



## Assessing Innovative Arsenic Adsorbents

### Objectives

According to a 1999 study by the National Academy of Sciences, arsenic in drinking water can cause several types of cancer, harm the central and peripheral nervous systems, cause serious skin problems, cause birth defects and reproductive problems. The USEPA published a Final Arsenic Rule in the Federal Register that established a revised Maximum Contaminant Level (MCL) for Arsenic of  $10\mu\text{g/L}$  (USEPA 2003). All public drinking water systems have to achieve compliance with this rule by January 2006. This new standard is estimated by the EPA to impact 4,000 community water systems nationwide.

This study focused on evaluating innovative adsorbent materials that can remove arsenic from water effectively. The adsorbents tested ranged from zero-valent iron (ZVI) and activated alumina (AA) to various forms of iron-oxides. The more innovative adsorbent forms include various combinations of iron and aluminum oxides and their coatings on diatomaceous earth (DE) and ceramic spheres.

### Methodology

Numerous adsorbent materials were tested in this study. Some had previously been evaluated by E. Hadnagy (2004) of the University of New Hampshire (UNH) such as granular ferric hydroxide (GFH), hydrous ferric oxide (HFO), iron hydroxide coated sand, ferric hydroxide coated calcinated diatomite (Media G2), sulfur modified iron (SMI), activated alumina (AA), zero-valent iron (ZVI) and goethite. All of the adsorbent materials used in the batch studies were in powdered form to facilitate equilibrium kinetics.

In addition, innovative adsorbents including DE coated with hematite (0609A), Iron nanoparticles on  $0.3\mu\text{m}$  aluminium oxide (J1), Iron nanoparticles on DE (J2), Iron nanoparticles on microlite ceramic spheres (J3), Iron nanoparticles on  $0.42\mu\text{m}$  aluminium oxide (J4), DE+ $\text{Fe}_2\text{O}_3$ + $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  on  $\text{Al}_2\text{O}_3$  (April set), Ceramic spheres coated with  $\text{Fe}_2\text{O}_3$  (S1),  $\text{Fe}_2\text{O}_3$  on  $\text{Al}_2\text{O}_3$  (S2),  $\text{Fe}_2\text{O}_3$  on  $\text{Al}_2\text{O}_3$  (S3),  $\text{Al}(\text{OH})_3$ + $\text{Fe}(\text{OH})_3$  (S4) and  $\text{Fe}_2\text{O}_3$ + $\text{Al}_2\text{O}_3$  (S5) were also evaluated.

This study can be divided in four parts:

- 1) Kinetic study.** This study provided information on the adsorption capacities of the materials tested and estimated the equilibrium time of the adsorption reaction. Through the results of this study it was also possible to tell if a constituent of the adsorbent (Fe or Al) leached into the solution.
- 2) Adsorption isotherms.** The objective of this isotherm study was to determine the amount of arsenic adsorbed at several adsorbent doses. The isotherm studies also indicated the adsorption density values (As removed/mass of adsorbent used) for the selected adsorbent materials in order to assess the arsenic removal capacity of each adsorbent, as a function of As concentration remaining in the solution. The adsorbent equilibrium removal capacities can then be compared. The more promising adsorbents can be further evaluated by conducting time consuming column studies.

**3) Column Study.** The adsorbents combining DE and iron oxides were tested in a column study. The aim of the column studies was to assess the removal of arsenic for the most competitive adsorbent with diatomaceous earth. Two columns were filled with DE coated with iron oxides which were compared to a control column filled with commercial DE (Hyflo Super Cell from Celite Corporation). The two adsorbent materials tested were: 1) DE coated with iron nanoparticles (J2) provided by Seldon Technologies LLC., Windsor, VT in July 04 and 2) DE embedded with Hematite (0609A) provided by Seldon Technologies LLC., Windsor, VT. The preparation of the adsorbent materials and the arsenic solution was the same as for the adsorption study. The influent pH was held constant at 8.

**4) ZVI Study.** The results of the tests of the adsorbent materials showed the interesting possibilities of using ZVI as an arsenic remover. The aim of this side assessment was to discern the factors that influence the efficiency of ZVI in adsorbing arsenic.

The prerusting of ZVI was tested first and then an Analysis Of Variance (ANOVA) was performed in order to identify whether Eh or pH (or both) master variables had an influence on the adsorptive properties of ZVI. The preparation of the adsorbent materials and the arsenic solution were prepared in the same way as those for the adsorption study. Prerusted ZVI (bubbled with fresh air) was tested under the same conditions as the other materials tested in the column studies.

The results of this experiment were used to run an ANOVA for a two level orthogonal array (Table 1).

Trial No	pH	Eh	pH*Eh Error
1	1 (pH=6)	1 (Nitrogen)	1
2	1 (pH=6)	2 (Air)	2
3	2 (pH=8)	1 (Nitrogen)	2
4	2 (pH=8)	2 (Air)	1

The two level orthogonal array provided information as to the percent contribution of the pH and the redox potential factors on the variability of the arsenic removal data. The question of what level of Redox potential and pH are required so that the ZVI can be most efficient at removing arsenic was explored at the conclusion of this study.

## Results

**Kinetic studies:** The kinetic studies (as depicted in Figure 1) showed a slow down in the reaction before 200 min for most of the adsorbents: Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (April set), AA, Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (S3), Al(OH)<sub>3</sub>+Fe(OH)<sub>3</sub> (S4) and for DE coated with hematite (0609A). Ceramic spheres coated with Fe<sub>2</sub>O<sub>3</sub> (S1), Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub> (S5), DE+Fe<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub> and goethite did not appear to react strongly. It is possible that they were already in equilibrium with the solution. ZVI and Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (S2) appeared to continue reacting with the arsenic even after 200 minutes. The kinetic studies demonstrated the

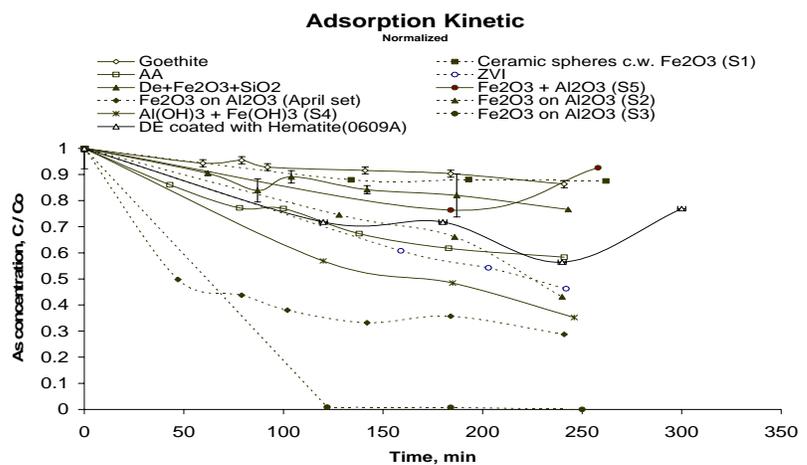


Figure 1: Freundlich Adsorption Isotherm of ZVI under different conditions

efficiency of the experimental procedure and that an equilibrium time of 200 minutes was generally sufficient in order to achieve equilibrium in the system.

Based on the results of this study, a new experiment is warranted to further investigate the kinetics of ceramic spheres coated with Fe<sub>2</sub>O<sub>3</sub> (S1), DE+Fe<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (April set) and Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (S2).

**Isotherm Studies:** The isotherm studies show the efficiency of each adsorbent in absorbing arsenic. Isotherm Freundlich and Langmuir curves were fitted to the adsorption data. The Freundlich Adsorption Isotherm Model and the Langmuir Adsorption isotherm model are summarized in Figures 2a and 2b.

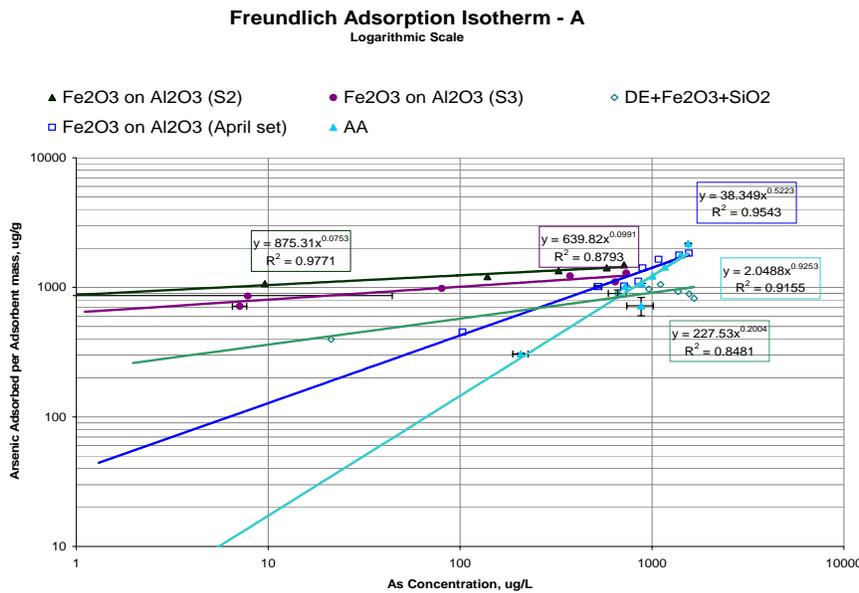


Figure 2a: Freundlich Adsorption Isotherms

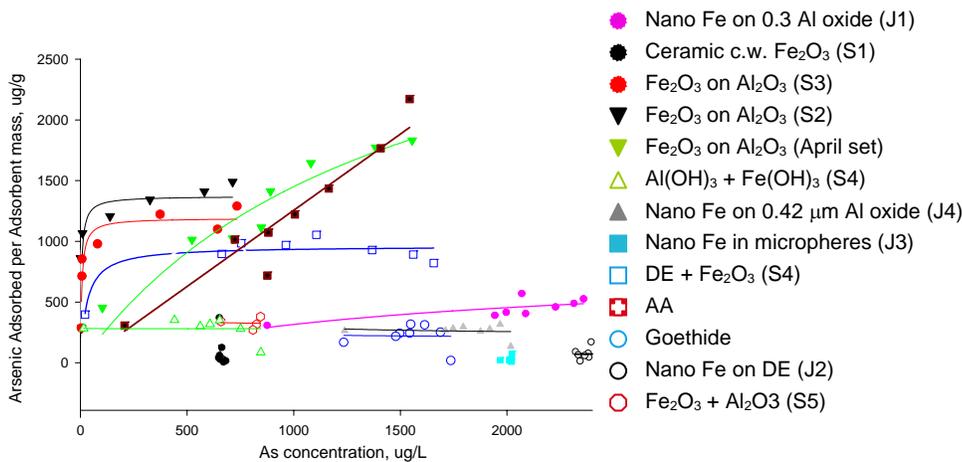


Figure 2b: Langmuir Adsorption Isotherms for all adsorbents

The numerical results of these approximations were summed up in Table 2 :

Table 2. Freundlich and Langmuir Approximation Model Coefficients
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	Results with Freundlich Approximation				Results with Langmuir Approximation		
	log (Kf)	1/n	n	R <sup>2</sup>	a'=Qo	1/b=b'	R <sup>2</sup>
Fe <sub>2</sub> O <sub>3</sub> on Al <sub>2</sub> O <sub>3</sub> (S2)	875.31	0.08	13.28	0.98	1,372.00	2.09E-01	0.42
Fe <sub>2</sub> O <sub>3</sub> on Al <sub>2</sub> O <sub>3</sub> (S3)	639.82	0.10	10.09	0.88	1,192.00	1.67E-01	0.63
AA	2.05	0.93	1.08	0.92	45,887,442.90	2.74E-08	0.91
Fe <sub>2</sub> O <sub>3</sub> on Al <sub>2</sub> O <sub>3</sub> (April set)	38.35	0.52	1.91	0.95	3,595.48	6.76E-04	0.91
DE+ Fe <sub>2</sub> O <sub>3</sub> on SiO <sub>2</sub>	227.53	0.20	4.99	0.85	960.54	3.42E-02	0.87

These isotherm curves showed a good adsorption potential for the following adsorbents listed in their order of efficiency from the most efficient to the least efficient:

Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (S2) > Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (S3) > DE+ Fe<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub> > Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (April set) > AA. The data for selected adsorbents other than those mentioned above were considered incomplete for a variety of reasons. It appears that in some cases not enough arsenic was absorbed, whereas in other cases it appears that none was absorbed. These ineffective adsorbents (at pH 8) included: ceramic spheres coated with Fe<sub>2</sub>O<sub>3</sub> (S1), Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub> (S5), nano Fe on DE (J2), nano Fe on microspheres (J3). Taking into consideration the cost of fabrication for the nanomaterials and miscellaneous items required, the use of the nano Fe on 0.3 um Al Oxide (J1), nano Fe on 0.42 um Al Oxide (J4) and Goethite were less efficient (at pH 8) when compared with : Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (S2, S3, April set), DE+Fe<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub> (S5) for removing arsenic.

The ability of ZVI for removing arsenic appear promising and the possibilities of using it as an arsenic removal treatment process also warrant further investigation.

**Column Studies:** The breakthrough of arsenic was expected to occur once 2000 bed volumes (BVs) had been filtered based on the work of Badruzzaman (2002). Breakthrough was expected to occur at 500 BV for iron nanoparticles coated on diatomaceous earth. DE coated with iron nanoparticles proved to be inefficient at the removal of arsenic as the breakthrough occurred very early (even before for the DE coated with hematite). The columns were not well operated as conditions such as pH were difficult to control.

**Assessment of ZVI:** The results of the ZVI's assessment (Freundlich Adsorption Isotherm) are shown in Figure 3. Previous studies (Lackovic et al. (2000), Su et al. (2001), and Farrell et al. (2001)) have shown that the arsenic removal mechanism is closely related to iron corrosion reactions. As expected prerusted ZVI (exposed to air) was an efficient arsenic remover. It appears that for a water at pH=8 (typical of groundwater), prerusted ZVI was more efficient and less expensive than many commercially available adsorbents previously tested. The ZVI isotherm adsorption curves showed a good adsorption potential for the following adsorbents listed in their order of efficiency from the most efficient to the least efficient:

Prerusted ZVI > Aired ZVI (Eh=152mV) > nitrogenized ZVI (Eh=82mV) > ZVI

One problem associated with the use of prerusted ZVI as an arsenic adsorbent is the possibility of iron leaching off and coloring the water. Nevertheless, prerusted ZVI could be very useful to facilities that had already installed an iron treatment system and were trying to get in compliance with the new arsenic regulations. Because of inconsistencies in the function of the Redox probe, no definitive conclusion could be made as to the tests performed in order to identify whether Eh or pH (or both) master variables had an influence on the adsorptive properties of ZVI. A more detailed and control study is required to assess the influence of pH and EH in terms of further understanding the adsorptive properties of iron oxides.

### Freundlich Adsorption Isotherm - ZVI

Logarithmic Scale

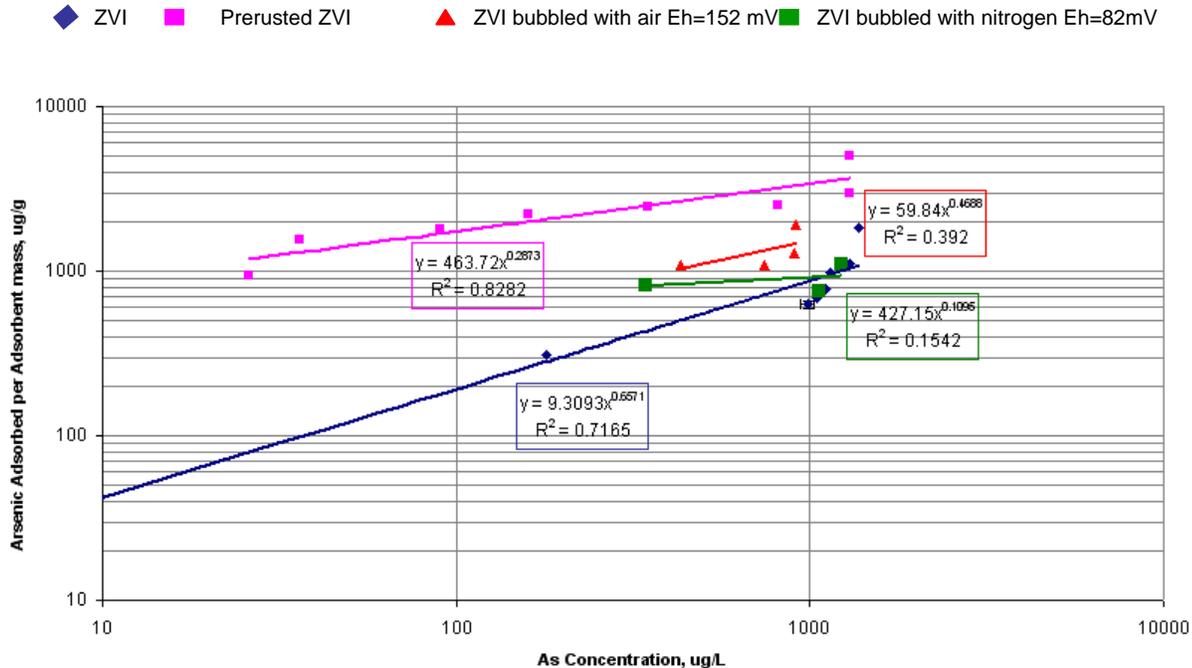


Figure 3: Freundlich Adsorption Isotherm of ZVI under different conditions

## Conclusions

The conclusion of the isotherm studies was that the materials, which combined DE technology and arsenic removal materials were not efficient at removing arsenic in water at pH=8. Some materials created by Seldon Technologies appeared to be more efficient at the removal of arsenic (Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (April set), Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (S2), Fe<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (S3)), whereas some appeared to be less efficient (ceramic spheres coated with Fe<sub>2</sub>O<sub>3</sub> (S1), Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub> (S5)). The remaining adsorbents tested appeared to provide average levels of efficiency.

The column studies showed that at pH=8 with an empty bed contact time (EBCT) of 2.5 to 5 min the DE coated materials were not very efficient. The prerusting of ZVI on the other hand appeared to be a very efficient and economical method for the removal of arsenic, despite the possibility of iron leaching, which could pose a problem for some water treatment facilities.

## Recommendations

DE coated materials warrant further study, especially under changing pH conditions of the effluent and the EBCT. The best way to integrate arsenic removal by ZVI to an existing water treatment plant should be researched in more detail.

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## Disclaimer

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