Arsenic Removal Using Synthetic Adsorbents: Kinetics, Equilibrium and Column Study

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INTRODUCTION

Arsenic contaminations are seldom of anthropogenic origin (mining, wood preservatives,…) being generally caused by the natural dissolution of minerals in surface or underground waters. In natural waters, arsenic is present either as As(III) or As(V). Both ions are toxic and carcinogenic. High concentrations of arsenic in the groundwater (>1000 mg/L) of natural origin have been found in some areas in countries like Bangladesh, West Bengala, India, Mexico and some areas in Argentina, Chile and U.S.A.

The main objective of this research is to establish a comparison between the performance of different sorbents for the removal of As(V): (i) a reference sorbent commercially known as ARM-300 (BASF Corporation) and two synthetic sorbents prepared at the laboratory, (ii) the hydrous ferric oxide (HFO) in suspension and (iii) loaded onto granular activated carbon (GAC). The research focused in the kinetics and chemical equilibrium using batch scale testing for the three systems.

EXPERIMENTAL

Materials

- The **suspension of hydrous ferric oxide (HFO)** was prepared immediately prior to each adsorption experiment. A solution of 0.5M NaOH was added drop wise with stirring to 150ml of 0.05 M $Fe(NO_3)_3$. The total volume of 0.5 M NaOH added was 45 ml; the final pH was approximately 8 (Wilke and Hering, 1996).

- **Hydrous ferric oxide loaded onto GAC (HFO/GAC)** was prepared using $Fe(NO_3)_3$. $9H_2O$ as a precursor for iron oxide incorporation into the pores of granular-size porous GAC. The GAC used was Riedel-de-Haën (reference 18002). The procedure adopted to achieve homogeneous impregnation was proposed by Mondal et al. (2008): 1.5 mL of ferric nitrate solution at concentrations of 1 g/mL was dispersed over 1 g of dried GAC and mixed thoroughly; GAC was then dried at room temperature for 24 h before placement in a rotary evaporator for curing (Fe oxide/hydroxide precipitation) at 80 °C for 12 h. After Fe oxide/hydroxide precipitation, the GAC was cooled to room temperature and then washed thoroughly with deionised water. The washed GAC was dried at room temperature for 24 h. Following this procedure, the Fe oxide/hydroxide precipitation occurred inside the pore structure of the GAC at elevated temperature in the acidic condition, without adding NaOH (Mondal et al., 2008).

- As a **reference material** , a specific adsorbent, **ARM 300**, was used whit no further preparation. ARM300 was purchase to BASF cooperation.

Methods

Arsenic determinations were carried by inductively coupled plasma optical emission spectroscopy with coupled hydride generation. Samples not analyzed on the same day as the adsorption experiment were acidified to about pH 1 with concentrated HCl and stored in acid washed high density polyethylene containers. All samples were analyzed within 7 days of collection.

A summary of the experimental conditions are presented in table 1.

Experiment	Adorbent	T (ºC)	$m_{adsorbent}$ (g)	V (mL)	$pH_{initial}$	$C_{initial}$ (ppb)	Q (mL/min)
Kinetic	HFO	20	2.409	651	3.6	5000	...
	HFO/GAC	20	5.005	1000	3.0	500	...
	ARM 300	20	5.000	1000	4.3	1000	...
Equilibrium	HFO	20	0.010-0.185	100	....	5000	...
	HFO/GAC	20	0.010-0.175	100	....	1000	...
	ARM 300	20	0.010-0.175	100	....	5178	...
Column	HFO/GAC	20	5.681	...	3.8	4674	8.00

RESULTS and DISCUSSION

Kinetics

Figure 1- Pseudo - first and pseudo-second order kinetics models of arsenic adsorption into (A) HFO, (B) HFO/GAC and (C) ARM 300
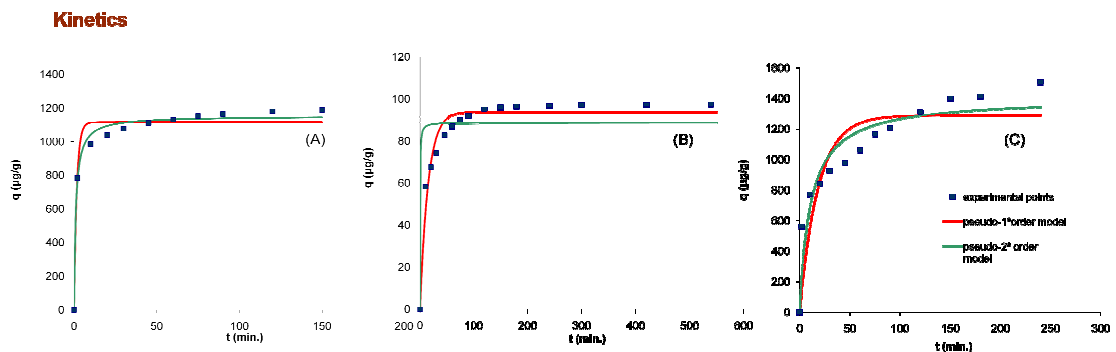
Figure 1- Pseudo - first and pseudo-second order kinetics models of arsenic adsorption into (A) HFO, (B) HFO/GAC and (C) ARM 300

	Pseudo-first order model				Pseudo-second order model			
Adsorbent	k_1 (min^{-1})	q_e $(\mu g/g)$	s^2	r^2	k_2 $(g/(\mu g. min))$	q_e $(\mu g/g)$	s^2	r^2
HFO	0.6 ± 0.2	1115 ± 48	4101	0.969	$8\times10^{-4} \pm 3\times10^{-4}$	1151 ± 33	1429	0.989
HFO/GAC	0.07 ± 0.02	94 ± 4	26.5	0.964	$4\times10^{-2} \pm 3\times10^{-1}$	97 ± 7	214	0.798
ARM 300	0.05 ± 0.03	1288 ± 171	37396	0.846	$7\times10^{-5} \pm 6\times10^{-5}$	1403 ± 183	21079	0.900

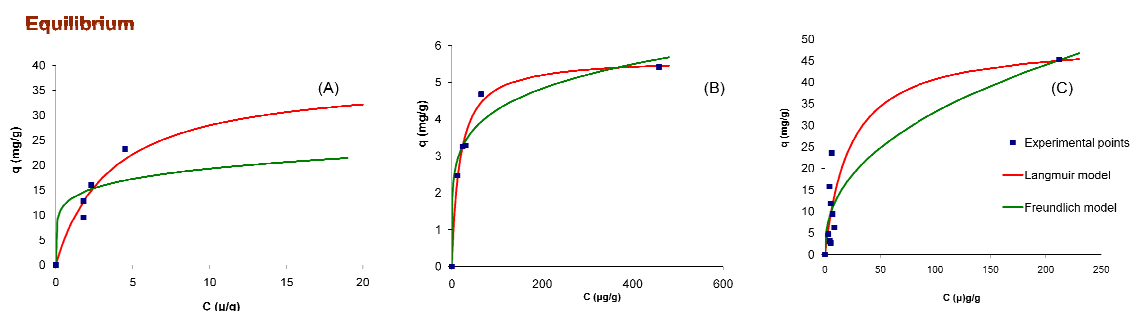Table 2 – Parameters obtained for pseudo first and second order kinetic models

Equilibrium

Figure 2- Langmuir and Feundlich equilibrium models of arsenic adsorption into (A) HFO, (B) HFO/GAC and (C) ARM 300

Table 3 – Parameters obtained for Langmuir and Freundlich models

	Langmuir isotherm				Freundlich isotherm			
Adsorbent	q_L (mg/g)	b $(L/\mu g)$	s^2	r^2	K_F $((mg/g)(L/\mu g)^{1/n})$	n	s^2	r^2
HFO	38 ± 2	0.3 ± 0.1	4.120	0.979	13 ± 6	6 ± 3	17.56	0.913
HFO/GAC	5.5 ± 0.5	0.06 ± 0.02	0.047	0.989	1.8 ± 0.9	5 ± 3	0.197	0.956
ARM 300	49 ± 20	0.06 ± 0.06	47.39	0.907	6 ± 6	3 ± 2	52.22	0.804
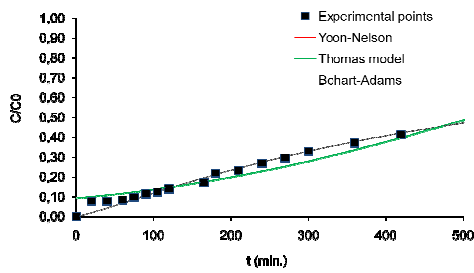
Figure 7 – Column models for HFO/ GAC

Table 4 – Parameters obtained for column models

Model	Parameters	HFO/GAC
Yoon-Nelson (YN)	k_{YN} (min^{-1})	$4.5 \times 10^{-3} \pm 6 \times 10^{-4}$
	τ_{YN} (min)	513 ± 33
	s^2	14×10^{-4}
	r^2	0.952
Thomas (T)	k_{TH} (mL(μg min)$^{-1}$)	$10 \times 10^{-4} \pm 2 \times 10^{-4}$
	q_{TH} (μg g^{-1})	3376 ± 219
	s^2	14×10^{-4}
	r^2	0.952
Yan (Y)	a_Y	1.2 ± 0.1
	q_Y (μg g^{-1})	3598 ± 268
	s^2	50×10^{-5}
	r^2	0.985
Fisher' test	F_{cal} (YN / Y; T / Y)	28
	F_c	2.27

AKNOWLEDGMENTS

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