

Modeling As(III) and As(V) adsorption and transport from water by a sand coated with iron-oxide colloids

Ilwon Ko, Cheol Hyo Lee, Kyoung-Woong Kim*

*OIKOS Co., Ltd., *Arsenic Geoenvironment Lab(NRL). Dept. of Environmental Science and Engineering
KJIST (e-mail: iwko@oikos.co.kr)*

<Abstract>

The development of a porous iron-oxide coated sand filter system can be modelled with the analytical solution of the transport equation in order to obtain the operating parameters and investigate the mechanism of arsenic removal. The adsorbed amount from the model simulation showed the limitation of adsorption removal during arsenic transport. A loss reaction term in the transport equation plays a role in the mass loss in column conditions, and then resulted into the better model fitting, particularly, for arsenate. Further, the competitive oxyanions delayed the breakthrough near MCL (10 µg/L) due to the competitive adsorption. This is the reason why arsenate can be strongly attracted in the interface of an iron-oxide coated sand, and competing oxyanions can occupy the adsorption sites. Therefore, arsenic retention was regulated by non-equilibrium of arsenic adsorption in a porous iron-oxide coated sand media. The transport-limited process seemed to be affect the arsenic adsorption by coated sand.

key word : Arsenic, Adsorption, Transport modeling, Iron-oxide, Sand

1. Introduction

Arsenic contamination is problematic in the geochemical distribution around metal mining areas and arsenic-related chemical spilling like pesticide around agricultural and industrial area. Many researchers developed the iron-oxide coated sand to remove arsenic and heavy metals. For a soil and groundwater restoration, a permeable reactive barrier system has been applied to locally contaminated groundwater using iron-oxide coated sand as a porous reactive material (Rakesh and Sudhir, 2003; Ko et al., 2002). Further, a large groundwater-contaminated area like Bangladesh, Nepal, etc, is restricted to use drinking water due to arsenic contamination, and then some home removal units is available to remove arsenic (Joshi and Chaudhuri, 1996).

Modeling can be performed to investigate the design factors for scaling up the technology and further understand the mechanisms of arsenic removal from contaminated water using iron-oxide

coated sand. This study performed the adsorption and transport modeling of arsenite and arsenate in iron-oxide packed system, that is, a column packed with a sand coated with iron-oxide colloids. Oxyanion competitive adsorption and arsenic inorganic speciation are also simulated with arsenic-loading water or groundwater during the column transport.

2. Results and discussions

2.1. Batch and column experiment

The removal of arsenite and arsenate by coated sand is shown in Figure 1. 1.0 mg/L of arsenic (arsenite and arsenate) was loaded into the coated sand, and sulfate and nitrate was chosen as competitive oxyanions. Both arsenite and arsenate adsorption showed a linear isotherm. It indicates that the surface adsorption sites of coated sand can be saturated in more than 1.0 mg/L. The presence of sulfate and nitrate inhibited both arsenite and arsenate adsorption onto surface of coated sand. The removal kinetics of arsenic can be described as a first-order reaction, and then the presence of competitive oxyanions reduced the removal kinetics.

For the column experiments, 1.0 mg/L of arsenic (arsenite or arsenate) passed through the iron-oxide coated sand media. The packing amount of coated sand in columns led to the slow breakthrough of arsenic concentration near the MCL (maximum contamination level) of 10 $\mu\text{g/L}$ (Figure 2a and 2b). Further, in the presence of competitive oxyanions, arsenic removal was restricted to the fast breakthrough near MCL, compared with a simple system including arsenic and coated sand (Figure 2c).

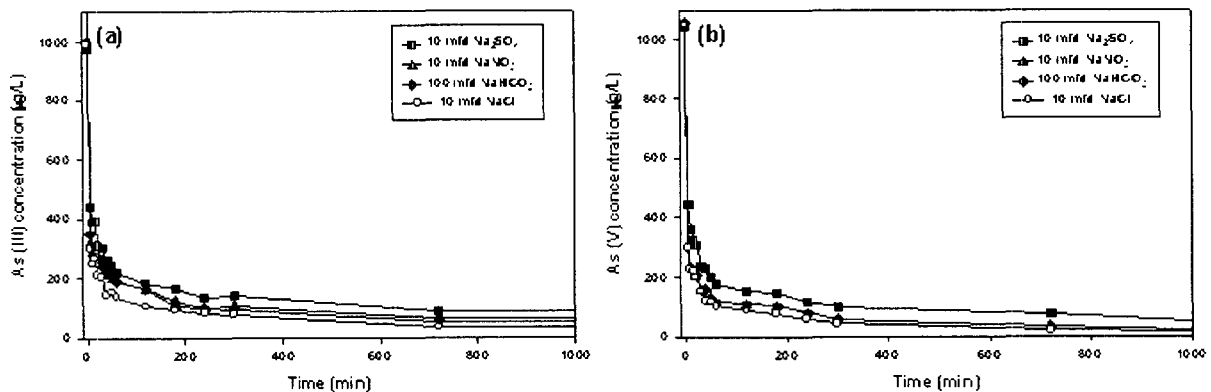


Figure 1. The removal kinetics of (a) arsenite and (b) arsenate in the presence of competing oxyanions.

2.2. Data analysis

Arsenic is transported into a coated sand-packed column by advection and dispersion processes. Surface adsorption can be a transport-limited process in a dynamic environment. The adsorption of arsenic onto coated sand is a removal process by both transport-limited and attachment-limited mechanisms. The fast equilibrium of adsorption was modeled with a linear adsorption, and the slow transport was modeled with a first-order loss reaction. Therefore, the one dimensional mass transport

equation can simulate the arsenic removal with a linear adsorption and a first-order loss reaction term. The non-equilibrium of arsenic removal was tested with and without a first-order loss reaction term.

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - kC,$$

where C is arsenic concentration in solution ($\mu\text{g/L}$), K_d ($\text{L}/\mu\text{g}$) is a linear equilibrium partitioning coefficient, D (cm^2/day) is a dispersion coefficient in a x -direction and k is a mass loss coefficient. R is a retardation factor and is computed from the following relationship.

$$R = 1 + \frac{K_{d\rho_s(1-n)}}{n}$$

where n is a porosity and ρ_s is a density of particle. By introducing the following initial and boundary conditions with continuous-input column experiments.

$$\begin{aligned} C(x,0) &= 0 \text{ for } x \geq 0 \\ C(0,t) &= C_0 \text{ for } t > 0 \\ \frac{\partial C}{\partial x} &= 0 \text{ for } x = \infty \end{aligned}$$

the analytical solutions with and without a first-order loss reaction term can be used, respectively,

$$\begin{aligned} C &= \frac{C_0}{2} \exp\left(-\frac{(v-u)x}{D}\right) \operatorname{erfc}\left[\frac{Rx-ut}{2(DRt)^{1/2}}\right] + \frac{C_0}{2} \exp\left(-\frac{(v+u)x}{D}\right) \operatorname{erfc}\left[\frac{Rx+ut}{2(DRt)^{1/2}}\right] \\ \text{and } C &= \frac{C_0}{2} \operatorname{erfc}\left[\frac{Rx-vt}{2(DRt)^{1/2}}\right] + \frac{C_0}{2} \exp\left(-\frac{vx}{D}\right) \operatorname{erfc}\left[\frac{Rx+vt}{2(DRt)^{1/2}}\right] \end{aligned}$$

where $u = v\left(1 + \frac{4kD}{v^2}\right)^{1/2}$ and C_0 is the initial concentration of arsenic.

An analytical solution was computed by a spreadsheet and simulated the breakthrough curves from the column data. The porosity was 0.38, dispersivity is 0.50, D is $140.3 \text{ cm}^2/\text{day}$ and the velocity of the water is 278 cm/day based on the tracer column test. The linear partitioning coefficient and the first-order mass loss coefficient were obtained by model calibration.

2.3. Model simulation

Experimental breakthrough curves were computed by the model fittings. The results of model simulation were compared with experimental results in order to determine the model fitness. The K_d and adsorbed amount represents the arsenic adsorption or co-precipitation onto surfaces of coated sand particles. Considering the K_d and amount of arsenic adsorption with respect to sorbent dose, that is, mixture amount of pure sand and coated sand, the increased amount of coated sand promoted the arsenic removal and more than 50% mixture of coated sand showed the plateau of adsorption amount of arsenic during the arsenic transport (Figure 2a). It is significant to retard arsenic transport at a

constant flow environment. The amount of sorbent dose can adsorb arsenite and arsenate to some extent. This implies that the transport-limited process become dominant, and then the dynamic flow process like advection and dispersion can control the adsorption equilibrium process in a fixed filter system. The loss reaction reflected the better fitting in the low breakthrough concentration ($<40 \mu\text{g/L}$ for arsenite), whereas the poor fitting in the high breakthrough concentration ($>40 \mu\text{g/L}$ for arsenite). In particular, the breakthrough curves of arsenate removal have less deviation for the loss reaction. This results from the strong adsorption affinity in the iron-oxide interface on sand, and then arsenate can be retained among sand particle pores. The oxyanionic competitive adsorption was also observed in the results of the model simulation (Figure 2b). The deviation between model fitting and experimental results increased in the presence of sulfate and nitrate. In particular, the groundwater spiked with arsenate has deviated from the model fitting at higher effluent time. This indicates that arsenic transport can be regulated by mass transfer inhibiting factors, such as competing oxyanion and surface complexation affinity.

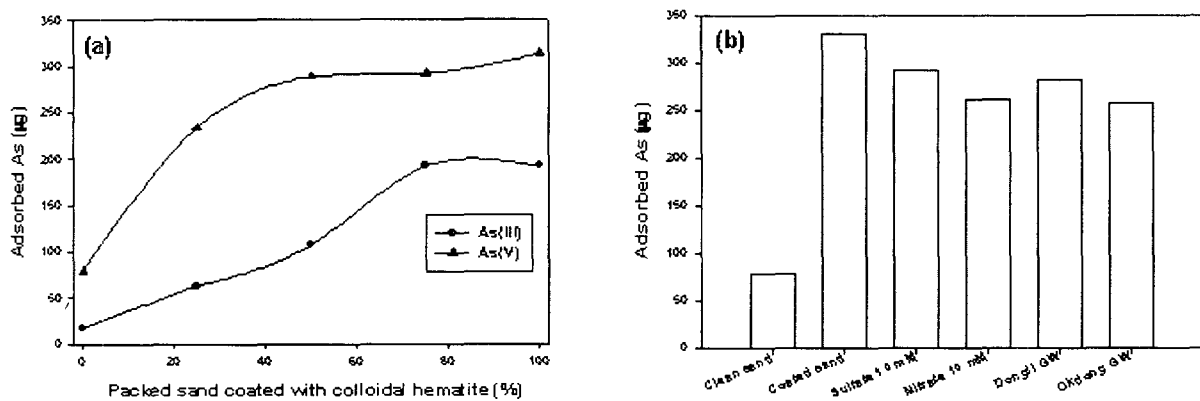


Figure 2. Adsorbed amount of As computed from model fitting during arsenic transport in a iron-oxide coated sand porous media.

3. Conclusions

Although the sand coated with iron-oxide colloids was effective in the arsenic removal, the operative parameters should be considered in the design of the removal system for a permeable reactive barrier of groundwater or for a home treatment unit of drinking water. In specific, the following conclusions suggest the factors and mechanisms controlling the arsenic adsorption and transport in a dynamic column environment.

- The analytical solution of the transport model reflected the significance of mass loss term. The better fitting in the low breakthrough concentration for arsenite was observed, but the fitting for arsenate was similar to that modeled without a loss reaction term. Further, the sorbent dose of coated sand showed the limited adsorption amount of arsenic during the flow environment.
- Arsenic retention was regulated by non-equilibrium of arsenic adsorption in a porous iron-oxide iron-oxide coated sand media. The model calibration determined the equilibrium partitioning coefficient and mass loss coefficient. Despite of the unproven chemical mechanism through

model fitting, the fast adsorption and slow transfer or diffusion of arsenic onto surfaces of coated sand is seem to be related with non-equilibrium processes.

- Model fitting also resolved the competitive adsorption in the presence of sulfate and nitrate. The delayed breakthrough near MCL (10 µg/L) occurs because the competitive oxyanions can inhibit the adsorption of arsenic in a dynamic column environment.

References

- Ko, I.W., Kim, J.Y., Kim, K.W., 2002, "Colloid barrier formation by nanoscale hematite particles", *4th Int'l Symp. on AEM, Cheju, Korea*.
- Joshi, A., Chaudhuri, M. J. of Environ. Eng. 122 (1996) 769.
- Rakesh, Chandra Vaishya and Sudhir, Kumar Gupta, 2003. Coated sand filtration: an emerging technology for water treatment *Journal of water supply research and technology - aqua*, 52(4), pp.299-306