

## Kinetic and Thermodynamic Investigations on Arsenic Adsorption onto Dolomitic Sorbents

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This work discusses the feasibility of arsenic uptake onto raw 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 raw dolomite. Experimental data were mathematically described using pseudo first-order and pseudo second-order models. 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.

### 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 (Budinova et al., 2009). 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 (Cano-Aguilera et al., 2005).

In light of this, the World Health Organisation (WHO) has set concentration limits for drinking water at 10 ppb (WHO, 2006). 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) (Sanchez de la Campa et al., 2008). At moderate or high redox potentials, arsenic can be stabilized as a series of pentavalent (arsenate) oxyanions,  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$ . Thus, to eliminate these toxic metals from water, a potential adsorbent must have the anion exchange properties (Yusof and Malek, 2009). 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 (Walker et al., 2003). 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  $AB(\text{CO}_3)_2$ , 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 (Walker et al., 2005).

## 2. Mathematical Modeling

The experimental data were 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:

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

Where:  $q_e$  and  $q_t$  are the amount of adsorbate adsorbed ( $\mu\text{g/g}$ ) at equilibrium and at time  $t$  (min),  $K_{1ads}$  is the adsorption rate constant. The values of  $K_{1ads}$  and  $q_e$  were 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:

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

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

To calculate the thermodynamic activation parameters such as enthalpy of activation,  $\Delta H^\circ$ , entropy of activation,  $\Delta S^\circ$ , and free energy of activation,  $\Delta G^\circ$ , the Eyring equation was applied,

$$\ln\left(\frac{K_{2ads}}{T}\right) = \left[\ln\left(\frac{k_B}{h_p}\right) + \frac{\Delta S^\circ}{R}\right] - \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) \quad (3)$$

$$\text{Where: } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

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

## 3. Experimental Materials and Methods

### 3.1 Adsorbent Characterization

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%  $\text{MgCO}_3$  and 53 %  $\text{CaCO}_3$ . The dolomite was ground and sieved on a series of test sieves.

### 3.2 Adsorbate Characterization

A 2000 ppb stock arsenic solution was prepared in 1L volumetric flask using deionized water. The stock solution was made from sodium arsenic dibasic heptahydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ), Aldrich Chemical Co. Inc, USA.

### 3.3 Experimental Methods

Preliminary 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.

Kinetic experiments were carried out using a standard ratio of  $1.0 + 0.0005$  g of the dolomite which was contacted with 500 mL of arsenic solution for eight hours on hot plate stirrers to adjust the temperature if required (standard temperature  $22^\circ\text{C}$ ). Magnetic stirrer was used for the agitation purpose. 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  $(1 \text{ mol/dm}^3)$  HCl or  $(1 \text{ mol/dm}^3)$  NaOH. Samples of the aqueous phase were taken at regular intervals by using needles and then were 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

Two simplified mathematical analyses: pseudo first-order and pseudo second order type kinetic models were used to describe the adsorption data. The sorption was rapid during the first 60 minutes and the dynamic equilibrium was attained in approximately 360 minutes for the three concentrations investigated. Figure 2 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 for especially at low initial concentrations. The pseudo second order rate constants,  $K_{2\text{ads}}$ , were calculated and are listed in Table 1 and show a large variation over the concentration range investigated. Moreover, the correlation coefficient ranged from  $R^2 = 0.922 - 0.975$ , indicating an adequate representation over the course of the experiment.

Figure 1 illustrates the applicability of pseudo-first order kinetics to the adsorption data. The best fit linearization (employing the sum of square errors squared method, 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. The correlation coefficient ranged from  $R^2 = 0.962 - 0.987$ , indicating an adequate representation of the kinetic data.

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	
	$K_{1ads}(\mu\text{g/g min})$	$q_e(\mu\text{g/g})$	$R^2$	$K_{2ad}(\mu\text{g/g min})$	$R^2$
50 ppb	$4.7 \times 10^{-3}$	43.13	0.987	$2.65 \times 10^{-4}$	0.922
500 ppb	$6.0 \times 10^{-3}$	280.96	0.962	$2.67 \times 10^{-5}$	0.926
2000 ppb	$6.8 \times 10^{-3}$	652.04	0.970	$1.75 \times 10^{-5}$	0.975

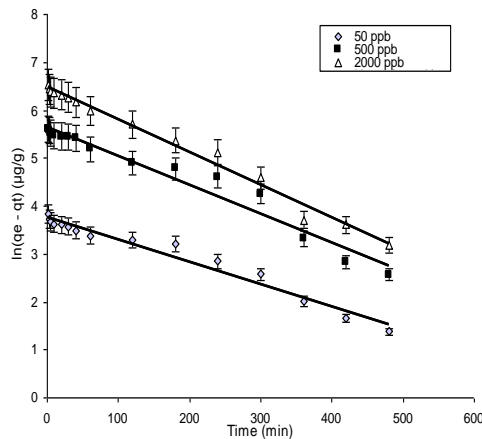


Figure 1: The linear first-order kinetic sorption isotherm for arsenic in single solute system by raw dolomite. Adsorbent ratio: 1g/L; pH = 2; particle size 710-2000 microns.

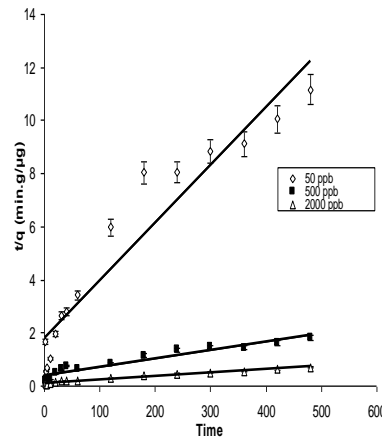


Figure 2: The linear second-order kinetic sorption isotherm for arsenic in single solute system by raw dolomite. Adsorbent ratio: 1g/L; pH = 2; particle size 710-2000 microns.

The samples were also analysed for the calcium and magnesium during the course of the kinetic experiment. The relationship between the arsenic removal and dissolution of calcium and magnesium is illustrated in Figure 3. The data indicate an increase in Ca and Mg with As 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 figure 3 between both calcium and magnesium versus arsenic removal are the same shape although the calcium is in 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 precipitation still occurs on the surface of the previously precipitated arsenic oxide.

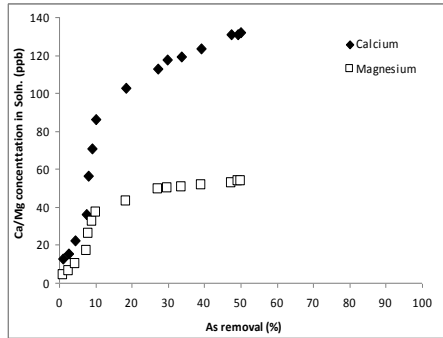


Figure 3: Ca and Mg relationship with As removal. Adsorbent ratio: 1g/L; pH = 2; particle size 710-2000 microns; Initial As concentration: 500 ppb.

#### 4.2 Adsorption Thermodynamic

In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. In order to investigate these parameters for our present As-dolomite system, adsorption kinetics were undertaken at 20, 45, 65 and 80 °C, from which the equilibrium partition constant  $K_c$ , were evaluated. A plot of  $\ln K_c$  as a function of  $1/T$  is illustrated Fig. 4. From this linear relationship,  $\Delta H^\circ$  and  $\Delta S^\circ$  can be calculated from the slope and intercept, respectively, with the values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  summarized in Table 2.

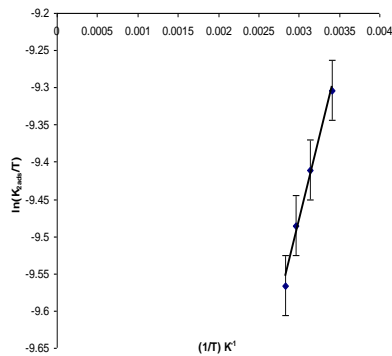


Figure 4:  $\ln(K_{2ads}/T)$  vs  $1/T$  for the diffusion of As(V) onto raw dolomite

The free energy of the process at the temperatures investigated was positive and increased with the rise in temperature. The calculated  $\Delta G^\circ$  were positive under the temperature range studied, which indicates that the adsorption reaction is chemisorptions. The negative value of the standard entropy,  $\Delta S^\circ$ , suggests decreased randomness at the solid/solution interface during the adsorption of the arsenic ions onto the adsorbent. The change of the standard free energy increases with increasing

temperatures. This indicates that an increase in the temperature is tended to decreasing the adsorption capacity. The value of the standard enthalpy change (3.67 kJ/mol) implies that there was loose bonding between the adsorbate molecules and the adsorbent surface.

Table 2 Thermodynamic parameters for the adsorption of As(V) on raw dolomite.

$\Delta G^\circ$ (kJ/mol)				$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)
T = 293	T = 318	T = 338	T = 353		
80.57	87.75	93.50	97.81	-3.67	-287.35

## 5. Conclusion

In order to optimize adsorption conditions for As (V) removal from aqueous solution using raw dolomite, various experimental parameters were investigated. Kinetic studies revealed that a pseudo first-order rather than a pseudo second-order mathematical model was successful in describing the process. Analysis of calcium and magnesium dissolution during arsenic sorption indicated a two stage arsenic removal process. 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 raw dolomite. Thermodynamic results indicate that the adsorption follows an exothermic chemisorption process.

## References

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