Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Arsenate Removal by Iron (Hydr)Oxide Modified Granulated Activated Carbon: Modeling Arsenate Breakthrough with the Pore Surface Diffusion Model

Kiril D. Hristovski[a]; Paul K. Westerhoff[a]; John C. Crittenden[a]; Larry W. Olson[b]
[a] Department of Civil and Environmental Engineering, Arizona State University, Tempe, AZ, USA [b] Environmental Technology, Arizona State University at the Polytechnic Campus, South Williams Campus Loop West, Mesa, AZ, USA

To cite this Article Hristovski, Kiril D. , Westerhoff, Paul K. , Crittenden, John C. and Olson, Larry W.(2008) 'Arsenate Removal by Iron (Hydr)Oxide Modified Granulated Activated Carbon: Modeling Arsenate Breakthrough with the Pore Surface Diffusion Model', Separation Science and Technology, 43: 11, 3154 — 3167

To link to this Article: DOI: 10.1080/01496390802221691

URL: http://dx.doi.org/10.1080/01496390802221691

Separation Science and Technology, 43: 3154–3167, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802221691

Taylor & Francis
Taylor & Francis Group

Arsenate Removal by Iron (Hydr)Oxide Modified Granulated Activated Carbon: Modeling Arsenate Breakthrough with the Pore Surface Diffusion Model

Kiril D. Hristovski,[1] Paul K. Westerhoff,[1] John C. Crittenden,[1] and Larry W. Olson[2]
[1]Department of Civil and Environmental Engineering, Arizona State University, Tempe, AZ, USA
[2]Environmental Technology, Arizona State University at the Polytechnic Campus, South Williams Campus Loop West, Mesa, AZ, USA

Abstract: This study focuses on evaluating the feasibility of using pore surface diffusion model (PSDM) to successfully predict arsenate breakthrough curves of continuous flow packed columns containing granulated activated carbon modified with iron (hydr)oxide. Two different treatment methods were used to synthesize modified granulated activated carbon media (M-GAC): (i) Fe(III)/alcohol treatment method (M-3–15), and (ii) $KMnO_4$/Fe(II) treatment method (Mn-0.5–15). Adsorption capacities were obtained and fitted by Freundlich isotherm model ($q = K \times C_E^{1/n}$) for initial arsenate concentration of 120 µg As(V)/L at either $pH = 7.3 \pm 0.1$ for M-3–15 or $pH = 8.3 \pm 0.1$ for Mn-0.5–15 in 10 mM $NaHCO_3$ buffered ultrapure water. Short bed adsorber (SBA) columns tests were conducted at the same water quality condition as the batch experiments and used to validate the PSDM.

Keywords: Adsorption, arsenate, granulated activated carbon, iron (hydr)oxide, pore surface diffusion model

Received 10 December 2007; accepted 15 April 2008.

Address correspondence to Kiril D. Hristovski, Department of Civil and Environmental Engineering, Arizona State University, Box 5306, Tempe, AZ 85287-5306, USA. Tel.: +1 480-727-1291; Fax: +1 480-965-0557. E-mail: kiril.hristovski@asu.edu

INTRODUCTION

Arsenic is a commonly occurring Class A human carcinogen and toxic element in natural waters (1). As such, USEPA and other environmental and health agencies throughout the world have regulated its presence in drinking water by establishing a maximum contaminant limit (MCL) of 10 μg/L (2–4). However, this presence of arsenic in aquifers and drinking water has become an evolving concern in the last decade due to the need to develop new or modify the old technologies to achieve the treatment levels required by the new regulations.

Modified granulated activated carbon (M-GAC) with many metal (hydr)oxides have been evaluated as media to remove arsenic from water in many studies (5–8). However, use of the homogeneous surface diffusion model (HSDM) or pore surface diffusion model (PSDM), which have been initially developed for homogeneous media such as GAC, to simulate arsenate breakthrough of a packed-bed adsorbent column containing M-GAC has not been shown (9–14). Such models are useful because they provide mechanistic insight and predict capabilities using limited data (isotherms and/or small column tests) instead long duration pilot tests. The goal of the study was to evaluate the feasibility of using the pore surface diffusion model to successfully predict arsenate breakthrough curve of a continuous flow adsorber column packed with modified granulated activated carbon modified. To achieve the goal of the study several tasks had to be completed:

(i) synthesize modified granulated carbon using same amounts of GAC and iron;
(ii) characterize the media;
(iii) conduct isotherms experiments;
(iv) conduct short bed adsorber (SBA) column tests; and
(v) validate the PSDM using the experimental data and predict the performance of a full-scale system using validated PSDM.

EXPERIMENTAL APPROACH

Material Synthesis and Characterization

Lignite based GAC (HD-3000, US mesh 8 × 30, NORIT Americas Inc., USA) was impregnated with iron (hydr)oxide using two different chemical synthesis techniques. In the first technique, GAC is pretreated with $KMnO_4$ and then treated with Fe(II)/water solution to form ferric (hydr)oxide (15). In the second technique Fe(III) precipitates as iron (hydr)oxide under alkaline conditions. HD-3000 GAC was selected as base support material because of its macroporous structure, large pore volume, and low cost of lignite coal (16). Both M-GAC media were synthesized using solutions with same iron concentrations and same amount of virgin GAC.

In general, 50 g of air-dried GAC were mixed with 500 mL $KMnO_4$ in 1 L amber glass bottles with Teflon caps at 30 rpm with 0.5 N MnO_4^- and for a period of 15 minutes. Treated GAC was decanted and rinsed repeatedly with ultrapure water ($<1\,\mu S/cm$) until no purple color was observed. The pretreated resin was then contacted with 1 M solution of $FeSO_4 \times 7\ H_2O$ for a period of 6 hours to oxidize the Fe(II) and precipitate the iron (hydr)oxide. During Fe(II) oxidation by the oxidized forms of manganese (e.g. Mn^{4+}), H^+ is generated resulting in pH decrease. To remove excess protons and iron (hydr)oxide precipitate, the product was repeatedly rinsed and soaked overnight in a solution of 1% $NaHCO_3$ in distilled water, and stored wet. The synthesized media were termed Mn-0.5–15 M-GAC.

A modified form of a proprietary synthetic method, developed by SolmeteX, using a solution of anhydrous $FeCl_3$ in alcohol was used to synthesize the modified GAC by precipitation of Fe(III) as iron (hydr)oxide under alkaline conditions (17). Synthesis involved mixing of 50 g of air dried GAC (US mesh size 8 × 30) with 500 mL of 1 M Fe(III)/alcohol solution in 1 L amber glass bottles with Teflon caps at 30 rpm for a period of 15 minutes. The iron impregnated GAC was filtered under suction and than vigorously mixed with a 7.5% NaOH solution for 15 minutes to form a precipitate. The product was repeatedly rinsed with distilled water to lower the pH and remove excess precipitate. The synthesized media were termed M-3–15 M-GAC.

After the synthesis, all fabricated materials were air dried, crushed, and sieved using US mesh 40 × 60, and stored wet. The iron content of the synthesized materials was quantitatively determined by acid digestion in concentrated HNO_3 and 30% H_2O_2 (US EPA SWA 846, Method 3050B) followed by Flame-Atomic Absorption Spectroscopy analysis (Varian Spectra 50B) (18). Before the acid digestion, M-GAC media were powdered and dried at 104°C to constant mass to remove any moisture. Scanning Electron Microscope (SEM) techniques were employed to determine the size and shape of the crushed M-GAC particles (XL 30 by FEI). The densities and porosities of the synthesized media were evaluated following a procedure described in Sontheimer et al., (11).

Multi-Point Equilibrium Adsorption Experiments

In order to predict the arsenate breakthrough, the pore surface diffusion model (PSDM) requires Freundlich isotherm parameters as input to describe the adsorption capacity of the media. Therefore, multipoint equilibrium adsorption experiments were conducted at $\mathrm{pH} = 7.3 \pm 0.1$ and 8.3 ± 0.1 (Final pH values) for M-3–15 M-GAC and Mn-0.5–15 M-GAC, respectively. The batch experiments were conducted in 500 mL HDPE bottles (Nalgene) in the presence of 10 mM $\mathrm{NaHCO_3}$ buffered ultrapure water. The initial arsenate concentration was $\sim$ 120 µg/L As (V) and the adsorbent dosages were ranging between 0.09 and 3.5 g dry M-GAC/L. Samples were continuously agitated for 3 days prior to filtering the M-GAC media through 0.8 µm acetate membrane filter.

Isotherms were developed for arsenate adsorption and analyzed using the Freundlich adsorption isotherm model (Equation 1).

$$q = K \times C_E^{\frac{1}{n}} \tag{1}$$

Where q is adsorption capacity (µgAdsorbate/g Adsorbent), K is the Freundlich adsorption capacity parameter ((µg Adsorbate/g Adsorbent)$\times$ $(L/\mu\text{g Adsorbate})^{1/n}$), C_E is the equilibrium concentration of adsorbate in solution (µg Adsorbate/L), and 1/n is the Freundlich adsorption intensity parameter (unitless).

Modeling Arsenate Breakthrough in Continuous Flow Columns

Initial estimates for the external mass transport coefficient were based on the Gnielinski correlation (11):

$$k_f = \frac{[1 + 1.5(1 - \varepsilon)] \times D_l}{d_p} \times (2 + 0.644 \times \mathrm{Re}^{1/2} \times \mathrm{Sc}^{1/3}) \tag{2}$$

$$\mathrm{Re} = \frac{\rho_l \times \Phi \times d_p \times v_l}{\varepsilon \times \mu_l} \tag{3}$$

$$\mathrm{Sc} = \frac{\mu_l}{\rho_l \times D_l} \tag{4}$$

Constraints: $\mathrm{Re} \times \mathrm{Sc} > 500$; $0.6 \leq \mathrm{Sc} \leq 10^4$; $1 \leq \mathrm{Re} < 100$; $0.26 < \varepsilon < 0.935$.

k_f is the external mass transport coefficient (calculated $k_f \approx 5.5 \times 10^{-3}$ cm s^{-1} for M-3–15 M-GAC; $k_f \approx 6.2 \times 10^{-3}$ cm s^{-1} for Mn-0.5–15 M-GAC); Re is the Reynolds number (unitless); Sc is the Schmidt number (unitless); d_p is the adsorbent particle diameter ($d_p = 0.6 \times 10^{-3}$ m); D_l is the free liquid diffusivity for arsenate ($D_l = 9.05 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$) (19); ε is the bed void fraction ($\varepsilon \approx 0.384$ for M-3–15 M-GAC; and $\varepsilon \approx 0.308$ for Mn-0.5–15 M-GAC); μ_l is the dynamic viscosity of water at 20°C (1.002×10^{-3} N s m^{-2}); ρ_l is the density of water at 20°C ($\rho_l = 998.2\,\text{kg m}^{-3}$); Φ is the particle shape factor ($\Phi = 1.2$); v_l is the liquid superficial velocity ($v_l \approx 3.45 \times 10^{-3}\,\text{m s}^{-1}$).

Because M-GAC is very porous (the particle porosity $\varepsilon_P \approx 0.78$), pore diffusion was the assumed dominant intraparticle mass transport over the surface diffusion, and the impact of surface diffusion was assumed negligible. As suggested by Sontheimer *et al.* (11), the pore diffusion coefficient was estimated using Equation (5):

$$D_P = \frac{\varepsilon_P \times D_l}{\tau} \tag{5}$$

The tortuosity was estimated using the correlation suggested by Mackie and Meares (Equation 6) for electrolyte solutions (20):

$$\tau = \frac{(2 - \varepsilon_P)^2}{\varepsilon_P} \tag{6}$$

Where τ is the toruosity factor; and ε_P is the particle porosity. The estimated toruosity value was $\tau \approx 1.91$, which resulted in estimated value for the pore diffusion coefficient of $D_P \approx 3.67 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$.

The pore and surface diffusion model (PSDM) was used to provide initial predictions of the arsenate breakthrough curve (9,12,21). PSDM is a dynamic packed bed model that incorporates a set of assumptions and governing partial differential equations describing the adsorber dynamics in a packed bed setup. PSDM simulations were conducted using AdDesignS$^{\text{TM}}$ software (Michigan Technological University) (22).

To validate calculated k_f and D_P values, a short bed adsorber (SBA) test was conducted. SBA tests are continuous flow column experiments with a packed bed sufficiently long enough to describe dissolved pollutant mass transfer zone (14,23,24). The initial model estimates predicted that a SBA column with diameter of 1.1 cm, bed depth of ~2.8 cm, and M-GAC particle size of 600 µm should be sufficiently long enough to describe dissolved pollutant mass transfer zone at loading rate of $\sim 5\,\text{L m}^{-2}\,\text{s}^{-1}$, initial arsenate concentration $C_0 \sim 125\,\mu\text{g L}^{-1}$ and temperature of 20°C. Such loading rates are typical for full scale fixed bed column absorbers (17,25,26).

For the SBA test, a 2.8 cm deep adsorbent media bed was packed atop a support of quartz sand and metal support screen in a glass column with diameter (d_{Column}) of 1.1 cm (Ace Glass). Glass beads were placed above and below to provide evenly distributed flow. The SEM analysis of the sieved adsorbent media suggested that the particle sizes generally ranged from approximately 400 to 800 µm so mean particle size of 600 µm was used in the calculations, which provided d_{Column}/d_p ratio of ~ 36. According to Benenati and Brosilow (27) and Chu and Ng (28), the wall effect on the mass transfer can be neglected for d_{Column}/d_p ratios >20. Since a minimum of 30 mL of sample volume was needed to conduct the necessary analyses, effluent from the SBA test was collected in ~ 20 bed volume (BV) sample aliquots.

The relative importance of internal and external mass transport resistance was evaluated by estimating the pore (Bi_P) Biot numbers using the relationship given by Sontheimer et al, (11):

$$Bi_P = \frac{k_f \times d_P}{2 \times D_P} \tag{7}$$

Where d_P is the arithmetic mean of the media (cm).

The maximum number of bed volumes that could be treated with the media was estimated using the relationship given by Sontheimer *et al.*,(11):

$$BV_{MAX} = \frac{q_0 \times \rho_{BED}}{C_0} \times 1000 \tag{8}$$

where ρ_{BED} is the bed density of the media in the packed bed ($\mathrm{g\,cm^{-3}}$), and the multiplication factor result from unit conversion.

The PSDM was used to simulate the performance of full scale fix bed systems operating at $12\,\mathrm{m^3\ m^{-2}hr^{-1}}$, and different empty bed contact times (EBCTs) (20, 40, and 80 minutes). To maintain the same loading rate, the length of the packed bed was changed to achieve the desired EBCTs. The modeling was conducted with realistic values of $C_0 = 25\,\mu\mathrm{g\,L^{-1}}$. Since the external mass transport is a function of the loading rate and the particle size, k_f was recalculated for $d_p = 1\,\mathrm{mm}$ and $\Phi = 1.2$ using Equation (3). The water chemistry, pH, and bed porosity were assumed the same as ones used in the SBA test.

Arsenic and Iron Analysis

Arsenate and iron concentrations in the effluent were analyzed using a graphite furnace atomic absorption spectrophotometer (GF-AAS) Varian Zeeman Spectra 400 (29).

RESULTS AND DISCUSSION

Material Characterization

The iron content of the M-3–15 M-GAC and Mn-0.5–15 M-GAC was 9% and 16% implying that greater iron content can be obtained via the $KMnO_4/Fe(II)$ method although both media were synthesized using solutions with same iron concentrations and same amount of virgin GAC.

The equilibrium adsorption experiments revealed that Mn-0.5–15 M-GAC has greater adsorption capacity than the M-3–15 M-GAC even though the experiments for Mn-0.5–15 M-GAC were conducted at higher pH (Fig. 1). The adsorption capacity (K) parameter for Mn-0.5–15, which was 47.3 (μg As/g dry media)(L/μg As)$^{1/n}$, in comparison to the adsorption capacity parameter of M-3–15 M-GAC, which was 10.6 (μg As/g dry media)(L/μg As)$^{1/n}$, illustrates this greater capacity. The Freundlich intensity parameters were $1/n < 0.66$ for both media, corresponding to favorable adsorption.

The SEM analysis revealed that the crushed M-GAC particles generally ranged from approximately 400 to 800 μm so mean particle size of 600 μm was used in the calculations. The estimated particle porosity of both media was $\varepsilon_P \approx 0.78$, and the estimated material densities were $\rho_M \approx 2.00 \pm 0.15$.

Continuous Flow Column Tests and Adsorption Modeling

Figure 2a presents the data and PSDM prediction for arsenate breakthrough in the SBA test conducted with M-3–15M-GAC at loading rate of 3.5 L m^{-2} s^{-1} (5.1 gal min^{-1} ft$^{-2;}$ Re × Sc ≈ 7,150) and initial arsenate concentration $C_{0(As)} \approx 130\,\mu g\,L^{-1}$. As illustrated, rapid breakthrough occurred initially due to the short bed depth, reaching 50% breakthrough ($C/C_0 \approx 0.5$) at approximately 70 bed volumes (BV). A complete breakthrough ($C/C_0 \approx 0.95$) was reached much later, at approximately 4,250

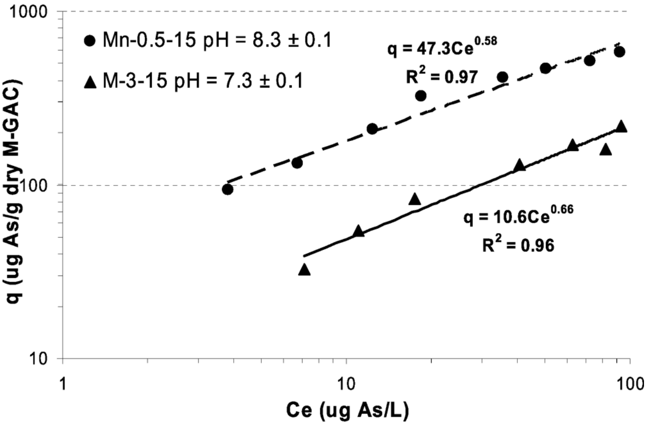
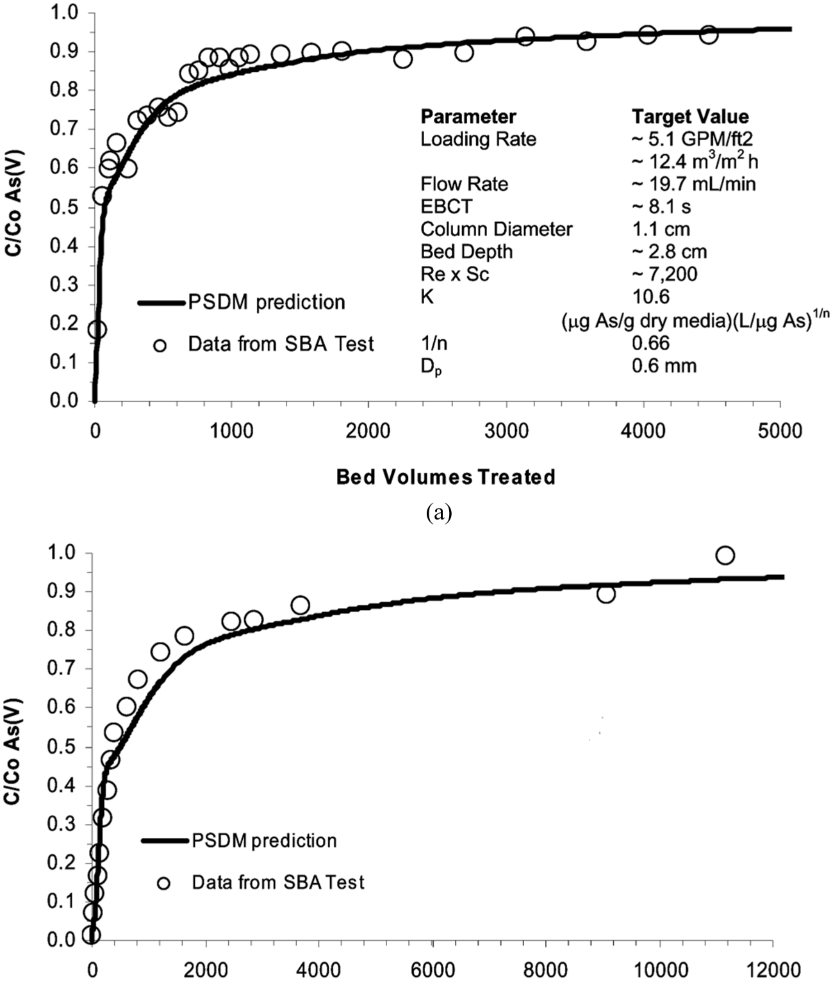


Figure 1. Equilibrium adsorption experiments for M-3–15 M-GAC and Mn-0.5–15 M-GAC adsorbent media in 10 mM $NaHCO_3$ buffered ultrapure water (Contact time = 3 days; $C_{0\text{-}As(V)} \sim 120\,\mu g\,L^{-1}$).



(a)

(b)

Figure 2. PSDM prediction (line) and experimental data (open symbols) from the SBA tests for (a) M-3–15 M-GAC adsorbent. ($pH_{Effluent} \approx 7.3 \pm 0.1$; $C_{0\text{-As(V)}}$ $\sim 130\,\mu g\,L^{-1}$; 10 mM $NaHCO_3$ buffered ultrapure water); and for (b) Mn-0.5–15 M-GAC adsorbent. ($pH_{Effluent} \approx 8.3 \pm 0.1$; $C_{0\text{-As(V)}}$ $\sim 121\,\mu g\,L^{-1}$; 10 mM $NaHCO_3$ buffered ultrapure water).

BV. The initial rapid breakthrough was expected as the adsorption sites located on the outermost surfaces of the particle become quickly occupied with arsenate, and the only available sites are located inside the media particle. Later, the gradual breakthrough (approximately 600 BV) occurs as the intraparticle mass transport becomes more limiting due to the longer time necessary for arsenate to diffuse inside the media particle.

Figure 2b presents the data and PSDM prediction for arsenate breakthrough in the SBA test conducted with Mn-0.5–15 M-GAC. Although the arsenate breakthrough curve for Mn-0.5–15 exhibited similar pattern when compared to the breakthrough curve of M-3–15, 50% breakthrough ($C/C_0 = 0.5$) occurred much later at approximately 500 BV. A complete breakthrough ($C/C_0 = 0.95$) also occurred much later at approximately 13,000 BV. The later breakthroughs are expected considering that the Mn-0.5–15 M-GAC exhibited several times greater adsorption capacity than the M-3–15 M-GAC.

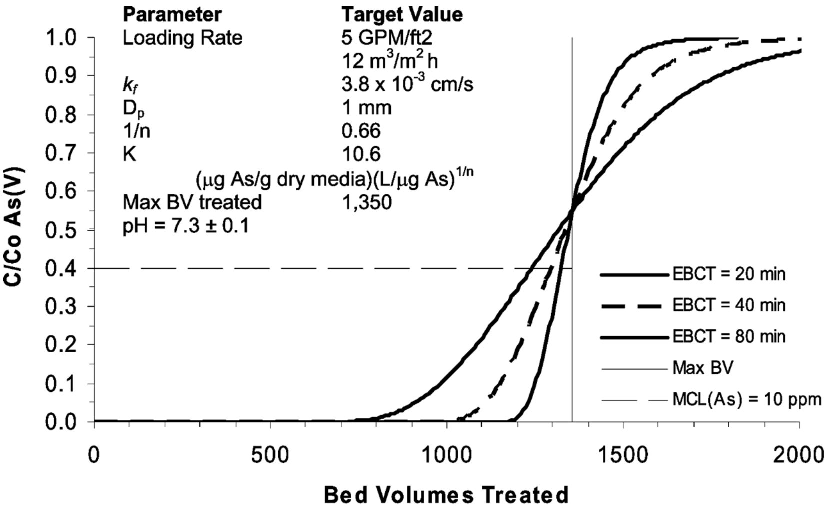
Based upon the theoretically calculated values of $k_f \approx 5.5 \times 10^{-3}$ cm s^{-1} and $k_f \approx 6.2 \times 10^{-3}$ cm $s^{-1}$for M-3–15 M-GAC and Mn-0.5–15 M-GAC, respectively, and $D_P \approx 3.67 \times 10^{-6} cm^2\ s^{-1}$ from equations 3 and 6, PSDM provided a good prediction (lines in Fig. 2) of the arsenate breakthrough, and validated that the PSDM can be used to predict a full scale system packed with both types M-GAC adsorbent.

The estimated pore Biot numbers $Bi_P > 58$ for both media. A Biot number ≥ 20 implies intraparticle diffusion controls the overall mass transport of the system (11).

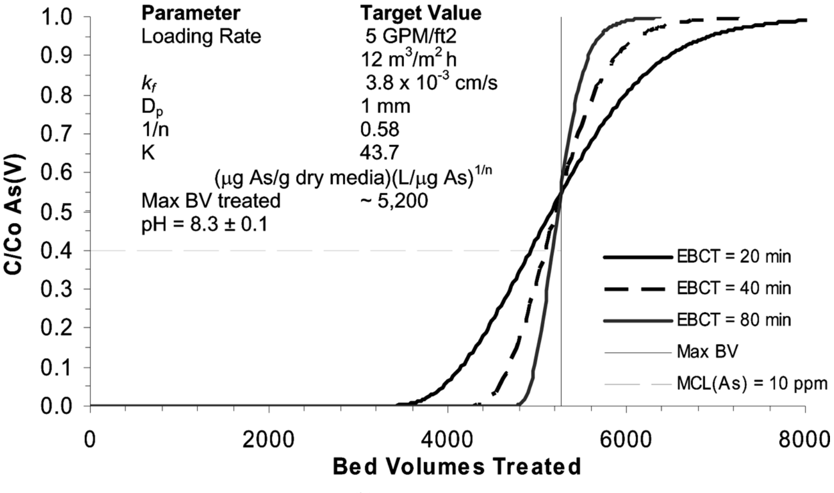
The iron trace analysis (MDL = 1 μg Fe/L) of the effluent revealed that no iron leached out of the M-GAC during the short bed column tests. This suggests that the packed bed was stable and did not release any iron.

Performance of Full-Scale Packed Bed Systems

Using the validated PSDM, predictions for arsenate breakthrough at longer empty bed contact times (EBCTs) were simulated for a full scale packed bed system (Fig. 3a and 4a). The number of bed volumes that can be treated until the MCL goal of 10 μg/L As(V) ($C/C_0 = 0.4$) is reached increases with increasing EBCT. For M-3–15 M-GAC, the PSDM predicts that approximately 1,240 BV can be treated at EBCT of 20 min, while this number is approximately 4,150 BV for Mn-0.5–15 M-GAC, which is significantly greater. With doubling of the EBCT to 40 minutes, the model predicts that M-3–15 M-GAC and Mn-0.5–15 M-GAC can treat approximately 1,290 BV and 4,700 BV, respectively. At EBCT of 80 min, the number of bed volumes that can be treated is approximately 1,320 BV for M-3–15 M-GAC and 4,970 BV for Mn-0.5–15 M-GAC and it is approaching the maximum number of bed volumes that can be treated which were estimated using equation 8.



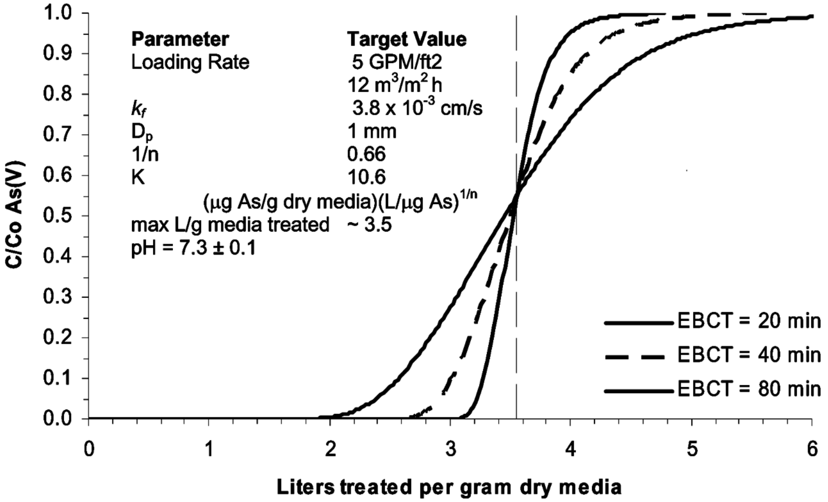
(a) M-3-15 M-GAC



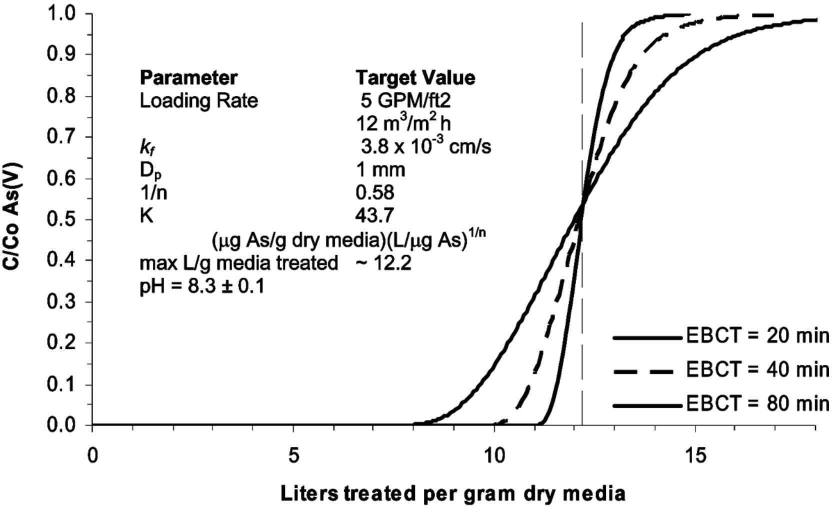
(b) Mn-0.5-15 M-GAC

Figure 3. Arsenate breakthrough predictions at EBCTs of 20, 40, and 80 minutes for a simulated full scale packed bed system expressed as bed volumes (BV) treated for evaluated M-GAC ($C_{0\text{-As(V)}} \sim 25\,\mu\text{g}\,\text{L}^{-1}$).

For M-3–15 M-GAC, the estimated number of bed volumes that can be treated was $BV_{MAX} \approx 1{,}350$ BV, while this number was $BV_{MAX} \approx 5{,}200$ for Mn-0.5–15 M-GAC. The greater number of bed



(a) m-3-15 M-GAC



(b) Mn-0.5-15 M-GAC

Figure 4. Arsenate breakthrough predictions at EBCTs of 20, 40, and 80 minutes for a simulated full scale packed bed system expressed as liters treated per gram dry media for the evaluated M-GAC ($C_{0\text{-As(V)}} \sim 25\,\mu\text{g}\,\text{L}^{-1}$).

volumes treated that can be achieved with Mn-0.5–15 M-GAC is directly related to the greater adsorption capacity of this media in comparison to M-3–15 M-GAC.

Figures 3b and 4b illustrate the arsenate breakthrough prediction expressed on the basis of liters of treated water per g dry media, which can be used to compare the performance of the media with other commercially available media when evaluated using column tests under similar conditions. As illustrated in Fig. 3b, approximately 3.5 L (or 87.5 μg As) can be treated per g of dry M-3–15 M-GAC media, which is at least an order of magnitude lower than the reported values reported by Barduzzaman et al. (25), Badruzzaman (30), and Westerhoff et al. (26) for commercially available GFH and E33 even when these media are tested in waters that contain ions competing with arsenate for available adsorption sites. However, although lower, the value of 12.2 L (or 305 μg As) that can be treated per g of dry Mn-0.5–15 M-GAC media, is comparable with the lower values of the range reported for the commercially available media which is from 300 μg to 11 mg As per g of dry media (25,26,30,31).

When engineering a packed bed adsorber, it is critical to be able to capture the mass transfer zone (MTZ) within the packed bed. Shorter mass transfer zone would reduce the EBCT and contribute to increase the number of bed volumes treated. Since pore diffusivity controls the overall mass transport, media with greater porosity would increase the overall mass transport and shorten the MTZ. Another approach is to reduce the particle size of the media which would shorten the path of arsenate inside the pores of the media thus, but also increase the external mass transport. This, however, can contribute to operational issues such as increased head loss, channeling, or even clogging of the packed bed.

CONCLUSION

The study demonstrated that the pore surface diffusion model can be successfully used to predict the performance of a packed bed adsorber column containing media with heterogeneous surface such as iron (hydr)oxide modified GAC. The arsenate removal performance of M-3–15 M-GAC did not compare well with the performance of commercially available media for arsenate treatment such as GFH or E33 even when these media are tested in waters that contain ions competing with arsenate, while the performance of Mn-0.5–15 M-GAC was slightly lower but comparable to commercially available media. The study emphasized that the adsorption capacity of the media is the crucial factor in determining the overall ability to remove arsenate in a packed-bed column setup. The full-scale packed bed simulation was significantly easier and faster than producing large quantities of media, which would be necessary to conduct long term pilot tests.

REFERENCES

1. US Department of Health and Human Services (Ed.). (2000) *Toxicological Profile for Arsenic*. US Department of Health and Human Services: Washington, DC.
2. EU Council. (1998) Council directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. *Offic. J. Europ. Communit.*, *L 330*: 32–54.
3. US EPA. (2002) *Implementation guidance for the arsenic rule*; EPA-816-K-02–018; Office of Water, US EPA: Washington DC.
4. WHO (Ed.). (2004) *Guidelines for Drinking-Water Quality*, 3rd Ed.; World Health Organization: Geneva.
5. Peraniemi, S.; Hannonen, S.; Mustalahti, H.; Ahlgren, M. (1994) Zirconium-activated charcoal as an adsorbent for arsenic, selenium and mercury. *Fresenius J. Anal. Chem.*, *349* (7): 510–515.
6. Gu, Z.M.; Fang, J.; Deng, B.L. (2005) Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Env SciTechnol*, *39* (10): 3833–3843.
7. Chen, W.; Parette, R.; Zou, J.; Cannon, F.S.; Dempsey, B.A. (2007) Arsenic removal by iron modified activated carbon. *Water Res*, in press.
8. Mohan, D.; Pittman C.U. Jr. (2007) Arsenic removal from water/wastewater using adsorbents – A critical review. *J Haz Mater*, *142*: 1–53.
9. Crittenden, J.C.; Hutzler, N.J.; Geyer, D.G.; Oravitz, J.L.; Friedman, G. (1986) Transport of organic compounds with saturated groundwater flow: Model development and parameter sensitivity. *Water Resour. Res.*, *22*: 271–284.
10. Crittenden, J.C.; Speth, T.F.; Hand, D.W.; Luft, P.J.; Lykins, B. (1987) Evaluating multicomponent competitive adsorption in fixed-beds. *J. Env. Eng.-Asce*, *113* (6): 1363–1375.
11. Weber, W. I.; Sontheimer, H.; Crittenden, J.C.; Summers, S. (1988) *Activated Carbon for Water Treatment*, 2nd Ed.; DVGW-Forschungsstelle, Engler-Bunte Institut, Universitat Karlsruhe: Karlsruhe, Germany.
12. Hand, D.W.; Crittenden, J.C.; Hokanson, D.R.; Bulloch, J.L. (1997) Predicting the performance of fixed-bed granular activated carbon adsorbers. *Water Sci. Technol.*, *35* (7): 235–241.
13. Crittenden, J.C.; Trussell, R.R.; Hand, D.W.; Howe, K.J.; Tchobanoglous, G. (Eds). (2005) *Water treatment: Principles and Design*, 2nd Ed.; Hoboken, New Jersey, USA: Wiley & Sons, Inc.: Hoboken, New Jersey, USA.
14. Weber, W.J.; Smith, E.H. (1987) Simulation and design models for adsorption processes. *Env. Sci. Technol.*, *21* (11): 1040–1050.
15. Sengupta, A.K.; Cumbal, L.H. (2005) *Method of manufacture and use of hybrid anion exchanger for selective removal of contaminating fluids*. US Patent Application 20050156136, July 21, 2005.
16. Lee, M.C.; Snoeyink, V.L.; Crittenden, J.C. (1981) Activated carbon adsorption of humic substances. *J. AWWA*, *73* (8): 440–460.
17. Hristovski, K.; Westerhoff, P.; Mooler, T.; Sylvester P.; Condit, W.; Mash, H. (2008) Simultaneous removal of perchlorate and arsenate by ion-exchange

media modified with nanostructured iron (hydr)oxide. . *J. Haz. Mater.*, *152*: 397–406.

18. US EPA. (1996) *SW-846 Test Methods for Evaluating Solid Waste, Physical/-ChemicalMethods*; *US, EPA : Washington, DC, USA.*
19. Lide, D. (ed). (2006). *CRC Handbook of Chemistry and Physics*; 87th Ed.; Talor and Francis Group: Boca Raton, Florida.
20. LeVan, D.M.; Carta, G.; Yon, C.M. (1997) Adsorption and Ion Exchange, Chapter 16. In: *Perry;s Chemical Engineers' Handbook*, Perry, R.D.; Green, D.W., eds.; 7th Ed.; McGraw-Hill: New York, USA.
21. Friedman, G. (1984) *Mathematical Modeling of Multicomponent Adsorption in Batch and Fixed-bed Reactors*, Master's Thesis. Michigan Technological University: Houghton, Michigan.
22. Mertz, K.A.; Gobin, F.; Hand, D.W.; Hokanson, D.R.; Crittenden, J.C. (1999) *Manual: Adsorption Design Software for Windows (Ad-DesignS)*; Michigan Technological University: Houghton, Michigan.
23. Weber, W.J. (1984). Evolution of a technology. *J. Env. Eng.-Asce.*, *110* (5): 899–917.
24. Smith, E.H.; Weber, W.J. (1988). Modeling activated carbon adsorption of target organic-compounds from leachate-contaminated groundwaters. *Env. Sci. Technol.*, *22* (3): 313–321.
25. Badruzzaman, M.; Westerhoff, P.; Knappe, D.R.U. (2004) Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH). *Water Res.*, *38* (18): 4002–4012.
26. Westerhoff, P.; Highfield, D.; Badruzzaman, M.; Yoon, Y. (2005) Rapid small-scale column tests for arsenate removal in iron oxide packed bed columns. *J. Env. Eng.-Asce.*, *131* (2): 262–271.
27. Benenati R.F.; Brosilow, C.B. (1962) Void fraction distribution in bed of spheres. *AIChE J.*, *8* (3): 351–361.
28. Chu, C.F.; Ng, K.M. (1989) Flow in packed tubes with a small tube to particle diameter ratio. *AIChE J.*, *35* (1): 148–158.
29. Franson, M.A.H.; Eaton, A.D.; Clesceri, L.S.; Greenberg, A.E. (Eds.). (1995) *Standard Methods for the Examination of Water and Wastewater*, 19th Ed.; American Public Health Association: Washington DC, USA.
30. Badruzzaman, M. (2005) *Mass Transport Scaling and the Role of Silica on Arsenic Adsorption onto Porous Iron Oxide (hydroxide)*; Ph.D. Dissertation, Arizona State University: Tempe Arizona, USA.
31. Sperlich, A.; Werner, A.; Genz, A.; Amy, G.; Worch, E.; Jekel, M. (2005) Breakthrough behavior of granular ferric hydroxide (GFH) fixed-bed adsorption filters: Modeling and experimental approaches. *Water Res.*, *39* (6): 1190–1198.