

# Combined hydrous ferric oxide and quaternary ammonium surfactant tailoring of granular activated carbon for concurrent arsenate and perchlorate removal

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## Introduction

Arsenic in groundwater causes serious toxicity and potential health risks for human beings and other living organisms. Arsenic is a highly toxic metalloid that is now regulated at 10 ppb by the US Environmental Protection Agency (USEPA); and the World Health Organization (WHO) recommends the same standard. Arsenic contamination of drinking water has adversely affected about 40–60% of the Bangladesh population (i.e. 60–80 million affected people); and many in West Bengal, India (Goldberg and Johnston, 2001). Also, perchlorate ( $\text{ClO}_4^-$ ) has contaminated numerous U. S. water sources since it has been used in rocket fuels. Perchlorate has been shown to inhibit iodide uptake by the thyroid gland; and in large doses, it has been linked to anemia and fetal brain damage (Li et al., 2001). Even though there is no nationally established drinking water standard for perchlorate, Texas and California have taken the initiative to establish 4–6 ppb as statewide standards and/or action levels; and Massachusetts has also adopted an even lower standard.

A few groundwaters in southern California and Arizona are contaminated by both arsenic and perchlorate species; and the work herein appraised whether both species could be removed concurrently by a novel dual media. Virgin activated carbon is a relatively ineffective adsorbent for removing either perchlorate or arsenic. Indeed, when employing mere lignite activated carbon, perchlorate breakthrough to 6 mg/L occurred within 1100 bed volumes (BVs) when the influent native water contained 60 mg/L perchlorate (Parette and Cannon, 2005). Moreover, mere lignite activated carbon yielded arsenic breakthrough within 100 BV (Chen et al., 2007). As a novel concept, the authors have devised a protocol for sequentially implanting both amorphous hydrous ferric oxide (HFO) and quaternary ammonium surfactants into the pores of activated carbon so as to create a sorptive material that in an engineered system could concurrently sorb both arsenic and perchlorate. The HFO removed arsenate or arsenite, but not perchlorate; while the quaternary ammonium removed

perchlorate but not arsenic. The co-sorption of two anionic oxyanions via distinct mechanisms has yielded intriguing phenomena.

Hydrous ferric oxide (HFO) has been extensively studied as a promising adsorptive material for removing both arsenate and arsenite from the aqueous phase due to its high iso-electric point (IEP 8.1), high surface area, and selectivity for arsenic species (Dixit and Hering, 2003; Raven et al., 1998; Jang et al., 2006). Jang et al. (2008) achieved iron preloading by means of an incipient wetness impregnation protocol, and observed that when this media was cured at 60 °C, the media removed arsenic better than did preloaded iron that was cured at 80 °C. As per X-ray diffraction analyses and arsenic sorption tests at varied pH, Jang et al. (2008) found that the Fe oxy/hydroxide that was cured at 60 °C exhibited the amorphous characteristics of hydrous ferric oxide; whereas the media cured at 80 or 90 °C exhibited partly crystallized characteristics.

The authors herein employed incipient wetness iron loading with 60 °C curing; and then followed this with postimpregnation of a cationic surfactant. Specifically, we used the quaternary ammonium surfactants Arquad 2C-75 or cetylpyridinium chloride (CPC); and we loaded these into the iron-tailored carbon via either incipient wetness or a recirculation impregnation method. Cationic surfactants are found in a variety of everyday products including personal care products and mouthwash. The Arquad 2C-75 contains a quaternary ammonium functional group, which is composed of a positively charged central nitrogen atom with 4 bonds to carbon atoms. We also used a pyridinium surfactant (CPC); and the pyridinium is within the category of quaternary ammoniums. Quaternary ammonium-based compounds have a high pKa, rendering the positive charge virtually independent of pH in natural waters. Studies have shown that cationic surfactants could also greatly increase the removal of ClO<sub>4</sub><sup>-</sup>, nitrate and chromate in ultrafiltration processes (Gzara and Dhabbi, 2001; Yoon et al., 2003; Morel et al., 1991).

Several researchers have observed that cationic functional groups on polymers aid the diffusion of anions through positively charged media via the Donnan effect; and this has been particularly cited relative to membrane phenomena. For example, Cumbal and SenGupta (2005) revealed that cationic functional groups on the surface of a membrane can attract negatively charged species such as arsenate or arsenite; and the membrane can thereby concentrate arsenic species in the pore phase. The Donnan effect can be defined as the behavior of charged particles failing to distribute evenly across the two

sides of the membrane due to the presence of differently charged substances (Cumbal and SenGupta, 2005; Beolchini et al., 2006; Puttamraju and SenGupta, 2006). These differently charged substances cannot pass through the membrane; and they thus create an uneven electrical charge.

For the work herein, activated carbon was used as a hosting material for these cationic surfactants; and the arsenate sorption behavior revealed that this media achieved a similar Donnan effect enhancement of anionic arsenic diffusion through activated carbon pores, as discussed below.

The work herein has built on earlier work by our team, where cationic surfactants were preloaded onto activated carbon to remove perchlorate ( $\text{ClO}_4^-$ ) from groundwater (Parette and Cannon, 2005; Parette et al., 2005). The removal mechanism of perchlorate with cationic surfactants is likely based on ion exchange. This is different from the surface complexation mechanism that has been invoked for explaining arsenic sorption onto iron (hydr)oxide (Jackson and Miller, 2000).

The significance of this distinction was observed during preliminary Penn State tests, where we preloaded cetyl trimethyl ammonium chloride (CTAC) onto activated carbon, and then monitored arsenic removal through this media. This RSSCT employed Penn State University groundwater that was spiked with 150–220 ppb arsenate. Within 100 BVs, arsenic had broken through; and this was nearly the same result as for virgin activated carbon that was not preloaded with CTAC (data not shown herein).

However, the same activated carbon, when loaded with CTAC, CPC, or Arquad 2C-75, exhibited excellent perchlorate removal, out to 30,000–35,000 BV for a natural water from Redlands, CA that contained 60 ppb perchlorate (Parette and Cannon, 2005). These three quaternary ammonium surfactants offered better perchlorate removal than did other quaternary ammonium surfactants. A small proportion (<10%) of the quaternary ammonium surfactant could bleed off of this GAC, and was fully resorbed by a polishing bed of subsequent conventional GAC.

### Diffusion rates as discerned by differential column batch reactors

As discussed above and below, the authors hypothesized that the arsenate diffusion rate would be affected by the Donnan phenomenon. Diffusion rates can be appraised via differential column batch reactors (DCBRs); and these were used herein. Specifically, for arsenic kinetic results, a pseudo-second-order

kinetic equation was found to fit well for many chemi-sorption processes using heterogeneous materials (Reddad et al., 2002). Therefore, all of the kinetic data from our experiments were fitted with a pseudo-second-order kinetic model in estimating the rate constants, initial sorption rates, diffusivities, and adsorption capacities for total arsenic. Ho and McKay (1998a–c) described the pseudo-second-order kinetic rate model, which can be solved with the following equations:

*Please refer to the full text*

Where  $q_{eq}$  is the sorption capacity at equilibrium,  $q$  is the solid phase loading of arsenic. The  $k_2$  ( $g\ mmol^{-1}\ min^{-1}$ ) is the pseudo-second order rate constant for the kinetic model. By integrating Eq. (1) with the boundary conditions of  $q = 0$  (at  $t = 0$ ) and  $q = q_t$  (at  $t = t$ ), the following linear equation can be obtained:

*Full text is available at :*

<http://www.ncbi.nlm.nih.gov/pubmed/19476961>

<http://www.sciencedirect.com/science/article/pii/S0043135409002668>