within a particle [11]. The negative value of the activation energy suggested that the rise in the solution temperature did not favour arsenic adsorption onto dolomite. The negative value also indicates an exothermic reaction.

To summarise, these thermodynamic data indicate the adsorption process was exothermic. The values of ΔG° , ΔH° , ΔS° and E are indicative of both a physical diffusion process followed by chemical adsorption on the solid surface of the dolomite.

5. Conclusions

In order to optimize adsorption conditions for As(V) removal from aqueous solution using dolomite, various experimental parameters were investigated. Kinetic studies revealed that a pseudo-first-order rather than a pseudo-second-order mathematical model was more successful in describing the process. The adsorption was found to be dependent on: the ratio of mass dolomite – volume of solution and particle size of dolomite. Equilibrium was reached in approximately 6 h. The presence of salts was found to be an important parameter, as the adsorptive capacity of the dolomite decreased significantly in the presence of phosphate. The extent of the competition between arsenate and the other anions was found to be dependent on the affinity of each anion to the surface. Adsorption and precipitation as arsenic oxide and possibly as arsenic carbonate were the reaction mechanisms that contributed to the removal of As(V) by the dolomite. Thermodynamic analysis indicate that the adsorption follows an exothermic chemisorption process

Analysis of calcium and magnesium dissolution during arsenic sorption indicated a two stage arsenic removal process: (i) an initial stage involving an ion exchange type process which can be described by a pseudo-first-order chemical reaction model resulting in the formation and precipitation of arsenic oxide/carbonate on the surface of the dolomite; (ii) in a second process, due to the increase surface coverage of the dolomite by the precipitate, further dissolution of Ca/Mg is limited and the predicted uptake profiles of the reaction models are not achieved, although some As precipitation still occurs on the surface of the previously precipitated arsenic oxide/carbonate.

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