

Drinking Water Purification for U.S.A.-Mexico Border Region

Final Report submitted to WRRI, New Mexico State University

by

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September 29, 2008

1. INTRODUCTION

Fluoride is a naturally occurring element present in the environment. It is released to the air from naturally fluoride-containing substances, such as coal, minerals, and clays, when they are heated to high temperatures in coal-fired power plants; aluminum smelters; phosphate fertilizer plants; glass, brick, and tile works; and plastics factories. Relative small amounts of fluoride are also present in water, air, plants, and animals. Fluoride is being found beneficial in improving dental caries; therefore it is frequently added to drinking water supplies at approximate concentrations of 1mg/l (1 ppm). It has been found that when excess of fluoride is added to waters, it can results in denser bones and cause skeletal damage. The International Agency for Research on Cancer (IARC) has determined that the carcinogenicity of fluoride to humans is not classifiable. The EPA determined that the maximum amount of fluoride allowed in drinking water is 4.0 milligrams per liter (mg/L) (USDHHS, 2003).

Excess of fluoride in contaminated waters have been treated using precipitation, membrane and adsorption processes (Rongshu et al., 1995; Srimurali et al., 1998). Disadvantage of precipitation is the generation of unwanted chemicals and waste disposal problems. Membrane processes include reverse osmosis, nanofiltration, electrodialysis and donnan dialysis. Disadvantage of these techniques are low economic viability and maintenance cost. Adsorption on alumina, charcoal, ash, lime, clay minerals, and spent leaching earth is also being reported as inexpensive method of choice to obtain drinking water (Bhargava, 1997, Mahramanlioglu, 2002). Hybrid processes combining adsorption with donnan dialysis have also been developed (Sathish, 2007). Recently new materials have been used as adsorbents in the adsorption process, such as biomass, biopolymer chitosan, coconut shell carbon, laterite, aligned carbon nanotubes, and amorphous alumina supported on carbon nanotubes (Sathish, 2007; Sarkar et al., 2007). However, by using these materials, the lowest limit obtained for fluoride removal is greater than 2 mg/l and the majority of them require working at pH values relatively low, which are not suitable for drinking water (Tripathy, 2006). Activated alumina has also been studied to adsorb fluoride (Ku, 2002, Ghorai, 2004, Karthikeyan, 2004, Chauhan, 2007). Reports indicated that these processes are very highly pH dependent. More recently studies have been conducted on the use of modified activated alumina for the removal of fluoride from drinking water. Tripathy (2006) studied the ability of alum-impregnated activated alumina for the removal of fluoride and reported 99% adsorption capacity at pH 6.5.

In a recent work Deng et al. (2006) synthesized a novel sol-gel mesoporous activated alumina and conducted adsorption equilibrium and breakthrough studies to determine its fluoride adsorption capacity. The novel material was used to clean contaminated drinking water from wells in Columbus, NM and Palomas, Mexico. He reported promising adsorption properties with a fluoride diffusion time of $1.9 \times 10^{-5} \text{ s}^{-1}$. The present work presents results on the adsorption kinetics of fluoride by modifying the novel mesoporous activated alumina synthesized in previous work. CaO and MnO₂ were used as coated materials. Results are compared with two commercially alumina-based adsorbents.

2. METHODS

A. Preparation of stable boehmite sol adsorbent

Stable 1M boehmite sol (γ -ALOOH) was prepared following the Yoldas process (Yoldas, 1975) Initially, the sol was synthesized in a sol-gel granulation apparatus by dissolving drop-wise 454 ml of alumina-tri-secondary butoxide in one liter of deionized water at an initial temperature of 75°C. Double deionized water was used as the solvent for the prepared solutions. The solution was continuously and vigorously stirred during the dissolution process. After dissolution the solution was heating at 90°C for one hour and the resulting slurry containing γ -ALOOH precipitates was peptized with 70 ml of 1.0 M HNO₃ (Yoldas). The peptized sol was then refluxed at 90-100°C for 10 hours, to obtain a stable boehmite sol. Sol droplets were generated by drying a given amount of the boehmite sol in a pretty dish under air atmospheric conditions of 40°C and 60% humidity. Gelated spherical wet-gel was separated by dropping oil to the solution and adding ammonia. After that the wet gel particles were washed, dried and calcined at 450oC for 3 hours to obtain γ -ALOOH with specific pore size. Detailed description of the synthesis process is presented in previous publications (Deng, 1998; Buelna, 1999).

B. Mesoporous activated alumina surface modification

Two different approaches were used to modify the sol-gel derived mesoporous activated alumina adsorbent for fluoride adsorption: 1) Loading with CaO, and 2) Loading with MnO₂.

The procedure for loading with CaO consisted on preparing 1L of 3 M CaCl₂ solution by dissolving analytical grade CaCl₂ in deionized water. 5g of sol-gel alumina were then put into 100mL of 3M of CaCl₂ solution and the solution was shaken for 24 hours. The solution was then filtered and the coated adsorbent was dried in the oven and then calcined at 450°C for about 12 hours with a slow heating ramp (5°C/min).

The procedure for loading with MnO₂ consisted on poring a solution containing a mixture of 2.5M MnCl₂ (10 ml) and 0.1ml of 10M NaOH over 10 g of AA in a heat-resistant dish. The mixture was then heated to 150°C for about 5 hours in a furnace. Afterwards, the same mixture was again heated to 500°C for 3 hours, then cooled to room temperature and washed with distilled water 2–3 times.

C. Kinetic Studies

The fluoride adsorption uptake with respect to time was conducted on five different activated alumina-based adsorbents, namely Sol-gel derived Activated Alumina (AA), MnO₂ coated Sol-gel AA; CaO coated Sol-gel AA; ALCOA, H-156 (40wt% zeolite, 60wt% AA); ALCOA, and F-200 AA (20% SiO₂, 80% AA). Synthetic zeolite 5A, a non alumina-based adsorbent, was also included for comparison purposes. To conduct the experiment a 10,000 ppm stock fluoride solution was prepared by dissolving 22.11 grams of sodium fluoride reagent grade with double distilled water to complete one liter of solution. From the stock solution seven 150 ml-solutions with concentrations ranging

from 1 to 1000 ppm was prepared and pH was adjusted to 6.0 with 0.1 M NaOH. The prepared solutions were tightly closed and placed in a shaker for 48 hours at 100 RPM to ensure equilibrium. The changes of fluoride concentration were measured at the beginning of the process every 15 minutes, and then with increasing intervals of time.

The equipment used to quantify the amount of fluoride ions was the Accumet XL-25 (pH and ion meter). TISAB III was used as the total ionic strength adjustment buffer in a ratio of 10:1mL of solution and buffer respectively. 200 ml high density polypropylene plastic bottles were used to conduct the experiment.

3. RESULTS AND DISCUSSION

The amount of fluoride removed was calculated using a mass balance. The kinetic data was correlated using the following equation (Ruthven, 1984):

$$\frac{q(t)}{q_{\infty}} = 1 - \frac{6}{\pi^2} \exp\left(\frac{-\pi^2 D_c t}{r_c^2}\right) \quad (1)$$

Where q_t/q_{\max} represents the amount of fluoride adsorbed with respect to the total possible amount adsorbed during the experiment or the fractional approach to equilibrium, D_c/r_c^2 represents the fluoride diffusion time constant (s^{-1}), and D_c represents the effective diffusivity (cm^2/s) for the fluoride. The equation is valid for adsorption approaching equilibrium, with $q_t/q_{\max} > 70\%$.

The adsorption uptake curves for the adsorbent materials at each of the seven different concentrations studied are presented in Figure 1. From the graph it was shown that the modified MnO_2 activated alumina adsorbent has the better adsorption capacity for all the concentrations studied. However, the commercially AA adsorbents showed a superior adsorption with respect to the sol-gel AA. The behavior of the MnO_2 coated AA may be attributed to an increase in its surface area and therefore in the available sites for adsorption.

The plots of $\ln(1 - q_t/q_{\max})$ versus time for the adsorbents materials are presented in Figure 2. The linerized fits provided the data to calculate the fluoride diffusion time constants from equation 1. The results are presented in Table 1. Correlated R^2 -values are also included.

It was found that the average diffusion time constant for fluoride was in the order of 1.5×10^{-6} to $2.34 \times 10^{-6} s^{-1}$, with the lowest corresponding to MnO_2 coated activated alumina and the highest to commercial F-200 activated alumina. Synthetic zeolite 5A reported a D_c/r_c^2 value of $2.82 \times 10^{-6} s^{-1}$, which is the highest of all the adsorbents studied. Assuming a particle radius (r_c) of 1 mm, the effective diffusivity (D_c) for all the adsorbent materials was in the order of magnitude of 1.5×10^{-8} to $2.3 \times 10^{-8} (cm^2/s)$. The D_c value for synthetic zeolite 5A was $2.82 \times 10^{-8} cm^2/s$.

The effect of adsorbate concentration on the diffusion time constants for fluoride is presented in Figure 3. It is observed that the three adsorbents have a tendency to reduce the diffusion time constant by increasing the initial concentration, however at very high concentrations the constant increases. This is specially observed with the sol-gel AA adsorbent. This may suggest that the pores of the adsorbent get saturated as the concentration increases.

5. CONCLUSIONS

The following conclusions on the adsorption of fluoride by activated alumina based adsorbents can be drawn:

- The MnO₂ coated activated alumina has higher fluoride capacity than commercially available AA-based adsorbents.
- The CaO and MnO₂ modified AA are better adsorbents than pure activated alumina.
- The MnO₂ coated AA has the highest fluoride capacity and smallest diffusion time constant.
- The diffusivity of fluoride in activated alumina based adsorbents is in the order of magnitude of 1.5×10^{-8} to 2.3×10^{-8} cm²/s.

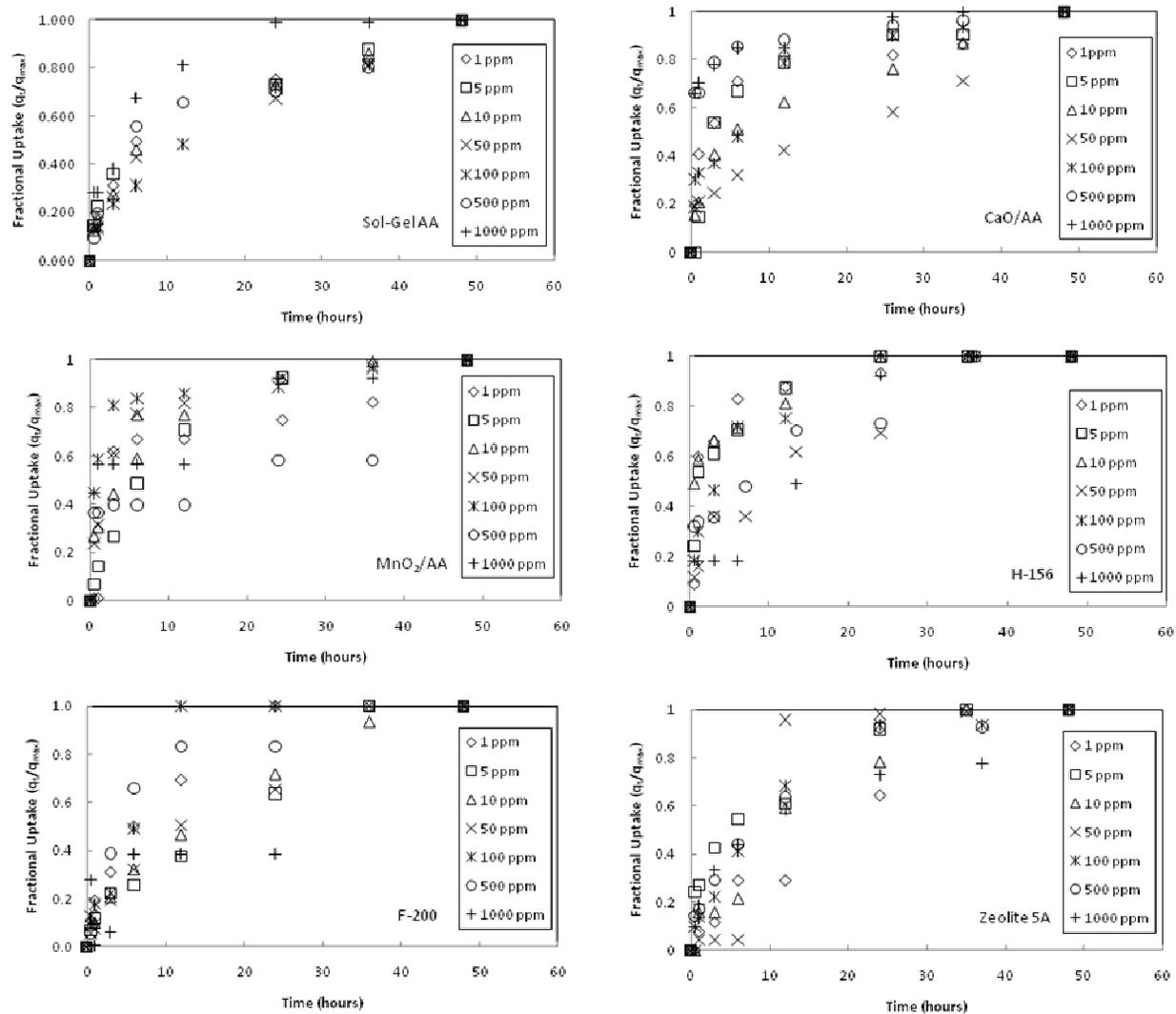


Figure 1. Adsorption uptake curves of fluoride on activated alumina-based adsorbents. Zeolite 5A is included for comparison purposes.

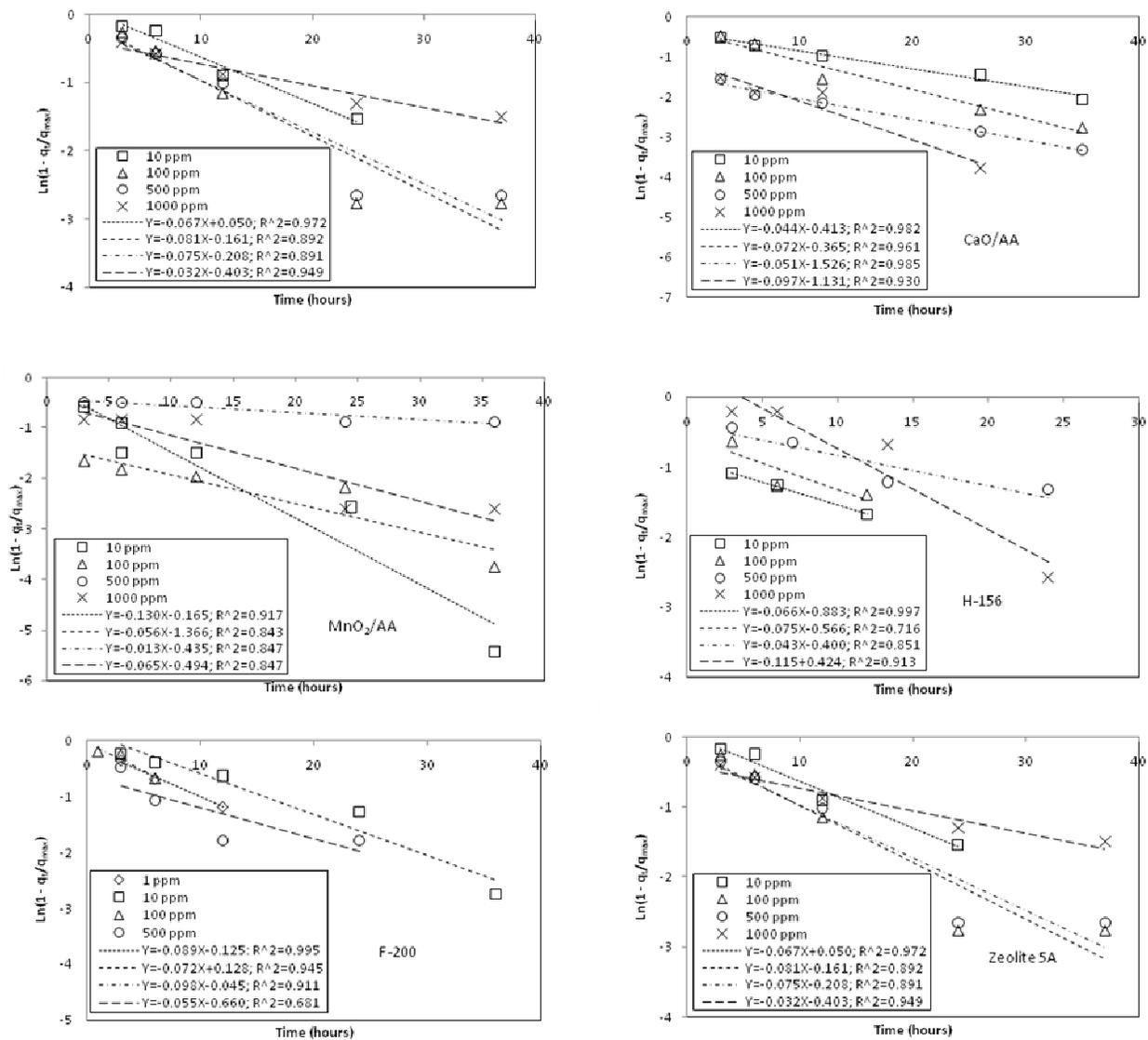


Figure 2. Linearized adsorption kinetic model for activated alumina-based adsorbents at different equilibrium concentrations. Zeolite 5A is included for comparison purposes.

Table 1. Fluoride diffusion time constants D_c/rc^2 (s^{-1}) and R^2 values for five activated alumina based adsorbent. Values for synthetic zeolite 5A are included for comparison purposes.

Sol-Gel AA	CaO/AA	MnO ₂ /AA	H-156	F-200	Zeolite 5A
<u>1.4 ppm</u> 1E-06 0.961	<u>1 ppm</u> 3.07E-06 0.748	<u>1.2 ppm</u> 4.59615E-07 0.963	<u>1 ppm</u> 2.98067E-06 0.898	<u>1 ppm</u> 3E-06 0.988	<u>1.5 ppm</u> 1.15857E-06 0.927
<u>4.5 ppm</u> 1.4E-06 0.982	<u>4.8 ppm</u> 1.88E-06 0.905	<u>5 ppm</u> 3.04E-06 0.998	<u>4.6 ppm</u> 3.60642E-06 0.991	<u>4.3 ppm</u> 1E-06 0.981	<u>4.8 ppm</u> 2.84605E-06 0.939
<u>9.6 ppm</u> 1.34E-06 0.983	<u>9.2 ppm</u> 1.23E-06 0.956	<u>10 ppm</u> 1.37E-06 0.917	<u>11 ppm</u> 1.86252E-06 0.997	<u>9.0 ppm</u> 2.05E-06 0.994	<u>11.5 ppm</u> 1.93945E-06 0.972
<u>48 ppm</u> 1.08346E-06 0.977	<u>46 ppm</u> 8.09E-07 0.966	<u>55 ppm</u> 1.8347E-06 0.984	<u>44 ppm</u> 1.48488E-06 0.903	<u>44 ppm</u> 1E-06 0.973	<u>56 ppm</u> 5.80239E-06 0.847
<u>140 ppm</u> 1.2609E-06 0.992	<u>95 ppm</u> 2.03E-06 0.965	<u>97 ppm</u> 5.51053E-07 0.843	<u>91 ppm</u> 2.13134E-06 0.716	<u>97 ppm</u> 2.64E-06 0.939	<u>109 ppm</u> 3.54173E-06 0.892
<u>513 ppm</u> 7E-07 0.865	<u>540 ppm</u> 1.73E-06 0.943	<u>520 ppm</u> 6.15155E-07 0.847	<u>548 ppm</u> 2.14952E-06 0.851	<u>497 ppm</u> 5.24E-06 0.988	<u>550 ppm</u> 3.32809E-06 0.891
<u>1053 ppm</u> 5.67E-06 0.970	<u>1116 ppm</u> 2.78E-06 0.853	<u>1033 ppm</u> 2.956E-06 0.847	<u>1180 ppm</u> 1.3831E-06 0.913	<u>1016 ppm</u> 1.45E-06 0.439	<u>1087 ppm</u> 1.11619E-06 0.949

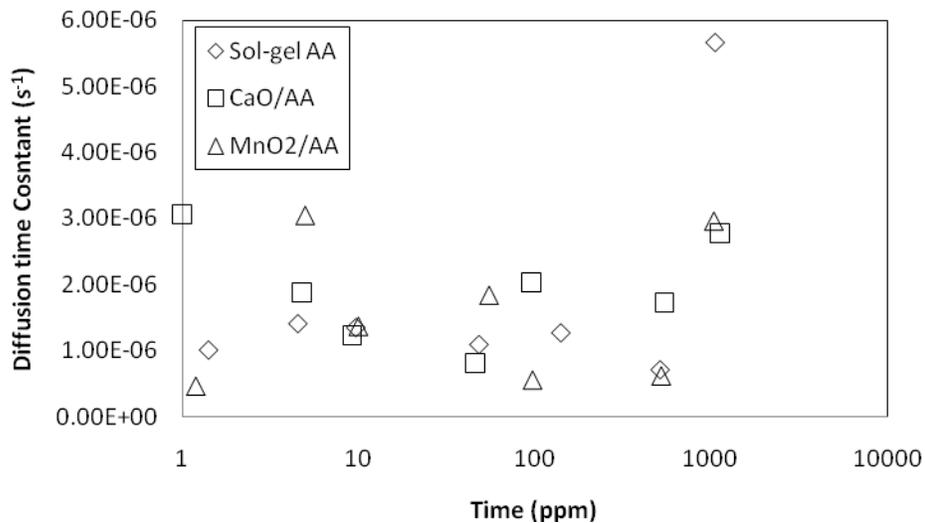


Figure 3. Effect of equilibrium concentration on diffusion time constant for coated AA and sol-gel

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6. ACKNOWLEDGEMENTS

This work was kindly supported by the Student Research Grant from WRII, New Mexico State University. The authors and their advisor greatly appreciate the continual supports from WRII and look forward to working with this organization in the near future.