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Arsenic removal *via* ZVI in a hybrid spouted vessel/fixed bed filter system

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Abstract

The description and operation of a novel, hybrid spouted vessel/fixed bed filter system for the removal of arsenic from water are presented. The system utilizes zero-valent iron (ZVI) particles circulating in a spouted vessel that continuously generates active colloidal iron corrosion products *via* the “self-polishing” action between ZVI source particles rolling in the moving bed that forms on the conical bottom of the spouted vessel. This action also serves as a “surface renewal” mechanism for the particles that provides for maximum utilization of the ZVI material. (Results of batch experiments conducted to examine this mechanism are also presented.) The colloidal material produced in this fashion is continuously captured and concentrated in a fixed bed filter located within the spouted vessel reservoir wherein arsenic complexation occurs. It is demonstrated that this system is very effective for arsenic removal in the microgram per liter arsenic concentration (*i.e.*, drinking water treatment) range, reducing 100 µg/L of arsenic to below detectable levels ($\ll 10$ µg/L) in less than an hour.

A mechanistic analysis of arsenic behavior in the system is presented, identifying the principal components of the population of active colloidal material for arsenic removal that explains the experimental observations and working principles of the system. It is concluded that the apparent kinetic behavior of arsenic in systems where colloidal (*i.e.*, micro/nano) iron corrosion products are dominant can be complex and may not be explained by simple first or zeroth order kinetics.

Keywords

Arsenic removal; Zero-valent iron; Spouted vessels; Environmental chemical engineering

1. Introduction

Removal of aqueous arsenic species with zero-valent iron (ZVI) is a well-known, abiotic process that occurs on ZVI materials as they corrode in water. Arsenic ions are removed from solution *via* a mechanism involving adsorption, co-precipitation, and surface complexation with ZVI-generated Fe(II) and Fe(III) oxides, hydroxides, and oxyhydroxides [1]. It is also known that the oxidation rate at the ZVI–water interface determines the nature of the oxides and oxyhydroxides formed on the iron surface, as well as the final corrosion products. These corrosion products include lepidocrocite and magnetite with green rust and bernalite as intermediates [2]. From EXAFS studies of the geometry of co-precipitated and adsorbed arsenate on the ZVI corrosion products ferrihydrite, goethite, akageneite, and lepidocrocite, Waychunas et al. [3] concluded that arsenate ligands primarily form an inner

sphere bidentate arsenate complex. Monodentate arsenate complexes have also been observed [4].

Once arsenic anions have been “fixed” on active sites in the iron corrosion products, they are unlikely to desorb. Lackovic et al. [5] found that only about 7–11% of adsorbed arsenic was released from exposed iron filings when flushed with 0.01 M NaNO_3 in DI water. Additionally, as the arsenic complexes age, the rate of desorption decreases significantly, attaining 5.01–5.72% after 30 days and 2.88–4.29% after 60 days.

In our laboratory we have been conducting studies on the application of spouted particulate electrodes to electrochemical removal of heavy metals from aqueous solutions [6–8]. This work led us to consider the application of spouted vessels [9] for the enhancement of arsenic removal with ZVI. The principal hypothesis is that the continuous abrasion or “self-polishing” action of circulating ZVI particles in the moving bed that forms on the conical spouted vessel bottom provides a continuous surface renewal mechanism for the generation of active colloidal iron corrosion products for arsenic complexation and surface renewal of the ZVI particles. Here we present some of our results with this approach.

2. Experimental

Three different types of experiments were conducted in an investigation of the effects of surface renewal on the removal of aqueous arsenic species by ZVI. One type consisted of batch samples of 50–300 mL of arsenic-containing working solution and carbon steel spheres. Other series of experiments were conducted in two separate continuous flow systems – a spouted vessel and a packed bed contactor that utilized the liquid recirculation loop of the spouted vessel system, operated in total recycle mode.

The spouted vessel used in the current work was constructed by Technic, Inc. (Cranston, RI). Schematics are presented in Fig. 1(a and b). Its operation is similar to that of a spouted particulate electrode that was used and described in our previous work [6–8]. Essentially, ZVI particles are entrained in the arsenic-containing liquid jet and convected upwards in the central draft tube. The entrained particles disengage from the liquid flow as the velocity decreases in the freeboard region, and then fall onto the inverted conical distributor. The collector/distributor cone channels the particles to the periphery, where they fall onto and become part of the particulate moving bed, which transports them inward and downward on the conical vessel bottom back to the entrainment region. The pumping action of the spout circulates the particles through the vessel in a toroidal fashion – upwards in the spout, and downwards in the moving bed.

Schematics of the packed column apparatus are presented in Fig. 2(a and b). As shown, it was constructed to utilize the spouted vessel liquid recirculation system. For packed column operation, both the drain valve and the throttling valve of the spouted vessel system were kept open, the circulation pump for spouted operation was turned off, and the working solution was circulated through the packed bed flow loop with another pump.

Arsenic solutions were initially prepared as 1000 mg/L standard solutions of either As(III) or As(V). The As_2O_3 standard was prepared with sodium hydroxide, and then subsequently acidified with nitric acid (TraceSELECTTM). The resultant As(III) 30 mg/L stock solution was buffered at pH 4 with potassium hydrogen phthalate (KHP) and sodium hydroxide (1.492 g/L KHP, 8 mg/L NaOH). The As(V) 30 mg/L stock solution, including 1.5 g/L of NaCl, was prepared from the 1000 mg/L As(V) standard solution initially made up from 99.9% (arsenic basis) arsenic(V) pentoxide (Alfa Aesar).

Total arsenic concentrations were determined with a PerkinElmer 4100ZL Zeeman Effect Graphite Furnace Atomic Absorption Spectrometer (GFAAS), equipped with an AS-71 autosampler. Individual furnace methods were derived from U.S.E.P.A. guidelines, and optimized for each buffer solution [10].

In both the spouted vessel and packed bed contactor experiments, 8 L of reagent water, followed by 8 L of the desired stock solution, and then 8 L more of reagent water were added to the spouted vessel reservoir for a total of 24 L. The circulation pump was run to mix the solution, and the temperature controller was set to 45 °C. Samples of the working solution were collected in order to determine the pH, and appropriate amounts of 1.0 M nitric acid or 1.0 M sodium hydroxide were titrated into the working solution to achieve the desired pH. When the solution attained the desired operating temperature, 270.1 g of grade 100, 1/8 in. diameter, carbon steel spheres (98.2–99.2 wt% iron, 0.10–0.20 wt% carbon; S.G. 7.95; Salem Specialty Ball Company, Inc. [11]) added to the spouted vessel. These were used as the iron source in all the experiments.

In another series of spouted vessel experiments, a cylindrical (5 in. long, 2.5 in. O.D.) 20 µm FOS-398 304 stainless steel, in-line filter (ISC Sales, Inc.) was installed in the flow loop (*cf.* Fig. 1b) to remove and concentrate colloidal iron corrosion products from the bulk liquid solution. The filter was placed within the solution tank with its outlet connected to one of the two tank drain lines. The other drain line was fitted with a valve that was adjusted to equalize the pressure drop in the two outlet lines. The effective water flow rate through the filter was about 20 L/min.

3. Results

3.1. Batch experiments

In order to simulate the behavior of immobilized ZVI particles in a fixed bed, 104 carbon steel spheres (~13.7 g), were placed in a polypropylene mesh sample bag, which was then immersed in 300 mL of 99.8 µg/L arsenic solution at pH 4, prepared from an As(III) standard (AAS *TraceCERT*[™], 998 mg/L, Fluka) for a loading of 2.2 µg As/g Fe. The solution was stirred with a magnetic stir bar.

The effects of particle–particle abrasion were simulated in batch experiments conducted in ten 50 mL centrifuge sample tubes attached to a mechanical rotator, each containing 40 mL of buffered 99.8 µg/L arsenic solution and 14 carbon steel spheres (~1.82 g) for the same initial loading of 2.2 µg As/g Fe. The samples were rotated at 60 rpm, maintaining the ZVI particles in constant motion, creating abrasion among themselves and with the walls of the centrifuge tubes. One tube at a time was then taken off the rotator at selected times – the last at 24 h. If no visible corrosion products were visible in the tube, a 1 mL sample of the solution was taken and preserved. For the tubes where corrosion products were visible, the contents were filtered through a 60 mL fine Büchner filter funnel (pore size of 4.0–5.5 µm). If corrosion product material remained in the filtrate, 50 mg of CaCl₂ flocculant was dissolved in 10 mL of filtrate. After the corrosion material settled out, a 1 mL sample of the supernatant solution was collected.

The results of these experiments are presented in Fig. 3. As shown, the agitated particle experiments resulted in the removal of about 45% of the initial arsenic from solution (arsenic concentration of 55.6 ± 4.0 µg/L) in 24 h, while the immobilized particle samples showed no signs of arsenic removal over the same time period. In addition, visual inspection of the sphere surfaces from the immobilized sample experiments showed no signs of reaction. Although regular sampling of the solutions in the immobilized samples was terminated after 24 h, solution/particle contact was allowed to continue for an additional 8

days. Corrosion of the spheres was finally visually observable at about 198.5 h, at which point the arsenic concentration had decreased to $36.1 \pm 4.0 \mu\text{g/L}$. For the agitated samples, reddish-brown corrosion products were visible in the solution and on the steel particle surfaces after approximately 1 h, coincident with the observed decrease in arsenic concentration.

Although arsenic removal was observed for both the immobilized and agitated particle batch samples, the time scale was greater than that reported for other ZVI materials under similar experimental conditions [12,13]. Biterna et al. [13] observed nearly complete arsenic removal within 30 min for an initial concentration of $200 \mu\text{g/L As(III)}$ using 2 g/L of iron powder (325 mesh) at pH 4. At initial pH values of both 3 and 5, a loading of 150 mg/L ZVI powder removed 85% of the $500 \mu\text{g/L As(III)}$ in under 2 h, as reported by Katsoyiannis et al. [12]. The difference in the time required for arsenic removal is attributed primarily to differences in surface area of the ZVI materials and the dependence of the removal mechanism on the iron corrosion rates. Katsoyiannis et al. [12] reported a surface area of $0.1 \text{ m}^2/\text{g}$ for their ZVI powder. In comparison, the carbon steel spheres have an estimated surface area of $2.4 \times 10^{-3} \text{ m}^2/\text{g}$. In addition, ZVI materials develop an oxide layer from exposure to air over time, and unless precautions are taken to prevent their oxidation, such as described by Kanel et al. [14], then initial arsenic uptake can occur on pre-existing oxide layers. The ZVI materials used by both Biterna et al. [13] and Katsoyiannis et al. [12] were not pretreated prior to use. Although no pretreatment of the carbon steel spheres was performed in the current experiments, the large particle size allowed for visual inspection of the spheres. No corrosion was observable on the surfaces of the immobilized particles until about 8 days, which is also about the time of the onset of arsenic removal. So, in this case, under relatively anoxic conditions, it is likely that resistance to the transport of dissolved oxygen to the iron–water interface probably had an effect on the overall rate of corrosion and arsenic complexation.

The observed differences in performance are at least partially attributable to increased mass transfer rates of arsenic to available adsorption sites in the agitated system. Yu et al. [19] found a strong correlation between arsenic removal and increasing Reynolds number, suggesting that the mass transfer rate is of significant importance for arsenic removal by ZVI. These authors also compared arsenite removal at varying stirrer speeds with an initial concentration of $2.88 \text{ mg/L As(III)}$ and an iron loading of 50 g of ZVI (28–35 mesh) in 2 L of 0.1 M NaClO_4 solution. At 333 rpm a 99% As(III) removal was observed after 1 h. In comparison, 5 days were required to attain 96.5% As(III) removal at 5 rpm . Yu et al. [19] suggested that increased stirrer speed could shear iron oxide layers from the ZVI surface, which in turn exposes fresh iron material, thereby stimulating additional iron corrosion. In our batch experiments, in addition to enhanced mass transfer due to liquid shear, the continuous motion of the carbon steel spheres causes collisions between particles and with the centrifuge tube walls that continually removes corrosion products from the particle surfaces in a physical process that produces active high surface area colloidal material and exposes fresh ZVI material to continue/enhance the surface renewal/complexation process. This mechanism also occurs in the dense moving particle bed on the conical bottom of the spouted vessel.

3.2. Continuous flow experiments

Comparisons of the performance of continuous flow experiments in the spouted vessel and packed column systems, in terms of the generation of iron corrosion products, also support the preceding conclusions. In one set of experiments, the steel spheres in the spouted vessel exhibited a mass loss that was an order of magnitude greater than that in the comparable fixed bed experiment; 24.3 g in the former, and 2.5 g in the latter. Visual inspection of the carbon steel spheres from the spouted vessel experiments showed the expected signs of

corrosion. Those from the comparable packed column contactor experiments also exhibited corrosion products on the surfaces that were much thicker than those observed in the spouted vessel experiments. Indeed, in the packed column experiments, corrosion products filled much of the interstices between the spheres, “cementing” them together and providing much greater resistance to flow. Thus, the packed column contactor promoted the formation of corrosion products on the carbon steel sphere surfaces, whereas the spouted vessel promoted the formation of colloidal corrosion products in the bulk liquid phase.

The occurrence of colloidal corrosion products was also cited in the arsenic removal experiments reported by Bang et al. [15]. In the presence of dissolved oxygen, these authors observed that corrosion products readily formed as suspended particulates, as well as on the surfaces of ZVI filings. Furthermore, for a total As(V) removal of 72% after 90 min of mixing, only 44% was removed on the surfaces of the ZVI material, while the remainder was attributed to that on colloidal corrosion products. The role of colloidal corrosion products has also been discussed by Yu et al. [19] and Triszcz et al. [16].

In the current work, it was observed that exposed surfaces in the spouted vessel system were rapidly coated with colloidal corrosion products by operation with carbon steel spheres in the absence of arsenic. The carbon steel spheres and the solution were then removed, and the spouted vessel was filled with 24 L of fresh 100 $\mu\text{g/L}$ As(V) solution. The arsenic concentration in solution was monitored over time by collecting and analyzing 1 mL samples of the bulk solution. After just 0.5 h of contact time with the pre-coated colloidal corrosion products, the arsenic concentration had decreased from 92.4 to 35.3 $\mu\text{g/L}$, and the presence of arsenic in solution was undetectable after 24.2 h. The contents of the spouted vessel were then drained, and the system was dried with ambient air without removing any of the pre-deposited colloidal corrosion products. Next, the spouted vessel was filled with 240 mL of a 1000 mg/L As(III) standard and filled with water to 24 L to yield an arsenic concentration of approximate 10 mg/L. The solution was then allowed to circulate for 20 days with samples taken periodically and analyzed by GFAAS. The results showed essentially no discernible arsenic removal by the colloidal corrosion products at this high arsenic concentration (10 mg/L). These results are interpreted to mean that colloidal corrosion products are quite effective in removing arsenic at low concentrations, but not at much higher concentrations. It is anticipated that under these conditions, all the available complexation sites on the pre-deposited colloidal corrosion material are rapidly saturated, and no additional arsenic can be removed without the generation of fresh colloidal corrosion material. Thus, the relative importance of suspended and deposited colloidal material *vs.* bulk surface iron corrosion products for the removal of arsenic from solution must be understood and carefully considered in order to understand performance differences between different arsenic removal systems for widely varying arsenic concentrations, and in the effective design of ZVI arsenic removal systems.

In another series of experiments, a filter was installed in the reservoir of the spouted vessel apparatus (see Fig. 1). The results of arsenic removal at low concentrations ($\sim 100 \mu\text{g/L}$) are presented in Fig. 4. As shown, the spouted vessel with internal filtering is a very effective technique for arsenic removal at low concentrations. The arsenic concentration of the solution attained a value of $<2 \mu\text{g/L}$ in about an hour, which is significantly below the USEPA MCL of 10 $\mu\text{g/L}$ [10].

3.3. Analysis of arsenic removal in the spouted vessel system

Assuming that the fundamental arsenic removal rate is defined by the encounter frequency of arsenic species, A^* , with “complexation sites in active colloidal iron corrosion products” (*i.e.*, “active sites”), I^* , the rate of the removal process may be generally represented as:

$$\frac{d[A^*]}{dt} = -k[A^*][I^*], \quad (1)$$

where k is an effective second order rate constant that can incorporate mass transfer resistances that are often important in ZVI systems. Since $[A^*]$ and $[I^*]$ are local concentrations, Eq. (1) can result in LHHW-type rate expressions when based on bulk phase concentrations that exhibit variable apparent reaction orders between zero and first for some systems [17].

As established by the preceding experiments, the generation of “colloidal iron corrosion product material” (“colloidal material”) in the spouted vessel occurs primarily *via* the self-polishing action of iron-containing particles in the moving bed that forms on the spouted vessel bottom, since that is where the particles reside for approximately 97% of their circuit time [18]. If the generation rate of colloidal material is approximately constant, then the behavior of the active site concentration can be represented as:

$$\frac{d[I^*]}{dt} = \frac{k^*}{V_{\text{eff}}} - k[A^*][I^*] - k_d[I^*] \quad (2)$$

where k^* is the total generation rate of active sites in the moving bed (*e.g.*, number of active sites/time), V_{eff} is the effective volume over which the colloidal material is active, and k_d $[I^*]$ is the rate of iron complex deactivation which allows for depletion due to “age,” since it has been reported that fresh iron complexes are more active than more aged ones [17]. For a constant generation rate of active sites that is more rapid than its sinks (*i.e.*, complexation and aging), Eq. (2) becomes:

$$\frac{d[I^*]}{dt} \approx \frac{k^*}{V_{\text{eff}}}, \quad \text{and} \quad [I^*] \approx \frac{k^* t}{V_{\text{eff}}}, \quad (3)$$

which assumes $V_{\text{eff}} \approx \text{constant}$, and $[I^*] = 0$ at $t = 0$.

In order to develop expressions describing the arsenic concentration in the bulk liquid phase in the spouted vessel system, this general formulation must be modified to reflect the characteristics of each portion of the active site population in the system. These are identified as colloidal material: (1) in the filter; (2) on accessible surfaces in the system; (3) in the circulating bulk liquid phase; and (4) on the primary ZVI particle surfaces where they are generated. The latter is assumed to be negligible in the current work since the surface area offered by the spouted ZVI particles is orders of magnitude less than that of the colloidal material. In addition, the “self-polishing” action of the particles in the moving bed is very effective in removing (*i.e.*, “cleaning”) almost all the corrosion product material from the ZVI particle surfaces.

The colloidal material in the filter should be more effective for arsenic removal than the adsorbed colloidal material, and that in the circulating bulk liquid due to the high relative velocity between the “fixed” (captured) colloidal material and the bulk liquid solution. (The relative velocity should be close to zero on average in the bulk solution.) In addition, the filter is effective in removing almost all the colloidal material from the circulating bulk liquid solution. (The bulk liquid solution was always visually clear when operated with the filter.)

Insofar as the role of mass transfer resistance, Yu et al. [19] found a strong correlation between arsenic removal and the liquid phase Reynolds number, which suggests that the effective mass transfer rate is of significant importance for arsenic removal by ZVI. These

workers compared arsenite removal at varying stirrer speeds with an initial concentration of 2.88 mg/L As(III) and an iron loading of 50 g of ZVI (28–35 mesh) in 2 L of 0.1 M NaClO₄ solution. At 333 rpm, 99% As(III) removal was observed after 1 h. In comparison, at 5 rpm, 5 days were required to attain 96.5% As(III) removal [19]. It was suggested that increased stirrer speed could shear iron oxide layers from the ZVI surface, which, in turn, exposes additional surface area and stimulates further iron corrosion. In a similar fashion, in the current work, the continuous abrasion of the carbon steel spheres with one another and along the walls of the centrifuge tubes in the batch samples, and in the moving particulate bed on the bottom of the spouted vessel serve to continually remove corrosion products from the ZVI particles.

If it is assumed that arsenic removal in the hybrid spouted vessel/fixed bed filter system is dominated by the colloidal material accumulating in the filter, as our observations suggest, then substituting Eq. (3) into Eq. (1):

$$\frac{d[A^*]}{dt} = -k[A^*][I^*] \approx \frac{-k[A^*]k^*t}{V_f} \quad (4)$$

where V_f is the effective filter volume, which is assumed to remain constant.¹ Integration of this expression yields:

$$\frac{[A^*]}{[A^*]_0} = \exp \left[-\frac{kk^*t^2}{2V_f} \right], \quad (5)$$

As shown in Fig. 4, the arsenic removal rate is much more rapid with the filter installed. Also, the resultant curve is not fit very well by a simple exponential, as would be the case for a first order process. Indeed, as shown, Eq. (5) provides a much better fit of the data with the filter, with $kk^*/V_f = 2.6 \times 10^{-3} \text{ min}^{-2}$. In this experiment, 1.81 g of colloidal material was collected by the filter in 2.5 h, or about 0.72 g/h, which provides a rough estimate of k^* . Approximating the effective filter volume as the geometric volume of the filter multiplied by an estimated void fraction of $\varepsilon = 0.4$, $V_f = 156 \text{ cm}^3$, and $k = 34 \text{ ((g colloidal material/cm}^3\text{) min)}^{-1}$.

The other data set presented in Fig. 4, obtained in the absence of the filter, shows a considerably reduced arsenic removal rate. In this case, both the adsorbed colloidal material and that accumulating/circulating in the bulk liquid phase, may also be significant. The material in the bulk liquid phase also accumulates in time, such that the resultant formulation should be similar to Eq. (5); *i.e.*,

$$\frac{[A^*]}{[A^*]_0} = \exp \left[-\frac{k'k^*t^2}{2V_{\text{eff}}} \right] \quad (6)$$

Therefore, for the same constant rate of colloidal material generation, k^* , the timescale for arsenic removal is controlled by the ratio, k'/V_{eff} in Eq. (6), or k/V_f in Eq. (5).

¹The effective filter volume and its time dependence (if not constant) is a function of the nature of the filter and the detailed mechanism by which the colloidal material accumulates. For more accurate predictions, this functionality must be determined experimentally for the particular filter, colloidal material, and experimental conditions used. For the current purposes, constant V_f results in a linear time dependence for accumulation of colloidal material in the filter, which approximates the observed qualitative behavior.

Like the active colloidal material captured by the filter, the material adsorbed onto exposed vessel surfaces is captured and concentrated. However, unlike the material captured by the filter, its accumulation occurs relatively rapidly, due to the limited surface area per unit volume, and ceases when it attains its allowable thickness. This material will also experience deactivation due to loss of accessibility to active sites as a result of the diffusion barrier that develops in the multilayer deposit. Our observations support the rapid adsorption of this material onto system surfaces. Since we have not yet investigated the details of this mechanism, for the current purposes the behavior of this material is approximated by a simple model of a “step function” increase (*i.e.*, “rapid” adsorption), followed by a first order deactivation process:

$$[I_s^*] = [I_s^*]_0 \exp(-k_{d,s}t) \quad (7)$$

where $[I_s^*]$ is the available, active colloidal material per unit surface area on the system surfaces, $[I_s^*]_0$ is the total amount of active sites in the adsorbed layers, and $k_{d,s}$ is the first order deactivation rate constant of active sites due to decreasing accessibility and other factors. (Loss of active sites due to arsenic complexation is also a sink, but for low bulk phase arsenic concentrations, it is assumed to be negligible.) Substitution of this expression into Eq. (1) yields:

$$\frac{d[A^*]}{dt} = -k''a[A^*][I_s^*] = -k''a[A^*][I_s^*]_0 \exp(-k_{d,s}t) \quad (8)$$

where k'' is the apparent second order rate constant for complexation of arsenic species in the adsorbed material, and $a = S/V_b$ is the effective specific surface area of the spouted vessel system over which adsorption of active colloidal material occurs. The solution of this expression is:

$$\begin{aligned} \frac{[A^*]}{[A^*]_0} &= \exp \left[-k''a[I_s^*]_0 \frac{(1 - \exp(-k_{d,s}t))}{k_{d,s}} \right] \\ &\approx \exp \left[-k''a[I_s^*]_0 t \right] \quad (\text{for } k_{d,s}t \ll 1) \end{aligned} \quad (9)$$

Once this sink is exhausted, then the only remaining major sink is suspended, circulating colloidal material in the bulk liquid solution, which occurs at a much lower rate.

As shown in Fig. 4, the arsenic concentration-time history for operation without the filter is more complex than that with the filter. It is believed that this is due to contributions from more than one portion of the colloidal material population; *i.e.*, it is a composite. In accordance with this hypothesis, the data without the filter were fit to a linear combination of Eqs. (6) and (9):

$$\frac{[A^*]}{[A^*]_0} = C_1 \exp \left[\frac{-k'k^*t^2}{2V_{\text{eff}}} \right] + C_2 \exp[-k''a[I_s^*]_0 t]. \quad (10)$$

where the first term represents slower arsenic removal by the colloidal material in the bulk liquid phase, and the second (faster) term by colloidal material adsorbed onto the spouted vessel system surfaces. The resultant best fit parameter set for the data in Fig. 4 for this model without the filter is: $C_1 = 0.5$, $C_2 = 0.5$, $k'k^*/V_{\text{eff}} = 5 \times 10^{-6} \text{ min}^{-2}$, and $k''a[I_s^*]_0 = 3 \times 10^{-2} \text{ min}^{-1}$. These results indicate that about half of the total initial bulk arsenic will (eventually) be removed by the entrained, circulating colloidal material in the bulk liquid solution, and the other half by complexation with active colloidal material adsorbed onto the surfaces of the spouted vessel apparatus. Assuming k^* is similar for operation with/

without the filter, $(k/V_f/k'/V_{\text{eff}}) \approx 520$, and if the volume ratio is roughly $(V_{\text{eff}}/V_f) \approx (V_b/V_f) \approx 24,000/156 = 154$, then $k/k' \approx 520/154 = 3.4$, which suggests that the apparent rate constant for arsenic complexation in the filter is approximately a factor of three or so greater than that in the bulk liquid solution, which seems reasonable based upon estimated mass transfer resistance differences alone. Also, $k' \approx 10 \text{ ((g colloidal material/cm}^3\text{) min)}^{-1}$.

As shown, the performance of the hybrid spouted vessel/fixed bed filter system for arsenic removal is quite effective. With the filter in place, there is no appreciable arsenic complexation in the bulk liquid phase since there is little or no colloidal material available in that phase. For the same reason, as well as its more limited capacity, the adsorbed surface layer is also an ineffective sink for arsenic under these conditions. Therefore, arsenic removal occurs almost totally within the filter.

In the absence of the filter, active colloidal material is available in the bulk liquid phase for arsenic removal, and for rapid formation of the adsorbed surface layer. In the current work, apparently both of these sinks are comparable in terms of the total amount of arsenic removal over the long run. It is also apparent, however, that the adsorbed colloidal material complexes arsenic at a much greater rate than that in the bulk liquid phase, primarily due to the much lower effective active site concentration in the latter sink. However, the adsorbed material is also rapidly saturated due to its more limited capacity.

4. Conclusions

The hybrid spouted vessel/fixed bed filter system is demonstrated to be particularly efficacious for the removal of arsenic from aqueous solutions at low concentrations (*e.g.*, to meet drinking water standards). As shown, the effective treatment time can be reduced by an order of magnitude or two, with a proportionate increase in the effective water treatment rate.

The novel hybrid nature of the system lies in its dual-function character, whereby colloidal material is continuously generated in the moving bed on the spouted vessel bottom, and arsenic removal/complexation occurs in the fixed bed filter. This method of generation of colloidal material maximizes utilization of essentially all the ZVI material, in comparison to fixed systems where the effectiveness is reduced by the development of a diffusion barrier of corrosion products, such that only a relatively small fraction of the ZVI is actually ever utilized to remove arsenic.

It is also important to note that the hybrid system physically and mechanically separates the two basic kinetic processes of iron corrosion product formation and arsenic complexation, unlike most other approaches that incorporate *simultaneous* or *parallel* iron oxidation and arsenic complexation. The *decoupling* of the two processes makes the system less sensitive to the rate of iron corrosion, as long as the corrosion products are present in excess. This allows for a broader range of operation with respect to pH and iron corrosion rates.

Operation of the hybrid system is particularly simple and potentially cost effective. It requires essentially no attention other than periodic backwashing of the filter to remove the collected colloidal material, which can be readily automated. With the current system, under the operating conditions used, the filter begins to plug after about 28 h on stream. This cycle time is sufficient to remove essentially all the arsenic at an initial concentration of 100 $\mu\text{g/L}$ to less than detectable limits ($\ll 10 \mu\text{g/L}$) from about 800 L, or about 7.8 gal/h, utilizing only about 7.5% of the initial charge of ZVI material in a relatively small device. It can also be readily scaled-up (*e.g.*, with greater filter and liquid capacities, *etc.*). Moreover, it is expected that potentially significant improvements in performance beyond those reported here can be achieved *via* system optimization, including: the use of more optimal filter

types/capacities, geometry/operating conditions of the spouted vessel; and pH control to maximize corrosion product formation, *etc.*

The mechanistic analysis of arsenic behavior in the hybrid system demonstrates that the apparent kinetic behavior of arsenic in systems where colloidal (*i.e.*, micro/nano) iron corrosion products are a dominant factor can be complex and may not be explained by simple first or zeroth order kinetics.

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Fig. 1. Schematics of the spouted vessel system: (a) internals and reservoir tank. The “in-line filter,” shown with a dashed outline, replaces one of the water outlet tubes when installed; (b) spouted vessel operation showing particle circulation.

Fig. 2.
Schematic of the packed column apparatus.

Fig. 3.

Removal of 99.8 $\mu\text{g/L}$ As(III) in batch experiments with fixed (immobilized) and mixed (agitated) of carbon steel spheres in a pH 4 buffer electrolyte solution (6.3 mM NaOH and 2.4 M KHP) at ambient temperature. Fixed bed: $V_0 = 300 \text{ cm}^3$, $m_{\text{spheres}} = 13.7 \text{ g}$; mixed bed: $V_0 = 40 \text{ cm}^3$, $m_{\text{spheres}} = 1.82 \text{ g}$; 2.2 $\mu\text{g As/g Fe}$.

Fig. 4.

Comparison of arsenic removal from a solution of 100 $\mu\text{g/L}$ As(V) with 500 mg/L NaCl in a spouted vessel with and without filtering of colloidal corrosion products. The vessel contained 24 L of solution at 45 $^{\circ}\text{C}$, initially at pH 6.