Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Arsenic Removal from Aqueous Solution by Iron Oxide-Coated Biomass: Common Ion Effects and Thermodynamic Analysis

D. Pokhrel[a]; T. Viraraghavan[a]
[a] Faculty of Engineering, University of Regina, Regina, SK, Canada

To cite this Article Pokhrel, D. and Viraraghavan, T.(2008) 'Arsenic Removal from Aqueous Solution by Iron Oxide-Coated Biomass: Common Ion Effects and Thermodynamic Analysis', Separation Science and Technology, 43: 13, 3545 — 3562
To link to this Article: DOI: 10.1080/01496390802212609
URL: http://dx.doi.org/10.1080/01496390802212609

Separation Science and Technology, 43: 3545–3562, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802212609

Arsenic Removal from Aqueous Solution by Iron Oxide-Coated Biomass: Common Ion Effects and Thermodynamic Analysis

D. Pokhrel and T. Viraraghavan
Faculty of Engineering, University of Regina, Regina, SK, Canada

Abstract: A batch study showed that the presence of anions (sulfate, chloride, and nitrate) in solution did not affect the adsorption process of both As(V) and As(III) by iron oxide-coated *A. niger* biomass. It was found that the presence of Ca^{2+}, Fe^{2+}, and Mg^{2+} ions at a concentration of 200 mg/L in solution could increase the removal efficiency of As(V) by 86.5%, 95.4%, and 65.8%, respectively. Similarly, the presence of Ca^{2+}, Fe^{2+}, and Mg^{2+} ions at a concentration of 200 mg/L in solution could increase the removal efficiency of As(III) by 39.3%, 97%, and 8.4%, respectively. The batch adsorption-desorption study showed that the reactions between the arsenic species and the iron oxide-coated *A. niger* biomass were reversible. Desorption of As(V) and As(III) at neutral pH was approximately 15%. As(V) desorbed more than As(III) in acidic (pH 1.33) and alkaline (pH 12.56) solutions. At a pH of 1.33, 67% of the adsorbed As(V) desorbed, and the percentage of desorbed As(III) was only 47.1% in the same condition. At a solution pH of 12.56, 73.4% of the As(V), and 43.7% of As(III) desorbed. The thermodynamic study showed the spontaneous nature of the sorption of arsenic on IOCB. The high value of the heat of adsorption $\{\Delta H \approx -133\,\text{kJ/mol}$ for As(V), and $88.9\,\text{k/mol}$ for As(III)$\}$ indicated that the mechanism of arsenic sorption was chemisorption.

Keywords: Adsorption, purification, biosorption, batch processing, thermodynamics, ion effect

Received 13 June 2007; accepted 6 April 2008.

Address correspondence to T. Viraraghavan, Faculty of Engineering, University of Regina, 3737 Wascana Parkway, Regina, SK, S4S 0A2, Canada. Tel.: 306-585-4094, Fax: 306-585-4855. Email: t.viraraghavan@uregina.ca

INTRODUCTION

Arsenic may be released into the environment by volcanoes, burning of fossil fuels and coal mining, weathering of arsenic-bearing minerals and ores. Contamination of groundwater sources due to the dissolution of arsenic-bearing minerals has posed a serious threat to human health. Arsenic is a known carcinogen and long-term exposure is reported to cause numerous health disorders: gastrointestinal, hepatic, renal, cardiovascular, neurologic, dermal, respiratory, hematopoietic and reproductive system (1). Therefore, the World Health Organization (WHO) in 1993 (2) and the United States Environmental Protection Agency (US EPA) in 2001 reduced the limit of arsenic in drinking water to 10 μg/L from an earlier value of 50 μg/L (3).

Arsenic may occur in nature in various inorganic and organic species: arsenate {As(V)}, arsenite {As(III)}, methylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethylarsine oxide, tetramethylarsonium ion, arsenobetaine, arsenocholine, dimethylarsinoylribosides, trialkylarsonioribosides, and dimethylarsinoylribitol sulfate (4). The toxicity varies depending on the arsenic species present; As(III) is 25 to 60 times as toxic as As(V) and several hundred times toxic than methylated arsenicals (5). In natural waters As(V) and As(III) are the dominant species.

Iron oxides have been reported to be effective for metal ion removal. Iron oxide-coated sand and other materials were reported to be effective in the removal of arsenic from aqueous solutions (6,7,8). Oxides of iron, aluminum and manganese are the potential sources/sinks for arsenic in aquifer sediments because of their chemistry, occurrence and tendency to adsorb other particles (9). Pokhrel and Viraraghavan (10) investigated arsenic removal potential of chemically modified *A. niger* because arsenic removal was less than 20% using non-viable biomass. Among the various pretreatment studies, iron oxide-coated biomass (IOCB) enhanced arsenic removal efficiency to 95% and 80% for As(V) and As(III), respectively (10). Further, iron oxide-coated biomass may be a better option to use in the case of drinking water compared to other chemical modifications. A factorial design study identified temperature and the mass of adsorbent as important factors in the removal of arsenic by iron oxide-coated *A. niger* biomass (11). A detailed batch study indicated an optimum pH of 6 and an equilibrium time of 7 hours (12) for best removals. Arsenic removal using *A. niger* biomass is the first kind of study conducted so far to the best of our knowledge.

This study examines adsorption-desorption and thermodynamic behavior of the arsenic species and the effects of common ions on arsenic removal in aqueous solution using iron oxide-coated *A. niger* biomass, because such studies related to iron oxide-coated materials are limited in literature. The adsorption-desorption study examines the leaching behavior of the adsorbed arsenic at different environmental conditions. In this laboratory study, the arsenic- loaded-IOCB was contacted with acidic (pH 1.33), neutral (pH 7) and basic (pH 12.56) solutions and the arsenic desorbed was measured. The driving force of reaction between arsenic species and IOCB was determined in the thermodynamic study. As Ca^{2+}, Mg^{2+}, Fe^{2+}, NO_3^-, SO_4^{2-}, and Cl^- are common ions found in most groundwaters, the effects of these ions on arsenic adsorption process was investigated in this study.

MATERIALS AND METHODS

Preparation of Standards, Non-viable A. niger Biomass and Iron Oxide-coated Biomass

Detailed procedure for the preparation of standards and reagents, and non-viable *A. niger* biomass could be found elsewhere (10). Detailed procedure for the preparation of iron oxide-coated biomass (IOCB) from the non-viable *A. niger* biomass could be found in an earlier publication (11).

The crushed biomass powder passing through a 400 µm sieve was used in biosorption experiments. The iron oxide-coated biomass powder used in the experiments was found to have a surface area of $2\,m^2/g$, a density of $0.72\,g/cm^3$, and an iron content of 254 mg/g.

Adsorption-desorption Studies

Adsorption

Arsenic solution {As(III) and As(V) 100 µg/L} of 100 mL volume was contacted with varying masses (0.02, 0.04, 0.06, 0.08, and 0.1 g) of the iron oxide-coated biomass at a controlled pH of 6 using tris buffer solution and a speed of 175 rpm for 7 hours in a platform shaker. Tris buffer solution of strength 0.1 M was prepared and the pH was adjusted to 6 by adding a required quantity of 0.5 M HNO_3 solution. Three sets of separate adsorption experiments were conducted for As(V) as well as for As(III) and the filtrate was analyzed for arsenic. All the experiments were conducted in duplicate and the average values were used in data analysis. The quantity of arsenic adsorbed on IOCB was determined by dividing the difference in the mass of arsenic in solution (initial – final) by the mass of the biomass as shown below:

$$\text{Arsenic adsorbed } (\mu g/g) = \frac{(As_i - As_f) \times V}{m}$$

where, As_i = initial arsenic concentration in solution (μg/L)
As_f = arsenic concentration in solution after experiment (μg/L)
V = solution volume (L)
m = mass of IOCB (g)

Desorption

After each set of the adsorption experiment, the arsenic-loaded iron oxide-coated biomass was separated from the solution by filtration. The arsenic-adsorbed biomass was placed in a series of conical flasks. A volume of 100 mL of arsenic-free solution each with pH 7, pH 1.33 (0.1 M HNO_3), and pH 12.56 (0.1 M NaOH) was added to three separate sets of the conical flasks. The solutions were shaken at a speed of 175 rpm for 14 hours and the arsenic desorbed in solution from the iron oxide-coated biomass (IOCB) was determined. Arsenic desorbed in the solution at different solution pH values was calculated as shown below:

$$\text{Arsenic desorbed } (\mu g/g) = \frac{(As_d - As_0) \times V}{m}$$

where, As_d = arsenic desorbed in solution (μg/L)
As_0 = initial arsenic concentration in solution in desorption experiment (μg/L)
V = solution volume (L)
m = mass of IOCB (g)

Note: The mass of the biomass in desorption experiment was considered to be the same as in adsorption experiment.

Effects of Common Ions

Experiments were conducted with arsenic solution {As(III) and As(V) of 100 g/L concentration} of 100 mL volume with an adsorbent dose of 1 g/L. The dose of the common ions: NO_3^- ($NaNO_3$, Fisher Scientific USA), SO_4^{2-} (Na_2SO_4, Sigma Chemicals USA), Cl^- (NaCl, BDH Inc. Canada), Ca^{2+} ($CaCl_2.2H_2O$, Fisher Scientific USA), Fe^{2+} ($FeSO_4.7H_2O$, Sigma Chemicals USA), and Mg^{2+} ($MgSO_4$, Fisher Scientific USA) was varied from 200 to 1000 mg/L. The solutions were mixed at a speed of 175 rpm on a platform shaker for 7 hours at a pH of 6. Select experiments were conducted by varying the arsenic dose in solution while keeping the adsorbent dose and the Ca^{2+}, Fe^{2+}, and Mg^{2+} concentration constant. A controlled experiment was conducted without adding ions but varying the arsenic concentration while keeping the adsorbent dosage constant (1 g/L). All the experiments were conducted in duplicate and average values were used in further analysis.

Thermodynamic Study

Arsenic solution {As(III) and As(V) 100 μg/L} of 100 mL volume was contacted with varying masses (0.02, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, and 0.1 g) of the iron oxide-coated biomass powder at a constant pH of 6 and a rotational speed of 175 rpm for 7 hours. These experiments were conducted at controlled temperatures of 5, 10, 15, 20, and 25°C and residual arsenic {As(III) and As(V)} in the solution was analyzed. The temperature was controlled by using an air bath. All the experiments were conducted in duplicate and the average value was used in the data analysis.

Arsenic Analysis

Arsenic was analyzed on Varian type spectraAA-600 Zeeman GFAAS equipped with GTA 100-graphite tube atomizer and programmable sample dispenser. Details of the analysis procedure had been given in an earlier publication (11).

Data Analysis

The isotherm data for As(V) and As(III) removal (at different temperatures) were analyzed using the Langmuir equation by non-linear regression using the software package STATISTICA (Release 5.0) for Windows. The significance of the data fit was evaluated by the *t*-test.

THEORY (THERMODYNAMICS)

The changes in heat of sorption (ΔH) and entropy (ΔS) of the sorption process are the driving forces for the reaction. The changes in heat of sorption (ΔH) and entropy (ΔS) are related with the standard Gibb's free-energy change (ΔG) by equation (1) (13). The changes in ΔG is expressed in terms of the Langmuir equilibrium constant, "b (L/mol)" by equation (2) (14) and the Langmuir equation is shown as Eq (3).

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

$$\Delta G = -RT\ln(b) \tag{2}$$

where R is the universal gas constant (8.314 J/mol/°K) and T is temperature in °K

The Langmuir equation is expressed in the following form (15):

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \tag{3}$$

where q_e is the equilibrium adsorption of arsenic by the adsorbent (μg/g); q_m is the maximum adsorption capacity of the adsorbent (μg/g); b is the equilibrium constant (L/μg); and C_e is the equilibrium concentration (μg/L). The Langmuir model assumes homogeneous monolayer adsorption of adsorbate on adsorbent. This means that an adsorbent (IOCB in this study) has fixed adsorption sites on its surface to adsorb arsenic. The adsorption of adsorbate continues to the point that the reaction sites are available in the adsorbent. There is a point beyond which no adsorption takes place and a steady-state equilibrium condition reaches.

In order to determine the Gibbs free-energy change at different temperatures, the equilibrium constant ‘b’ was first calculated from the Langmuir equation (3). The value of ‘b’ (L/μg) was converted to L/mol mol by multiplying with a factor of 74.92×10^6 and the value of ‘b’(L/mol) for different temperatures was substituted in equation (2) to find ΔG. The values of ΔG were plotted against T and the data points were regressed to form a straight line. The value of enthalpy change (ΔH) was obtained at T = 0°K from the equation of the straight line and the magnitude of the entropy change (ΔS) was equal to the slope of the straight line.

RESULTS AND DISCUSSION

Adsorption-desorption Studies

The adsorption-desorption experiments showed that only a small quantity of As(V) {14.7% ± 1.9} and As(III) {13.7% ± 8} on an average was desorbed at neutral pH in a contact time of 14 h. The desorption of As(V) in a dilute acid solution (0.1 M HNO_3) of pH 1.33 and in an alkaline solution (0.1 M NaOH) of pH of 12.56 was 67% ± 5.9 and 73.4% ± 4.2, respectively. Desorption of As(III) in similar acidic and alkaline solutions was 47.1% ± 11.9 and 43.7% ± 7.6, respectively. The adsorption-desorption data for As(V) and As(III) are provided in Tables 1 and 2, respectively. Desorption of both As(III) and As(V) at neutral solution (pH 7) was similar. However, desorption of As(III) in acidic and alkaline solutions was much less than that of As(V) in similar conditions.

Table 1. Desorption of As(V) on neutral, acidic and alkaline solutions

Adsorbent dose (g)	Ads. pH 6 (μg/g)	Des. pH 7 (μg/g)	Des. (%)	Ads. pH 6 (μg/g)	Des. pH 1.33 (μg/g)	Des. (%)	Ads. pH 6 (μg/g)	Des. pH 12.56 (μg/g)	Des. (%)
0.1	59.5	7.2	12.1	63.2	40.5	64.1	60.3	40.4	67.0
0.08	80.0	10.8	13.4	81.5	48.6	59.7	76.6	56.1	73.2
0.06	103.8	17.2	16.5	101.8	66.2	65.0	104.5	79.5	76.1
0.04	160.5	26.3	16.4	164.8	120.5	73.1	158.5	123.8	78.1
0.02	348.5	53.0	15.2	340.0	248.5	73.1	351.5	254.5	72.4
Average %			14.7 ± 1.9			67.0 ± 5.9			73.4 ± 4.2

Note: 'Ads.' means adsorption and 'Des.' means desorption.

Table 2. Desorption of As(III) on neutral, acidic and alkaline solutions

Adsorbent dose (g)	Ads. pH 6 (μg/g)	Des. pH 7 (μg/g)	Des. (%)	Ads. pH 6 (μg/g)	Des. pH 1.33 (μg/g)	Des. (%)	Ads. pH 6 (μg/g)	Des. pH 12.56 (μ g/g)	Des. (%)
0.1	47.4	3.3	7.0	37.1	15.2	41.0	34.9	16.4	47.0
0.08	67.4	2.8	4.1	38.0	16.5	43.4	55.1	19.6	35.6
0.06	36.0	6.2	17.1	42.3	19.7	46.5	45.2	21.7	48.0
0.04	55.8	8.8	15.7	43.8	16.3	37.1	51.3	26.8	52.2
0.02	38.5	9.5	24.7	46.0	31.0	67.4	101.0	36.0	35.6
Average %			13.7 ± 8			47.1 ± 11.9			43.7 ± 7.6

Note: ‘Ads.’ means adsorption and ‘Des.’ means desorption.

Table 3. Effects of common ions on As(V) removal {initial As(V) concentration 100 μg/L, adsorbent dose 1 g/L, pH 6, contact time 7 h and the residual As(V) [μg/L] is shown

Ions → Ion con. (mg/L) ↓	NO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Fe^{2+}
0	30.0 ± 7.0	43.9 ± 2.2	31.9 ± 2.9	45.0 ± 0.3	32.7 ± 1.2	26.2 ± 0.8
200	37.6 ± 1.3	42.8 ± 0.5	21.2 ± 0.4	3.0 ± 0.2	8.9 ± 0.3	2.6 ± 0.7
400	39.4 ± 1.4	40.9 ± 0.1	20.4 ± 0.4	1.2 ± 0.2	3.7 ± 0.1	2.3 ± 0.3
600	40.3 ± 4.5	44.0 ± 0.4	16.4 ± 0.1	0.1 ± 0.1	2.9 ± 0.1	2.3 ± 0.2
800	41.0 ± 1.3	45.4 ± 1.2	16.3 ± 0.4	1.0 ± 0.2	1.7 ± 0.2	2.9 ± 0.0
1000	41.0 ± 0.3	46.4 ± 1.0	16.1 ± 0.1	0.5 ± 0.0	2.3 ± 0.1	1.6 ± 0.1

Note: 'con.' means concentration.

Effect of Common Ions on Arsenic Removal

Nitrate, sulfate, chloride, calcium, magnesium, and iron(II) are commonly present in most groundwaters. The presence or absence of these ions in the aqueous medium may have significant influence on the arsenic removal process. The arsenic removal process can be optimized when the effects of these ions are known. The effect of common ions on As(V) and As(III) removal are shown in Tables 3 and 4, respectively.

The data showed that the presence of anions (sulfate, chloride and nitrate) had no significant effect on As(V) adsorption. Addition of cations such as calcium, magnesium and iron (II) improved the adsorption of As(V). A residual As(V) concentration of 3 μg/L or below was achieved at all times when Ca^{2+} and Fe^{2+} ions of 200 mg/L or greater were present in the solution when the initial As(V) was 100 μg/L (Table 3). The presence of Mg^{2+} ions in the solution was not as effective as Ca^{2+} and Fe^{2+} ions. However, Mg^{2+} ions of 400 mg/L or more might be required to lower As(V) below 5 μg/L from an initial As(V) of 100 μg/L.

The addition of anions such as nitrate, sulfate, and chloride did not have any influence on As(III) adsorption process (Table 4). The presence of cations (Ca^{2+} and Fe^{2+}) in the solution improved As(III) adsorption. The effect of Mg^{2+} on the As(III) adsorption was not quite high even with the increased dose of Mg^{2+} ions.

In another set of experiments, the dosage of Ca^{2+}, Mg^{2+} and Fe^{2+} was kept constant (200 mg/L), adsorbent dosage was also maintained at 1 g/L and the arsenic {As(V) and As(III)} concentration was varied in order to find out proper ratio of cations to arsenic for optimization

Table 4. Effects of common ions on As(III) removal initial As(III) concentration 100 μg/L, adsorbent dose 1 g/L, pH 6, contact time 7 h and the residual As(III) [μg/L] is shown

Ions → Ion con. (mg/L) ↓	NO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Fe^{2+}
0	21.9 ± 2.0	21.6 ± 0.1	33.2 ± 0.3	23.2 ± 0.8	41.8 ± 2.9	39.5 ± 0.6
200	20.5 ± 2.9	20.2 ± 4.0	23.5 ± 0.3	3.4 ± 0.1	33.4 ± 0.1	6.1 ± 0.3
400	24.2 ± 0.1	21.3 ± 0.6	28.1 ± 0.3	7.9 ± 1.6	27.9 ± 1.6	7.1 ± 1.0
600	16.7 ± 1.1	22.0 ± 0.9	21.2 ± 0.6	9.2 ± 1.8	24.7 ± 0.9	6.6 ± 0.6
800	20.2 ± 0.3	21.6 ± 2.2	25.0 ± 1.2	9.2 ± 1.1	26.3 ± 0.4	8.0 ± 0.4
1000	24.4 ± 1.2	24.1 ± 0.0	23.4 ± 3.1	9.9 ± 1.3	20.5 ± 0.8	9.3 ± 0.1

Note: ‘con.’ means ‘concentration’.

of experiments. Figures 1 and 2 show the increased removal of As(V) and As(III), respectively by IOCB due to the presence of the cations in the solutions. Comparing the residual arsenic in solution after the experiment with and without cations, it was found that As(V) removal increased to 86.5%, 95.4%, and 65.8% on an average due to the presence of Ca^{2+}, Fe^{2+}, and Mg^{2+} ions (concentration of cations in solution 200 mg/L), respectively. The As(III) removal increased by 39.3%, 97%, and 8.4%

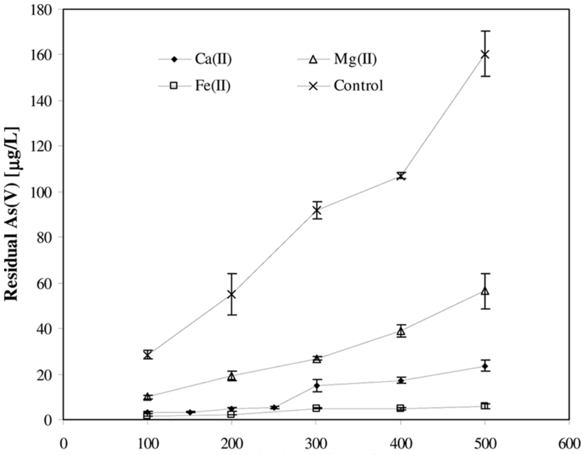

Figure 1. Residual As(V) *vs* initial As(V) at a fixed dose of cations [Ca^{2+}, Mg^{2+} and Fe^{2+} concentration 200 mg/L, adsorbent dose 1 g/L, pH 6, contact time 7 hours and error bars are shown in Figure].

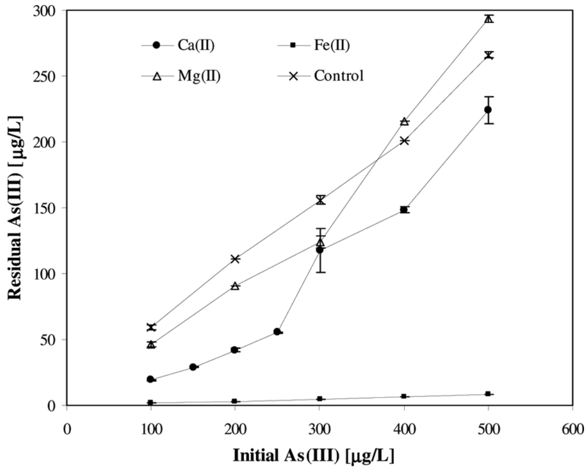

Figure 2. Residual As(III) *vs* initial As(III) at a fixed dose of cations [Ca^{2+}, Mg^{2+} and Fe^{2+} concentration 200 mg/L, adsorbent dose 1 g/L, pH 6, contact time 7 hours and error bars are shown in the Figure].

on an average due to the presence of Ca^{2+}, Fe^{2+}, and Mg^{2+} ions (concentration of cations in solution 200 mg/L), respectively.

It was found that the addition of Fe^{2+} at a dose of 200 mg/L could remove As(V) approximately at or below 5 µg/L for up to an initial As(V) concentration of 500 µg/L using IOCB as an adsorbent. With the presence of Ca^{2+} ions at a concentration of 200 mg/L, the residual As(V) was found to be approximately 5 µg/L or below for up to an initial As(V) concentration of 250 µg/L. For an initial As(V) concentration of 500 µg/L, the residual As(V) was approximately 24 µg/L, well below the drinking water standards in the developing countries such as Bangladesh (arsenic standard for Bangladesh is 50 µg/L). There was an improvement in increased adsorption capacity of As(V) due to the presence of Mg^{2+} ions in solution but it was not as effective as Ca^{2+} and Fe^{2+} ions. For an initial As(V) concentration of 500 µg/L, the residual As(V) was approximately 56 µg/L due to the presence of Mg^{2+} ions at a concentration of 200 mg/L.

Addition of Fe^{2+} ion in solution at a concentration of 200 mg/L could remove As(III) well below 10 µg/L for up to 500 µg/L of initial As(III) concentration. The presence of Ca^{2+} and Mg^{2+} ions in solution could improve the adsorption capacity of the IOCB for As(III) removal but the dose of Ca^{2+} and Mg^{2+} ions needed would be greater than 200 mg/L in order to achieve residual As(III) below 10 µg/L.

Table 5. The Langmuir isotherm parameters and Gibbs free-energy change (ΔG) for As(III) and As(V) adsorption by IOCB

	As(III)				As(V)			
Temp. (°C)	b (L/μg)	q_m (μg/g)	R^2	ΔG (kJ/mol)	b (L/μg)	q_m (μg/g)	R^2	ΔG (kJ/mol)
5	0.0027	200.2	0.13	−28.2	0.0986	108.6	0.61	−36.6
10	0.0052	181.8	0.20	−30.3	0.1040	188.2	0.91	−37.3
15	0.0020	522.9	0.43	−28.5	0.0426	334.5	0.96	−35.9
20	0.0991	103.5	0.25	−38.5	0.0052	1541.3	0.79	−31.4
25	0.0154	305.5	0.73	−34.6	0.0571*	526.0*	0.82*	−37.8*

Note: (1) * Data not significant at 95% confidence level. All other data are significant at 95% confidence level (*t*-test). (2) 'Temp.' means 'temperature'.

Thermodynamic Behavior

The isotherm data for As(V) and As(III) removal (at different temperatures) were fitted to the Langmuir equation to find the equilibrium constant 'b' in order to determine ΔG. The Langmuir isotherm parameters and the Gibbs free energy change (ΔG) values for As(V) and As(III) removal are presented in Table 5. Data that were not significant at 95% confidence level were not used for the calculation of thermodynamic parameters (ΔH and ΔS).

In most of the environmental engineering practice, both the change in energy (ΔG) and the change in entropy (ΔS) must be considered to determine the spontaneity of the process (16). The negative values of ΔG indicated the feasibility of the adsorption of both As(III) and As(V) by the IOCB and the spontaneity of the sorption process. The values of ΔH and ΔS for As(V) adsorption were −133 kJ/mol and −0.34 kJ/mol/°K, respectively (Fig. 3). The negative value of ΔH for As(V) confirmed that heat was produced during the adsorption of As(V) by IOCB indicating the exothermic nature of the process. The negative value of entropy (ΔS) change indicated a greater order of reaction during the adsorption of As(V) on IOCB (17) and also that stable complexes formed between the As(V) and the IOCB (18). The values of ΔH and ΔS for As(III) adsorption were 88.9 kJ/mol and 0.42 kJ/mol/°K, respectively (Fig. 3). The positive value of ΔH for As(III) confirmed the endothermic nature of the process. The positive value of entropy (ΔS) change showed the affinity of the IOCB on As(III) and also an increased randomness at the solid/liquid interface during the adsorption (19,20,21). A study by Zeng (21) reported exothermic nature of reaction between

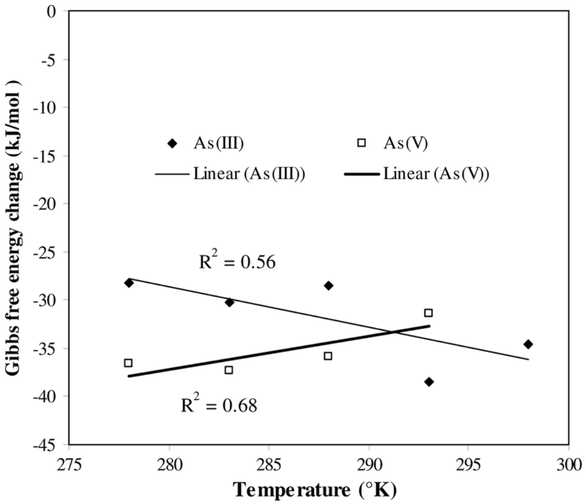

Figure 3. The Gibbs free-energy change *vs* temperature (°K).

As(V) and Fe(III)-binary oxide and endothermic between As(III) and Fe(III)-binary oxides. The adsorption of As(III) on iron oxide impregnated activated alumina was also found to be an endothermic (22). The reasons why As(V) adsorption was exothermic and As(III) adsorption endothermic need to be examined.

Discussion

Desorption of arsenic varied according to the arsenic oxidation state, adsorbents and leaching solutions (23). The desorption capacity of iron-pillared clay was 95% and 80% for As(V) and As(III), respectively (24) using 1 M HCl in a contact time of 4 h. In another study 70% of As(III) and 55% of As(V) desorbed from the waste tea fungal biomass using 0.5 N NaOH solution (25). The desorption percentage of As(V) through Fe_2O_3 with a solution pH of 7 was directly proportional with the initial As(V) concentration (26). The present study showed that desorption of arsenic varied according to the arsenic species and the solution pH.

Kundu and others (27) reported that SO_4^{2-} did not affect the adsorption of As(V) whereas presence of Cl^- and NO_3^- ions at or above 200 and 400 mg/L, respectively, decreased the removal of As(V). The presence of Ca^{2+}, Mg^{2+}, and Fe^{2+} ions in solution decreased arsenic removal efficiency. The presence of chloride and sulfate ions in solution improved the removal of As(V) using natural iron ores (hematite and goethite) (28). The presence of sulfate (SO_4^{2-}) had no effect on arsenic removal (at pH 7.4) using Fe(III)-Si binary oxide (21). The presence of Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-} ions had no effect on As(V) adsorption using Ce(IV)-doped iron oxide adsorbent (29). There was no effect of sulfate on As(V) removal using ferrihydrite but As(III) adsorption decreased below neutral pH (30) and the presence of sulfate above pH 7 had no effect on As(III) adsorption. A decreasing trend was observed in adsorption of As(III) and As(V) using hydrous ferric oxide in the presence of sulfate ion (31). The effect was greatest at a lower pH. The addition of Ca^{2+} ions in solution enhanced As(V) adsorption by hydrous ferric oxide, increasing the quantity of positive charge on oxide surface (31). The presence of Ca^{2+} ion enhanced As(V) adsorption by aluminum oxide above pH 8 (32). The reason for the enhanced removal of arsenic by the IOCB in the presence of cations (Ca^{2+}, Mg^{2+}, and Fe^{2+}) could be due to an enhanced positive charge similar to the mechanism suggested by other researchers (31). Arsenic is often found in the mineral deposit as a compound combined with cationic metal ions.

The forces of attraction between the solute molecules and the adsorbing surfaces could be classified into three major groups:

1. chemical,
2. electrostatic and
3. physical, and the energies associated with the attraction of solute by the adsorbent surfaces are due to the changes in enthalpy (ΔH) (33).

Chemical adsorption involves solute-sorbent bond characterized by a large heat of adsorption (100 to 400 kJ/mol or larger). Electrostatic adsorption involves Coulombic forces of attraction between oppositely charged species, with a heat of adsorption as high as 200 kJ/mol. Physical adsorption results due to the action of van der Waals forces, comprised by London dispersion forces and classical electrostatic forces. The heats of adsorption associated with the physical adsorption may be as high as 20 kJ/mol (33). The sublimation energy of physical adsorption ranges from 20 to 40 kJ/mol whereas in chemical adsorption it could range from 100 to 400 kJ/mol (14). The strength of physical adsorption could be 20 kJ/mol and chemisorption could be as high as 300 to 500 kJ/mol (34). It was noted that ΔG values of up to -20 kJ/mol were consistent with physical adsorption while the ΔG values greater than -40 kJ/mol involved charge sharing or formed a coordinate bond between the metal surface and the adsorbent (35). The energy of ligand exchange reaction may range from 8 to 60 kJ/mol whereas the change in enthalpy of chemisorption may be greater than 29 kJ/mol (36).

The high values of ΔG (≈ -28 to -39 kJ/mol) for both As(V) and As(III) as well as high ΔH values {-133 kJ/mol for As(V) and 88.9 kJ/mol for As(III)} indicated that the adsorption mechanism may be either chemisorption or electrostatic attraction. The surface charge of the IOCB was negative from a pH of 3 to 9(10) and the fact that arsenic species in these pH ranges are either in anionic or in neutral form, electrostatic attraction can not be the mechanism of adsorption. The high value of ΔH and the negative surface potentials of IOCB found earlier provide evidence that the major mechanism of arsenic {both As(V) and As(III)} adsorption on IOCB was chemisorption. In chemisorption an actual chemical bond, usually covalent, is formed between the adsorbate molecule and the adsorbent surface atoms and also some ligand exchange reactions are chemisorption processes (36). The adsorption capacity of the iron oxide-coated biomass was found to be 1080 μg/g for As(V) and 880 μg/g for As(III) in fixed bed column experiments (37).

CONCLUSIONS

The following conclusions were drawn based on the results:

1. There was no considerable effect of the presence of anions (NO_3^-, ${SO_4}^{2-}$, and Cl^-) on arsenic removal process using IOCB.
2. Addition of cations such as Ca^{2+}, Mg^{2+}, and Fe^{2+} enhanced arsenic {As(V) and As(III)} removal efficiency in general. The presence of Ca^{2+} and Fe^{2+} ions at a concentration of 200 mg/L could remove As(V) below 5 μg/L from an initial As(V) concentration of 250 μg/L L and 500 μg/L, respectively.
3. The presence of Fe^{2+} at a concentration of 200 mg/L could remove As(III) below 10 μg/L from up to an initial As(III) concentration of 500 μg/L. However, the Ca^{2+} and Mg^{2+} dose of 200 mg/L was not adequate to achieve effluent As(III) less or equal to 10 μg/L, the standard set by WHO for drinking water.
4. The adsorption-desorption study showed that the reactions between the arsenic species and the iron oxide-coated *A. niger* biomass were reversible.
5. Desorption of arsenic was dependent on the solution pH. At pH 7, desorption of both As(V) and As(III) was less than 15%. Desorption of As(V) was greater than that of As(III) in acidic (pH 1.33) and alkaline solutions (pH 12.56).

6. The value and sign of the thermodynamic parameters (ΔG and ΔS) showed the spontaneity of the adsorption of arsenic on IOCB.
7. The high value of the heat of adsorption (ΔH) indicated that the mechanism of arsenic adsorption by IOCB may be chemisorption.

ACKNOWLEDGEMENT

The study was supported by a grant from the Natural Sciences and Engineering Research Council of Canada to the second author. The authors would like to thank the reviewers for their constructive comments.

REFERENCES

1. Agency for Toxic Substances and Disease Registry (ATSDR) (2002) Arsenic toxicity: case studies in environmental medicine; U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry.
2. World Health Organization (WHO) (1993) *Guidelines for Drinking-Water Quality*; Geneva, Switzerland.
3. US EPA. (2001) http://www.epa.gov/safewater/ars/arsenic_finalrule.html.
4. World Health Organization (WHO) (2001) *Environmental Health Criteria 224: Arsenic and Arsenic Compounds*; Geneva, Switzerland.
5. Korte, N.E.; Fernando, Q. (1991) A review of arsenic (III) in groundwater. *Critical Reviews in Environmental Control*, *21* (1): 1–39.
6. Thirunavukkarasu, O.S.; Viraraghavan, T.; Subramannian, K.S. (2003) Arsenic removal from drinking water using iron oxide-coated sand. *Water, Air, and Soil Pollution*, *142*: 95–111.
7. Zouboulis, A.I.; Katsoyiannis, I.A. (2002) Arsenic removal using iron oxide loaded alginate beads. *Ind. Eng. Chem. Res.*, *41*: 6149–6155.
8. Ghimire, K.N.; Inoue, K.; Makino, K.; Miyajima, T. (2002) Adsorptive removal of arsenic using orange juice residue. *Separation Science and Technology*, *37* (12): 2785–2799.
9. Stollenwerk, K.G. (2003) Geochemical processes controlling transport of arsenic in groundwater: A review of adsorption. In: *Arsenic in Ground Water: Geochemistry and Occurrence*, Welch, A.H.; Stollenwerk, K.G., eds.; Kluwer Academic Publishers: USA, 67–100.
10. Pokhrel, D.; Viraraghavan, T. (2006) Arsenic removal from aqueous solution by a modified fungal biomass. *Water Research*, *40*: 549–552.
11. Pokhrel, D.; Viraraghavan, T. (2006) Arsenic removal from aqueous solution by iron oxide-coated fungal biomass: a factorial design analysis. *Water Air and Soil Pollution*, *173*: 195–208.
12. Pokhrel, D.; Viraraghavan, T. (2008) Arsenic removal from aqueous solution by modified *A. niger* biomass: batch kinetic and isotherm studies. *Journal of Hazardous Materials*, *150* (3): 818–825.

13. Daniels, F.; Alberty, R.A. (1966) *Physical Chemistry*; John Wiley & Sons, Inc.: New York, USA, 69–99.
14. Butt, H.-J.; Graf, K.; Kappl, M. (2003) *Physics and Chemistry of Interfaces*; Wiley-VCH Verlag GmbH & Co. KgaA: Weinheim, Germany, 177–179.
15. Langmuir, I. (1918) The adsorption of gases on plane surface of glass, mica and platinum. *J. Am. Chem. Soc.*, *40*: 1361–1403.
16. Sawyer, C.N.; McCarty, P.L.; Parkin, G.F. (2003) *Chemistry For Environmental Engineering And Science*; The McGraw-Hill Companies, Inc.: New York, USA, 52–63.
17. Khan, A.A.; Singh, R.P. (1987) Adsorption thermodynamics of carbofuran on Sn(IV) arsenosilicate in H^+, Na^+ and Ca^{2+} forms. *Colloids and Surfaces*, *24*: 33–42.
18. Biggar, J.W.; Cheung, M.W. (1973) Sorption of picloram (4-amino-3,5,6-trichloropicolinic acid) on panoche, ephrata, and palouse soils: a thermodynamic approach to the adsorption mechanism. *Soil Sci. Amer. Proc.*, *37*: 863–868.
19. Ho, Y.-S. (2003) Removal of copper ions from aqueous solution by tree fern. *Water Research*, *37*: 2323–2330.
20. Ozer, A.; Ozer, D. (2004) The adsorption of Cr(VI) on sulphuric acid-treated wheat bran. *Environmental Technology*, *25*: 689–697.
21. Zeng, L. (2004) Arsenic adsorption from aqueous solutions on an Fe(III)-Si Binary Oxide adsorbent. *Water Qual. Res. J. Canada*, *39* (3): 267–275.
22. Kuriakose, S.; Singh, T.S.; Pant, K.K. (2004) Adsorption of As(III) from aqueous solution onto iron oxide impregnated activated alumina. *Water Qual. Res. J. Canada*, *39* (3): 258–266.
23. Ladeira, A.C.Q.; Ciminelli, V.S.T. (2004) Adsorption and desorption of arsenic on an oxisol and its constituents. *Water Research*, *38*: 2087–2094.
24. Lenoble, V.; Bouras, O.; Deluchat, V.; Serpaud, B.; Bollinger, J.C. (2002) Arsenic adsorption onto pillared clays and iron oxides. *Journal of Colloid and Interface Science*, *255*: 52–58.
25. Murugesan, G.S.; Sathishkumar, M.; Swaminathan, K. (2006) Arsenic removal from groundwater by pretreated waste tea fungal biomass. *Bioresource Technology*, *97* (3): 483–487.
26. Puls, R.W.; Powell, R.M. (1992) Transport of inorganic colloids through natural aquifer material: implications for contaminant transport. *Environmental Science and Technology*, *26*: 614–621.
27. Kundu, S.; Kavalakatt, S.S.; Pal, A.; Ghosh, S.K.; Mandal, M.; Pal, T. (2004) Removal of arsenic using hardened paste of portland cement: batch adsorption and column study. *Water Research*, *38*: 3780–3790.
28. Zhang, W.; Singh, P.; Paling, E.; Delides, S. (2004) Arsenic removal from contaminated water by natural iron ores. *Minerals Engineering*, *17*: 517–524.
29. Zhang, Y.; Yang, M.; Huang, X. (2003) Arsenic(V) removal with a Ce(IV)-doped iron oxide adsorbent. *Chemosphere*, *51*: 945–952.
30. Jain, A.; Loeppert, R.H. (2000) Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. *Journal of Environmental Quality*, *29*: 1422–1430.

31. Wilkie, J.A.; Hering, J.G. (1996) Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occuring solutes. *Colloids and Surfaces*, *107*: 97–110.
32. Ghosh, M.M.; Teoh, R.S. (1985) Adsorption of arsenic on hydrous aluminum oxide, in 7th Mid Atlantic Industrial Waste Conference, Lancaster, Pennsylvania, 139–155.
33. Weber, W.J. Jr.; Digiano, F.A.. (1996) *Process Dynamics in Environmental Systems*; John Wiley & Sons, Inc.: New York, USA, 353–356
34. Houston, P.L. (2001) *Chemical Kinetics And Reaction Dynamics*; The McGraw-Hill Companies, Inc.: New York, USA, 174–177.
35. Horsfall, M. Jr.; Abia, A.A.; Spiff, A.I. (2006) Kinetic studies on the adsorption of Cd^{2+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions by cassava (*Manihot sculenta Cranz*) tuber bark waste. *Bioresource Technology*, *97* (2): 283–291.
36. Roy, W.R.; Krapac, I.G.; Chou, S.F.J.; Griffin, R.A. (1991) *Batch-Type Procedures For Estimating Soil Adsorption Of Chemicals*, United States Environmental Protection Agency: Cincinnati, Ohio, USA EPA/530-SW-87–006-F, 3–4.
37. Pokhrel, D.; Viraraghavan, T. (2008) Arsenic removal in an iron oxide-coated fungal biomass column: Analaysis of breakthrough curves. *Bioresource Technology*, *99* (6): 2067–2071.