

PILOT-SCALE STUDY ON ARSENIC REMOVAL WITH IRON-TAILORED ACTIVATED CARBON AND CARBON COUPLED WITH ZERO-VALENT IRON

Weifang Chen¹, Robert Parette², Fred S. Cannon² and Will Sheehan²

¹ 516 Jungong Rd. University of Shanghai Science and Technology, Shanghai, 200093 China

² 212 Sackett Building Department of Civil and Environmental Engineering Pennsylvania State University University Park, 16802 US

Introduction

Arsenic in drinking water is of environmental concern because it is a carcinogen. A new arsenic limit of 10 ppb became effective in 2006 for United States drinking water systems. This new regulation would make small public water facilities face heavy financial burdens, unless less costly methods of arsenic removal are developed.

Zero-valent iron (ZVI) for removing arsenic has attracted much attention in recent years [1,2]. The main issue with ZVI application is that when a ZVI filter is used alone, the unit clogs with iron oxides, and excessive iron may exit from the unit. Therefore, several studies have appraised whether zero valent iron can be solubilized and the resulting As-laden iron-hydroxide colloids be caught in a down stream filter [3,4].

The main objective of the research was to develop an arsenic removal system that couples the high pore volume, structural cohesiveness, and low costs of granular activated carbon (GAC) with the arsenic-sorbing propensity and low cost of iron.

Experimental

Pilot columns were produced from 5' long sections of nominal 3" schedule 80 clear PVC pipes (inside diameter of 2.875"). A gravel and sand layer (each 2" in depth) were installed first to prevent the activated carbon from exiting the bottom of the bed. Activated carbon with a bed depth of 3'4" was then added atop the sand. These tests employed a total 11 pilot columns. Each pilot column was installed with about 1.9-2.2 kg of either virgin or iron-tailored activated carbon.

Specifically, column #1 was the control column with virgin AquaCarb. In column #2, 0.445 kg of steel mesh was placed atop a bed of virgin AquaCarb. Columns #3 and 4 were columns for iron-tailored AquaCarb with no ZVI for comparison. In Column #5, plain steel rods were used as the iron source and placed in the center and at the full length of the virgin carbon bed.

Columns #6 to #11 were GAC carbons with branched plain steel rods arranged in the first 2/3 of the carbon bed. This structure offered an iron source that was more evenly distributed across the carbon cross section. The carbon beds were 3 feet deep, while the branched rod systems were located in the top 2 feet of the bed. This design was aimed to use the last 1/3 of the carbon bed as a scavenger of the iron products,

and thus prevent iron leaking. The branched rods in column #6-10 had a diameter of 1/4" and the rods in Column #11 were 1/8" in diameter. The influent in column #8 was adjusted to pH 7.9-8.1, so as to test the effect of pH. For the other columns, the influent pH, without adjustment, was 7.1-7.4.

All of these pilot columns operated in the down-flow mode with an empty bed contact time of 5 min unless specified. Samples were taken every other day from the influent and effluent ports of the pilot columns. Arsenic analysis was via a Shimadzu atomic absorption spectrophotometer-hydride vapor generation system (AAS-HVG).

Results and Discussions

In designing RSSCT columns, it is necessary to assume a relationships between empty bed contact times (EBCTs) in the RSSCT column and in the full-scale bed. The RSSCTs in this research have been designed by assuming that proportional diffusivity would be proper for ions the size of arsenic species (such as AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^-).

Table 1 summarizes the bed volumes to 10 $\mu\text{g/L}$ breakthrough by tailored temperature in RSSCT and pilot columns.

Table 1. Bed volumes to 10 $\mu\text{g/L}$ As breakthrough in RSSCTs and pilot columns with iron tailored carbons.

Column type	Water source	Iron-tailoring temp (°C)	Typical % Fe	BV to 10 $\mu\text{g/L}$ As Break-through	BV to 10 $\mu\text{g/L}$ As BT (normalized to 12.4% Fe)
RSSCT	Rutland	60	12.4±0.4	26,200	26,200
RSSCT	Rutland	100	11.7±0.3	25,500	27,000
RSSCT	As-spiked Tap	60	12.4±0.4	28,200	28,200
RSSCT	As-spiked Tap	100	11.7±0.3	26,500	28,000
Pilot column	As-spiked Tap	60	11.0	22,600	25,500
Pilot column	As-spiked Tap	100	11.0	22,800	25,700

As shown in Table 1, bed volumes to breakthrough by RSSCTs were only slightly longer than those for pilot columns. This could be attributed in part to distinctions in iron content. The tailored carbons made for the pilot columns had an iron content around 11%; while those used in RSSCTs have had an iron content of 11.7-12.4%. When the BV data is normalized to a uniform iron content of 12.4% Fe, the pilot columns achieved BV to 10 $\mu\text{g/L}$ arsenic breakthrough that were just 10% lower than the counterpart values with RSSCTs (last column of Table 1). In light of this, the results indicate that the proportional diffusivity similitude offers quite a good match to operations with full-scale GAC grains.

Column #1 was operated with virgin AquaCarb and no ZVI, as a control. There was immediate arsenic breakthrough from this column, indicating that virgin activated carbon had

little adsorption for arsenic.

Although no arsenic was detected throughout the duration of the column #2 run (steel mesh upstream of virgin GAC), the back pressure in this column reached such a level that the operation was forced to be terminated prematurely at around 6000 bed volumes, since little water was able to pass through at this pressure. Besides the problem with back pressure, column #2 also released iron in the effluent that was continuously higher than 0.3 mg/L. This is problematic since the US secondary drinking water standard for iron is 0.3 mg/L.

In column #5, two plain steel rods were installed vertically throughout the length of the carbon bed. For comparison, in column # 6 to 11, a branched rod with the same mass was installed, but only within the first 2/3 of the bed. The rest 1/3 of the carbon bed was set aside as a scavenger bed for capturing the iron that leached out from corrosion. Table 2 summarizes the arsenic breakthrough results from these columns.

Table 2. Bed volumes to 10 µg/L As breakthrough in pilot columns with zero-valent iron rod and GAC.

Col	pH	carbon	EBCT	rod	BV to breakthrough
5	7.1-7.4	virgin AquaCarb	5	1/4" straight	29,500
6	7.1-7.4	iron-tailored AquaCarb	5	1/4" branched	43,000
7	7.1-7.4	virgin AquaCarb	5	1/4" branched	36,500
8	7.9-8.1	virgin AquaCarb	5	1/4" branched	31,100
9	7.1-7.4	HD4000	5	1/4" branched	36,700
10	7.1-7.4	iron-tailored AquaCarb	2.5	1/4" branched	35,000
11	7.1-7.4	iron-tailored AquaCarb	5	1/8" rod	51,900

As shown in Table 2, pilot column with iron-tailored AquaCarb + branched rod (column #6) did not have breakthrough until about 43,000 bed volumes, which was 6,500 bed volumes longer than that of virgin AquaCarb+ branched rod (column #7). This indicates that iron-tailored AquaCarb did play a significant role in adsorbing arsenic. Column #7 and #8 both contained virgin AquaCarb. The only difference was that the influent pH for column #8 was 0.5-1 units higher. As a result, column #8 had arsenic breakthrough at 31,100 bed volumes which was 5,400 bed volumes lower than that of column #7. This concurred with previous studies, which showed that in a pH range of 6-8, lower pH corresponded to higher iron's sorption of arsenate [5,6].

Column #6 and #10 were set up to evaluate the effect of EBCT. When EBCT changed from 5 to 2.5 min, bed volumes to 10 µg/L As breakthrough dropped from 43,000 to 35,000. Longer EBCT provides more time for arsenic to diffuse into the carbon's pore structure, thus the higher removal efficiency.

Column #7 and #9 used virgin AquaCarb and a more mesoporous HD4000 carbon respectively. There was no significant difference in arsenic breakthrough with these two

columns. It appeared that the type of carbon used may not be a significant factor in the arsenic removal when excessive amount of iron was available. Column #11 employed smaller rods to increase the surface exposed for corrosion. The surface area of the iron rods were more than 3 time that of all the other columns. The BV to 10 µg/L As breakthrough increased from 43,000 bed volumes to about 51,900.

Iron concentrations in effluent were monitored for all the columns. For all the columns where the rods resided within the top 2/3 of the beds (columns #6-11), effluent iron continuously remained under 0.2 mg/L for the duration of the operation.

Conclusions

Pilot-scale studies appraised arsenic removal via technologies that Penn State had developed in rapid small-scale column tests (RSSCTs). The pilot units address scale-up issues for full-scale application. The results indicated that arsenic removal by a system of ZVI plus iron-tailored GAC showed great promise for practical applications. The best performance was achieved when zero-valent iron worked together with GAC that had been tailored by an iron-salt evaporation method. The most favorable column was able to operate for 51,900 bed volumes before 10 µg/L As breakthrough, with no adverse pressure buildup. Iron-tailored carbon played a significant role in scrubbing arsenic from the water and extended the bed life. In addition, iron concentration was kept under 0.2 mg/L when the bottom third of the GAC bed was used as a scavenger for the colloidal iron.

Pilot scales studies were further compared with results from RSSCTs. The similarity in arsenic breakthrough curves between these two systems serves to prove that it is appropriate to assume proportional diffusivity for arsenate removal in RSSCT design.

References:

- [1] Biterna, M., Arditsoglou, A., Tsikouras, E., Voutsas, D. (2007) Arsenate removal by zero valent iron: batch and column test. *Journal of Hazardous Materials* 149, 548-552.
- [2] Beak, D.G., Wilkin, R.T. (2009) Performance of a zero valent iron reactive barrier for the treatment of arsenic in groundwater: Part 2. Geochemical modeling and solid phase studies. *Journal of Contaminant Hydrology*, 106, 15-28
- [3] Carabantea, I., Grahna, M., Holmgrena, A., Kumpieneb, J. and Hedlunda, J. (2009) Adsorption of As (V) on iron oxide nanoparticle films studied by in situ ATR-FTIR spectroscopy. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 346,106-113.
- [4] Gu, Z. M., Fang, J., and Deng, B. L. (2005) Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Environmental Science & Technology*, 39(10), 3833-3843.
- [5] Chen, W.F., R.B. Parette, F.S. Cannon, B.A. Dempsey. (2008) Arsenic Adsorption via Iron-Preloaded Activated Carbon and Zero-valent Iron. *Journal American Water Works Assoc.* 100 (8) pp. 96-105.
- [6] Jang, M.; W.F. Chen, F.S. Cannon. (2008) Preloading hydrous ferric oxide into granular activated carbon for arsenic removal. *Environmental Science and Technology* ,42, 3369-3374.