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Project Summary

The Equilibrium Arsenic Capacity of Activated Alumina

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Arsenic(V) can be effectively removed from water by adsorption onto activated alumina. Variables affecting the extent of adsorption include pH, temperature, and the presence of other ions in solution. Adsorption isotherms establishing a relation between solid and liquid phase arsenic concentrations at equilibrium can be developed by batch tests of 7 days or more. Despite the fact that batch tests exposed alumina to uncharacteristically high initial arsenic concentrations, the resulting capacities were close to those obtained by minicolumn tests that exposed alumina to low arsenic concentrations for 21 days.

Batch tests performed with granular Alcoa* F-1 type activated alumina (28 x 48 mesh) required as many as 7 days to reach an equilibrium solid phase loading of 13.5 mg As(V)/g at a liquid phase concentration of 1.0 mg As(V)/L in an artificial ground water containing 266 mg Cl^-/L and 367 mg SO_4^{2-}/L (pH 6, 25°C). Minicolumn tests performed under similar conditions obtained a solid phase loading of 16.1 mg As(V)/g alumina at 1.0 mg As(V)/L, but they yielded results identical to the batch tests at equilibrium liquid phase concentrations less than 0.50 mg As(V)/L. These results verified the feasibility of batch tests for modeling column capacities in that range.

Minicolumn tests showed As(V) adsorption to be extremely dependent on pH, as expected, since the latter determines both the surface charge on the alumina and the valence of the arsenate. Maximum adsorption occurred at pH 6. Increased temperature resulted in increased adsorption, as batch tests performed at 40°C yielded As(V) solid phase loadings 33 percent higher (at 1.0 mg As(V)/L) than tests performed at 25°C. This increased adsorption was attributed to kinetic rather than energetic considerations. Arsenic adsorption from pH 6.0 deionized water reached a maximum loading of 25 mg As(V)/g alumina at 1.0 mg As(V)/L, which decreased by over 50 percent in the presence of 720 mg SO_4^{2-}/L and 16 percent in the presence of 532 mg Cl^-/L. These decreases were greater than expected on the basis of previous experiments with fluoride adsorption onto the same type of alumina.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Arsenic is a natural constituent of a significant percent of the world's surface and ground water. In several areas, arsenic contamination of water supplies has been reported at levels as high as 10 mg/L — far in excess of the 0.05 mg/L maximum contaminant level (MCL) set by the U.S. Environmental Protection Agency (EPA). When arsenic is present in surface water, it is usually removed by conventional water treatment methods, including lime softening and filtration, or coagulation by alum or ferric sulfate. But where communities rely on untreated well water containing arsenic for their water supply, treatment for arsenic contamination removal must be considered. For the treatment of well water, a packed bed process is generally preferred; and one of the most promising column media for arsenic removal is activated

*Mention of trade names or commercial products does not contitute endorsement or recommendation for use.

alumina, which has been used successfully in this manner to remove fluoride.

This study of arsenic removal by adsorption onto activated alumina was designed to accomplish the following objectives:

1. To determine the capacity of activated alumina for As(V) by both batch and column methods, and to compare the isotherms thus obtained.
2. To determine the optimum pH for adsorption of As(V) onto activated alumina.
3. To determine the effect of competition by chloride and sulfate ions on the adsorption of As(V) onto activated alumina.

The work was undertaken as laboratory support for future pilot-scale studies to be performed in the University of Houston/EPA Mobile Drinking Water Treatment Research Facility.

Materials and Methods

Alcoa F-1 type granular activated alumina used in the experiments was manually screened to a mesh size of 28 x 48 and conditioned with two cycles of 1 percent NaOH and 1 percent H_2SO_4, with 80 bed volumes of each solution passed through the conditioning column for each cycle. Conditioned alumina was exhaustively rinsed with deionized water to pH 5.0. The As(V) solutions were prepared with reagent grade KH_2AsO_4. Except for tests of adsorption from deionized water, all arsenic solutions contained total anion concentrations of 15 meq/L made up of chloride, bicarbonate, and sulfate ions at the concentrations specified in Table 1. Graphite furnace atomic absorption spectroscopy was used to determine arsenic, with $Ni(NO_3)_2$ added to prevent premature volatilization. Three different arsenic sources — As_2O_3, KH_2AsO_4, and a purchased standard — were used for standardization and cross-checking.

Batch Tests

In the batch tests, identical volumes and concentrations of arsenic in solution were exposed to different quantities of activated alumina. The control contained only arsenic solution, without alumina. final arsenic concentrations were determined, and the difference between batch-test and control final concentrations was attributed to adsorption of arsenic onto activated alumina.

The procedure for batch tests was as follows:

1. Aliquots (150-ml) of 5.0-mg As(V)/L solution were pipetted into 200-ml glass bottles along with measured quantities (10 to 500 mg) of granular activated alumina (28x48 mesh).
2. Bottles were capped and placed on an Eberback shaker operating at 140 5-cm excursions/min.
3. After shaking, the bottles were removed and their contents were decanted and filtered through a 0.45-μm Millipore filter.
4. Each concentration of alumina was tested in duplicate. All samples were analyzed for arsenic concentration and pH, and the results were recorded.

Column Tests

Column tests to determine the equilibrium loading of As(V) onto activated alumina consisted of passing an As(V) solution through glass minicolumns containing fixed amounts of activated alumina until the effluent concentration reached 90 percent of the influent concentration — that is, until As(V) removal was reduced to < 10 percent. Control columns containing no alumina were included for each arsenic concentration and pH tested. Arsenic removed was determined as the difference between the arsenic in the influent and that in the total effluent collected. The arsenic loading on the alumina was calculated by dividing the total weight of As(V) removed by the weight of alumina in the column. A diagram of the column apparatus appears in Figure 1.

Operation of the columns included regular sampling, repeated preparation of influent solution, and measurement and sampling of collected effluent. In addition, alumina in the minicolumns was periodically reclassified (broken up) by inversion to prevent the channeling and cementation that occurred in the upper layers of the column.

Results and Discussion

Equilibrium

Figure 2 compares As(V) isotherms developed from batch tests conducted under similar conditions for different lengths of time. As can be seen, the isotherm representing results of the 14-day batch tests indicates significantly greater adsorption at each liquid phase concentration than does that for either the 1- or 2-day tests. On the other hand, isotherms obtained by 7- and 14-day tests appear to be in close agreement, indicating that most of the various concentrations of alumina had reached equilibrium with the liquid phase arsenic within 7 days at 40°C.

Furthermore, a comparison of equilibrium isotherms derived under similar conditions from batch tests and column tests (Figure 3) indicates that the results obained by these two methods agree very well at liquid phase concentrations of less than 0.50 mg As(V)/L. Above that concentration, however, the column isotherm predicts solid phase loadings progressively higher than those obtained by the 7-day batch tests.

One explanation for this divergence is suggested by Figure 2, which indicates greater deviation between the 7- and 14-day isotherms at higher liquid phase arsenic concentrations. This result implies that the higher loadings achieved by the column method might be obtained by batch tests performed for some period of time longer than 7 days. Nevertheless, the batch method seems adequate for

Table 1. *Make-Up of Artificial Ground Water for Use in Arsenic (III) and Arsenic (V) Adsorption Experiments*

	pH 4 to 6		pH 7 to 10	
Ions	*mg/L*	*meq/L*	*mg/L*	*meq/L*
Cations:				
Na^+	345	15	345	15
Anions:				
Cl^-	266.2	7.5	177.5	5
HCO_3^-	---	---	305	5
SO_4^{2-}	367.5	7.5	240	5
Total Dissolved Solids	978.7	---	1067 5	---

Total concentration of ions: C_T = 15 meq/L = 0.015 N
Ionic strength of pH 4 to 6 solutions: I = 0.0263 M
Ionic strength of pH 7 to 10 solutions: I = 0.0225 M

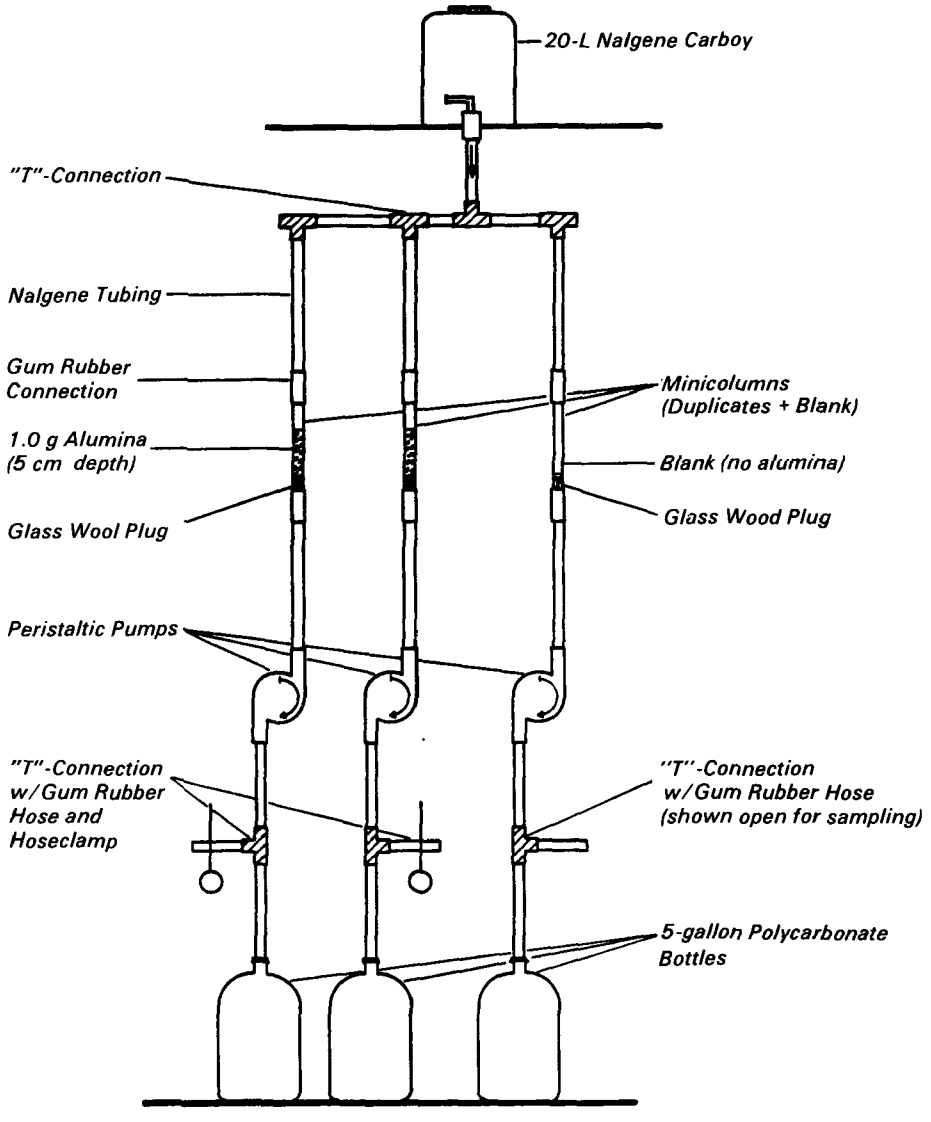

Figure 1. *Minicolumn apparatus for arsenic(V) adsorption onto alumina by the column method.*

predicting column capacity in the low range (< 0.50 mg/L) of arsenic concentrations likely to be encountered in contaminated ground water.

Data from the column tests used to determine the equilibrium isotherm in Figure 3 are plotted on a log-log scale in Figure 4 according to the linearized form of the Freundlich equation with a correlation coefficient (r^2) of 0.9982. Constants derived from this plot by the slope-intercept method yield a Freundlich equation such that

$$q_e = 16.2\ C_e^{(0.43)}$$

where q_e and C_e are the solid (mg/g) and liquid phase (mg/L equilibrium As(V) concentrations, respectively.

The Freundlich model, which fits the data better than the Langmuir model, allows for both heterogeneous adsorption site energies and multilayer adsorption. Although the isotherms obtained at pH 8 (Figure 2) have a shape more characteristic of the BET isotherm model, saturation concentration was not obtained at pH 6 in the column test results shown in Figure 3. Determination of such a saturation concentration at optimum pH may be considered an area for further study.

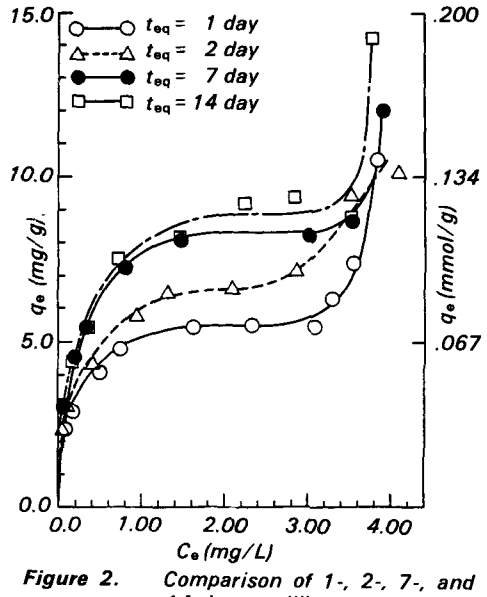

Figure 2. *Comparison of 1-, 2-, 7-, and 14-day equilibrium isotherms for adsorption of arsenic(V) onto activated alumina.*

(T = 40°C; C_o = 5 mg As(V)/L; pH = 8; TDS = 1067 mg/L; Cl^- = 5 meq/L; HCO_3^- = 5 meq/L; SO_4^{2-} = 5 meq/L)

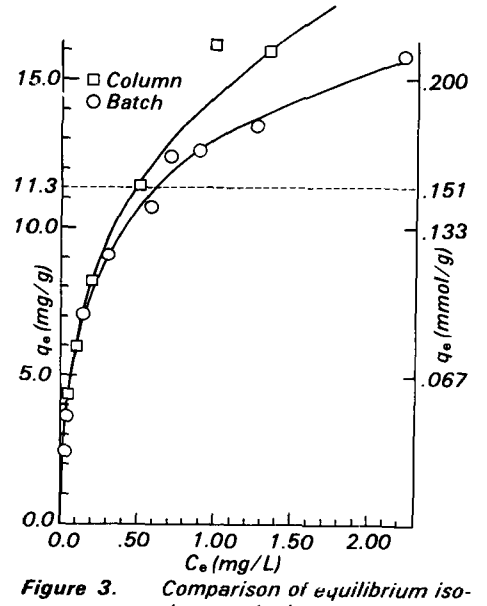

Figure 3. *Comparison of equilibrium isotherms obtained by batch and column methods at optimum pH.*

(T = 25°C; pH = 6; TDS = 979 mg/L; Cl^- = 7.5 meq/L; SO_4^{2-} = 7.5 meq/L)

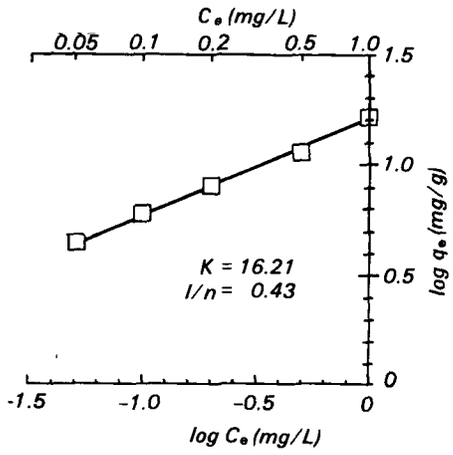

Figure 4. *Linearized Freundlich isotherm for adsorption of arsenic(V) onto activated alumina by column method at 25 °C.*

(pH = 6; TDS = 979 mg/L; Cl^- = 7.5 meq/L; SO_4^{2-} = 7.5 meq/L)

Arsenic Adsorption and pH

An optimum pH for adsorption of As(V) onto activated alumina was found at pH 6, as indicated in Figure 5. These results are similar to those obtained for fluoride and arsenic by other researches. At pH > 6.0, the alumina becomes progressively less positively charged; at pH < 6.0, the anions from the acids added to lower the pH compete with the arsenate anion for adsorption sites.

Arsenic Adsorption and Temperature

Isotherms for adsorption of As(V) onto activated alumina at two different temperatures are presented in Figure 6. As can be seen arsenic adsorption increased when the temperature of the batch tests was raised from 25° to 40°C. This result appears to contradict the prevailing assumption that adsorption is an exothermic reaction, since an increase in temperature would then tend to drive the reaction in the direction of desorption from the solid phase.

One explanation for this apparent anomaly, however, is that a higher temperature could increase the rate of diffusion into the solid phase and thus increase the solid phase loading at a given pH and time to equilibrium. This hypothesis agrees with the findings of both batch and minicolumn tests — that the adsorption reaction was largely controlled by kinetic constraints.

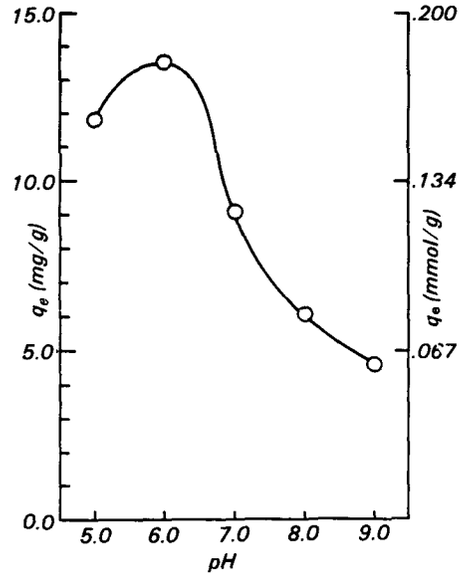

Figure 5. *Effect of pH on adsorption of arsenic(V) onto activated alumina by column method.*

(C_o = 1 mg As(V)/L; TDS = 979 [pH 5.6], and 1067 mg/L [pH 7-9])

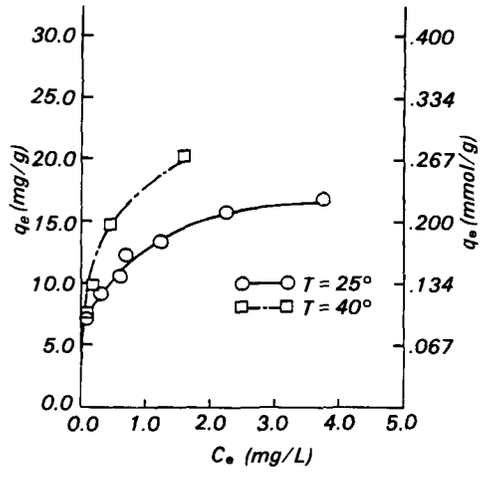

Figure 6. *Effect of temperature on adsorption of arsenic(V) onto activated alumina by batch method.*

(C_o = 5 mg AS(V)/L; pH = 6; TDS = 979 mg/L; Cl^- = 7.5 meq/L; SO_4^{2-} = 7.5 meq/L; t_{eq} = 7 days)

Arsenic Adsorption and Ion Competition

Figure 7 compares equilibrium isotherms for adsorption of As(V) onto activated alumina with those of solutions containing different concentrations of competing anions. It indicates that arsenic adsorption is significantly reduced in the presence of chloride and sulfate. At an equilibrium concentration of 1.0 mg As(V)/L in the liquid phase, solid phase loading was reduced by 16 percent in the presence of 532 mg Cl^-/L (15 meq/L), and by more than 50 percent in the presence of 720 mg SO_4^{2-}/L (15 meq/L), as compared with adsorption from deionized water. Similarly, in an artificial ground water composed of 7.5 meq/L each of chloride and sulfate, adsorption was reduced by more than 40 percent.

These results agree with the proposed selectivity sequence for competitive adsorption onto activated alumina, which predicts a greater reduction from sulfate competition than from chloride competition. However, the sensitivity of As(V) adsorption to competition from chloride ions was greater than that expected on the basis of previous work with fluoride adsorption onto the same type of alumina.

The full report was submitted in fulfillment of Cooperative Agreement No. CR-807939-02 by the University of Houston under the sponsorship of the U.S. Environmental Protection Agency.

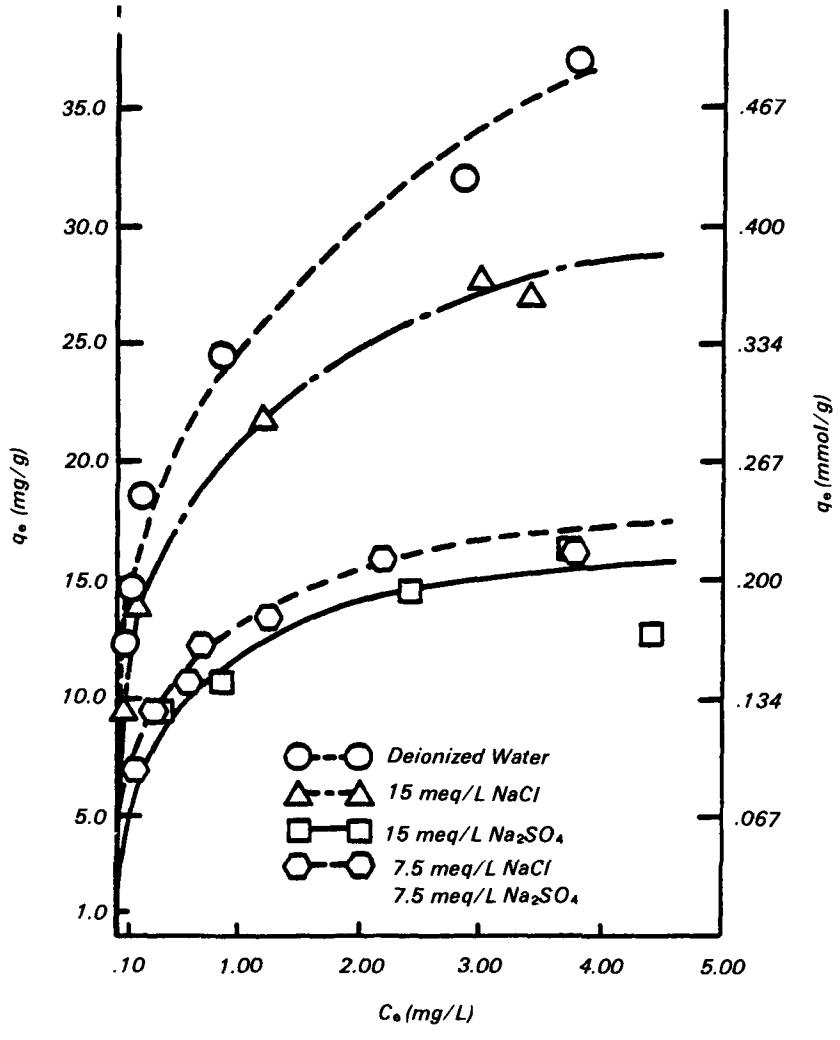

Figure 7. *Effect of competition by chloride and sulfate ions on adsorption of arsenic(V) onto activated alumina.*

($T = 25°C$, $C_o = 5$ mg AS(V)/L; pH = 6; $t_{eq} = 7$ days)

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Tom Sorg *is the EPA Project Officer (see below).*
The complete report, entitled "The Equilibrium Arsenic Capacity of Activated Alumina," (Order No. PB 84 110 527; Cost: $11.50, subject to change) will be available only from:

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