Published in final edited form as:

Chemosphere. 2012 February ; 86(6): 648–654. doi:10.1016/j.chemosphere.2011.11.012.

Intra-particle migration of mercury in granular polysulfide-rubber-coated activated carbon (PSR-AC)

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Abstract

The depth profile of mercuric ion after the reaction with polysulfide-rubber-coated activated carbon (PSR-AC) was investigated using micro-x-ray fluorescence (μ -XRF) imaging techniques and mathematical modeling. The μ -XRF results revealed that mercury was concentrated at 0–100 μ m from the exterior of the particle after three months of treatment with PSR-AC in 10 ppm HgCl_2 aqueous solution. The μ -X-ray absorption near edge spectroscopic (μ -XANES) analyses indicated HgS as a major mercury species, and suggested that the intra-particle mercury transport involved a chemical reaction with PSR polymer. An intra-particle mass transfer model was developed based on either a Langmuir sorption isotherm with liquid phase diffusion (Langmuir model) or a kinetic sorption with surface diffusion (kinetic sorption model). The Langmuir model predicted the general trend of mercury diffusion, although at a slower rate than observed from the μ -XRF map. A kinetic sorption model suggested faster mercury transport, which overestimated the movement of mercuric ions through an exchange reaction between the fast and slow reaction sites. Both μ -XRF and mathematical modeling results suggest mercury removal occurs not only at the outer surface of the PSR-AC particle but also at some interior regions due to a large PSR surface area within an AC particle.

Keywords

intra-particle transport; diffusion; mercury; polysulfide-rubber polymer; activated carbon

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1. INTRODUCTION

Mercury species in nature include various complexes, e.g., HgCH_3^+ , HgS^0 , and colloidal NOM (natural organic matter)-bound mercury in the aqueous phase as well as clay (or other particulate matter)-bound mercury in the solid phase. Since the stability constants between mercuric ion and natural organic matter (Haitzer et al., 2002) are comparable to those between mercuric ion and reduced sulfur groups (Reddy and Aiken, 2001; Hesterberg et al., 2001), NOM is expected to be associated with a large portion of mercuric ions in organic-rich sediments (Slowey, 2010).

Although the bioavailable portion of the total mercury has not been fully characterized, a number of studies indicate that mercury sorption on particulate matter (Perdicakis et al., 1999; Roux et al., 2001) in sediments reduces the bioavailability of mercury to methylating bacteria. However, the dissolution of sparingly soluble cinnabar by dissolved organic matter (DOM) (Ravichandran et al., 1998; Ravichandran, 2004) poses potential ecological risks.

The extent of solid-phase mercury dissolution may depend on reaction with DOM (Slowey, 2010; Waples et al., 2005). Therefore, suppressing the contact between DOM and the immobilized mercury would decrease the risk of increased bioavailability and transport. Similarly, physical isolation of the mercuric ion from bacteria would also help reduce the bioavailability of mercury for methylation. Therefore it is imperative to understand accessibility of immobilized mercury in order to estimate the bioavailability of immobilized mercuric ion in the presence of DOM and methylating bacteria. In this study, we investigated the accessibility of the immobilized mercury on particles of polysulfide-rubber-coated activated carbon (PSR-AC). One proxy for the accessibility of the mercury retained by PSR-AC is the distance between the particle exterior and the mercuric ion inside the particle.

Previous studies on the intra-particle diffusion of hydrophobic organic compounds (HOCs) into activated carbon (Ahn et al., 2005) showed sorption-retarded radial diffusion of the HOC molecules (Ball and Roberts, 1991; Grathwohl, 1998), where solute transport through a particle was described using parallel processes of macropore and micropore diffusions (Peel et al., 1981). Mercuric chloride can diffuse into activated carbon (AC) faster than hydrophobic compounds due to a greater diffusion coefficient and a smaller AC/water partition coefficient. However, AC surface modification or infusion of reactive components into the AC could significantly impede the diffusion of mercuric ion via surface reactions.

Mercuric ion removal efficiencies by AC can be enhanced by polysulfide-rubber (PSR) coating on AC (Kim et al., 2011) as mercuric ion forms a chemical bond with sulfur atoms in the PSR polymer. However, it is not clear whether the reaction takes place primarily at the edges and the particle exteriors, as in metal complexation models (Henry et al., 1992) for minerals, or whether mercuric ions are able to penetrate PSR-AC by intra-particle diffusion (Axe and Trivedi, 2002; Wu et al., 2001). Since the polymer coating on AC can change the porosity and the extent of solute retardation, the mercury movement within the PSR-AC particle is expected to depend on the polymer distribution in AC. If the polymer coating seals up the outer surface with a thin sulfur-polymer film, mercury diffusion rates in PSR-AC should be the same as in PSR thin films. If the PSR polymer is more evenly distributed throughout the AC particle, the reaction site densities should be fairly uniform across the particle. Therefore, the mercury transport within the PSR-AC particle would be analogous to the retarded diffusion of HOCs into an AC particle with a smaller porosity and a different partition coefficient for mercuric ion.

The purpose of this study is to understand the micro-scale movement of the mercuric ion through a reactive porous sorbent with polysulfide-rubber. The results suggest a reactive

intra-particle diffusion of mercuric ion into PSR-AC, which is conceptually similar to the intra-particle diffusion of hydrophobic organic compounds into virgin AC.

2. Materials and methods

2.1 Polymer coating on activated carbon

The polymer was synthesized following the procedure described by Kalaei et al (2009). Condensation polymerization between sodium tetrasulfide and 1,2-dichloroethane, using methytributylammonium chloride as a phase transfer catalyst, produced a yellowish elastic solid in water. The polymer block was boiled twice in deionized water for one day each to remove residual salts. The polymer was dried in an oven at 105°C over night.

One gram of the polysulfide polymer in 200 mL toluene was refluxed until the polymer completely dissolved to make a homogeneous solution. The solution was cooled to room temperature and 2.0 g of the HD3000 activated carbon (Norit Inc.) was added. The slurry was refluxed for 24 hours followed by stirring at room temperature for 48 hours. The product was collected by vacuum filtration on a Teflon membrane filter and it was rinsed with toluene and methylenechloride to remove the residual polymer on the particles. The filtered AC was dried at 50°C until constant mass.

The modified AC was characterized by BET (Coulter SA 3100) to estimate the changes in the pore size distribution and the surface area. The sulfur content of the AC before and after the modification was determined in duplicate by an elemental analysis at Atlantic Microlab, GA, United States.

2.2 Mercury contact scheme

Mercuric chloride (Sigma Aldrich) was used to prepare 8.11 g Hg L^{-1} stock solution in a 2M HCl, which was diluted to make 10 mg Hg L^{-1} (49.9 μM) HgCl_2 solution. The mercury bound PSR-AC samples used for μ -XRF analyses were prepared by adding 50 mg PSR-AC (S: 12.5 wt%, 3.91 mmol g^{-1}) in 200 mL of 10 mg Hg L^{-1} HgCl_2 solution at pH 7 for three months after which the particles were filtered, gently washed with DI-water, and dried in a glove box.

Initial HgCl_2 aqueous solutions varying from 5 to 50 mg Hg L^{-1} in 0.01M pH 7 phosphate buffer were used for adsorption isotherm studies. Ten mg of adsorbents were reacted with 40 mL mercury solution in duplicate. The vials were shaken at 300 rpm for three months.

2.3 Total mercury analysis

One mL of duplicate samples was taken out and filtered through 0.45 μm polyvinylidene fluoride (PVDF) membrane filter. The filtrate was oxidized with 0.5% BrCl in order to preserve the mercuric ion. The samples were diluted by 800 to 640,000 fold to ensure mercury concentrations were within the detection range of 0.5 to 400 ng L^{-1} . The total mercury concentrations were measured by Tekran 2600 cold vapor atomic fluorescent spectrometry (CVAFS) following the US EPA (Environmental Protection Agency) method 1631 revision E.

2.4 μ -X-ray fluorescence imaging

Synchrotron micro-X-ray fluorescence (μ -XRF) imaging was performed on beamline 10.3.2 at the Advanced Light Source (ALS) and beamline 2–3 at the Stanford Synchrotron Radiation Lightsource (SSRL). The PSR-AC particles reacted with mercuric chloride were dried and cured in EPOTEK 301-2FL resin. Samples were then thin sectioned to 30 μm thickness, and mounted on a quartz slides. The thin section was mapped at 12400 and 3912

eV with $40 \times 40 \mu\text{m}$ step size at ALS. Selected areas were mapped again at 12300 eV with $2 \times 2 \mu\text{m}$ step size at SSRL where mercury micro-X-ray absorption near edge spectroscopy (μ -XANES) analysis was performed. Mercury intensities on maps collected at SSRL were calibrated with AgHg standard to calculate mercury concentrations in $\text{fmoles } \mu\text{m}^{-3}$. Mercury speciation across the particle was determined by XANES fittings; scans were collected from 12054 to 12565 eV. Linear combination XANES spectral fitting was performed using SIXPACK (Webb, 2005) to deduce the proportion of HgCl_2 and HgS characteristics while minimizing reduced chi square values. HgCl_2 salt and HgS (metacinnabar, black) were used as fitting standards.

3. Results and discussion

3.1 Particle analysis of PSR-AC

Table 1 summarizes the bulk properties of HD3000 activated carbon (AC) before and after the polymer coating with PSR. Micropore surface area diminished significantly after the polymer coating and the particle density increased due to the pore-filling effect. Assuming the contribution of microporous area of PSR-AC (1.4% of the total BET area) to the overall reaction is negligible, the major intra-particle mercury transport process should be associated with the macropores that facilitate a relatively fast infusion of mercuric ions in the aqueous phase. The reduced micropore surface area likely resulted from the dead volume formed in the particle core if PSR clogged some macropores in the particle interior. However, according to the cross-sectional sulfur distribution obtained by μ -XRF shown in Figure 1, the PSR polymer covers the AC surface throughout the particle. This results in a fairly uniform distribution of sulfur. Therefore, for assessing the performance of PSR-AC, the creation of more modeling parameters that depend on the PSR depth profile is not necessary.

3.2 Mercury adsorption isotherm with granular type PSR-AC

Mercury adsorption over a wide range of aqueous concentrations was assessed for granular type PSR-AC with 12.5 wt% S, for which the physical properties are described in Table 1. The adsorption isotherm with the initial mercury concentrations ranging from 5 – 50 mg Hg L^{-1} is shown in Figure 2. The results were fitted by a Langmuir equation, $Q_{\text{ac}} = \frac{Q_{\text{acmax}} * K * C_{\text{aq}}}{(1 + K * C_{\text{aq}})}$ to get $Q_{\text{acmax}} = 0.579 \text{ g Hg g}^{-1} \text{ PSR-AC}$ and $K = 2.10 * 10^7 \text{ cm}^{-3} \text{ g}^{-1} \text{ Hg}$, where C_{aq} is aqueous total mercury concentration [g Hg cm^{-3}], and Q_{ac} is the immobilized mercury concentration in PSR-AC [$\text{g Hg g}^{-1} \text{ PSR-AC}$]. Since the initial aqueous mercuric ion concentration for the PSR-AC thin section preparation was $1.0 * 10^{-5} \text{ g Hg cm}^{-3}$, which corresponds to $Q_{\text{ac}} = 0.577 \text{ g Hg g}^{-1} \text{ PSR-AC}$, the reaction begins at a near-saturation point of PSR-AC for mercuric ion. These data indicate that aqueous mercury concentrations decrease by three orders of magnitude during three months of reaction. The non-linear sorption isotherm data suggest a wide range of surface reaction efficiencies during the intra-particle mercury transport processes.

3.3 μ -X-ray fluorescence imaging

μ -X-ray fluorescence images shown in Figure 1 show the distribution of sulfur and mercury across the PSR-AC particle. Sulfur is uniformly distributed across the particle while mercury is concentrated at about a 100 μm -deep layer. The overlay of the two images shows that the mercury layer is not a result of mercury precipitation on the particle exterior, but mercury shares the same zonation with sulfur atoms. On the basis of linear combination XANES fitting, a large proportion of mercury exists as HgS (Table S1), which indicates that that mercury transport in PSR-AC accompanies a chemical reaction between PSR and mercury. Similar result was also observed in our previous study (Kim et al., 2011). This validates the incorporation of mercury sorption reactions in a mass transfer model. The particle at the

lower left corner in Figure 1 has sparse distribution of sulfur compared with the rest of particles; however, it has a thicker mercury layer of relatively lower concentrations. This finding qualitatively illustrates that low sulfur density (i.e., less number of reaction sites for mercuric ions) and better internal connectivity to the liquid phase seem to facilitate a faster diffusion of mercury.

The penetration of mercury into the PSR-AC particle was explained by high resolution μ -XRF depth profile images (Figure 3). The data points for the μ -XRF image in Figure 4 correspond to 35 depth profiles for mercury along the radial axis from the areas X, Y, and Z as depicted in Figure 3-a and 3-b. The μ -XRF spatial resolution is about 2 μ m, and the error bars in Figure 4 represent the standard deviations. The mercury concentrations obtained from the μ -XRF data produced a skewed bell-shape depth profile curve. The observed decreasing mercury concentration near the particle exterior in the μ -XRF images may result from the unequal thicknesses of the thin section near the edge (Figure S1) due to the irregular shape of the PSR-AC particle. As a result, the X-ray beam perturbs a smaller amount of mercury at the edge of the section, yielding less fluorescence. As the thickness of the section increased toward the interior up to $r \approx 770$ μ m (Figure 4), the X-ray beam perturbs more mercury, yielding more fluorescence.

3.4 Intra-particle mass transfer modeling: parameters, equations

An intra-particle mercury diffusion model was used to assess mercury penetration into the porous particles. The terms and units for this model are listed in Table 2. The model was based on the traditional two phase (aqueous and solid) diffusion transport equations of a single homogeneous reaction domain in the solid phase using spherical coordinates (equation (1)).

$$\frac{d}{dt}[\varepsilon C_1 + (1 - \varepsilon)\rho \overline{C}_1] = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_1}{\partial r} \right) \quad (1)$$

The distance from the particle exterior was translated into r by assuming the PSR-AC particle radius is uniformly 0.08 cm. C_1 and $\overline{C}_1$ denote single phase concentrations in water and solid respectively. Therefore the multiplication of $\overline{C}_1$ by the particle density, $(1 - \varepsilon)\rho$, gives a concentration based on a unit volume of the particle. The equation describes the temporal changes of solute mass in water and solid at $r = x$ cm ($0 \leq x \leq R$), which equals the accumulated flux of solute due to concentration gradients near $r = x$ cm ($0 \leq x \leq R$). The equation does not reflect the heterogeneity in the diffusion processes but the diffusion coefficient $D \equiv \varepsilon D_{aq}/\tau$ is globally adjusted with porosity (ε) and tortuosity (τ) factors. Here, the tortuosity is approximated to be an inverse of porosity, and the diffusion coefficient of HgCl_2 , $D_{aq} = 10.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was taken from the literature (Garland et al., 1965). The major mercury species at pH 7 with a chloride ion concentration of 20 mg L^{-1} is HgClOH (Kim et al., 2011), which has a similar molecular size, and thus a similar diffusion coefficient to HgCl_2 when hydration effects are neglected.

Equation (2) describes the bulk aqueous phase concentrations (C_1 at $r=R$) that change with the total immobilized mercury concentrations ($\overline{C}_1$) and porewater concentrations (C_1) in a single PSR-AC particle over time (Ahn et al., 2005).

$$\frac{dC_1(r=R)}{dt} = -\frac{v_{AC}}{v_{aq}} \cdot \frac{d}{dt} \left[\frac{3(1 - \varepsilon)\rho}{R^3} \int_0^R r^2 \overline{C}_1 dr + \frac{3\varepsilon}{R^3} \int_0^R r^2 C_1 dr \right] \quad (2)$$

Depending on the adsorption behavior of a solute, the solid concentration, $\overline{C}_1$, can be estimated using an appropriate model, such as a linear adsorption isotherm, a nonlinear Freundlich model or a Langmuir sorption isotherm model. A Freundlich or Langmuir non-linear sorption isotherm model can represent the mercury retardation more accurately than the linear sorption isotherm model in terms of correlation between wide ranges of the solid and liquid mercury concentrations. According to the Langmuir equation,

$Q_{ac} = Q_{acmax} * K * C_{aq} / (1 + K * C_{aq})$, the mercury immobilization efficiency is lower at a higher aqueous concentration. Therefore the mercury retardation at the early stage with a high mercury concentration should be less than that after the aqueous concentration decreases by orders of magnitude. The sorption-retarded diffusion transport equation (3) assumes a fast equilibrium between the porewater and the solid surface following a Langmuir sorption isotherm model when the solute resides inside the particle.

$$\frac{d}{dt} \left[\varepsilon C_1 + (1 - \varepsilon) \rho \frac{Q_{acmax} K C_1}{1 + K C_1} \right] = \frac{\varepsilon D_{aq}}{\tau r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_1}{\partial r} \right) \quad (3)$$

Nano-scale reaction volume of the inner-particle pore facilitates a fast reaction inside PSR-AC, which would make a local equilibrium assumption used in equation (3) relevant. However, the reaction rates below the PSR polymer/porewater interface may not be fast enough to neglect kinetic factors depending on the polymer thickness. Figure S2 depicts the two different reaction sites that correspond to the fast (i.e., in equilibrium state) and the slow reaction sites. Unlike the Langmuir model (3), a kinetic sorption model (equation (4) and (5)) differentiates diffusion rates at fast reaction sites from that at slow reaction sites, and it incorporates a kinetic term accounting for the change in solute mass from fast to slow reaction sites.

$$f \frac{dC_{fast}}{dt} = f \frac{D_\varepsilon}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{fast}}{\partial r} \right) - k_f (C_{fast} - C_{slow}) \quad (4)$$

$$(1 - f) \frac{dC_{slow}}{dt} = k_f (C_{fast} - C_{slow}) \quad (5)$$

Equations (4) and (5) describe mass balances at the fast and the slow reaction sites respectively. Here, C_{fast} (g Hg cm⁻³) is the porewater mercury concentration in the fast reaction regime, equivalent of an equilibrium state, and C_{slow} (g Hg cm⁻³ PSR-AC) is the porewater concentration of mercury in the slow reaction regime. The contribution of the fast reaction sites to the overall mercury transport rate is proportional to f , the fraction of the fast reaction sites. Mass transfer behavior at the fast reaction sites is analogous to the traditional diffusion transport model as described in equation (1), except that the exchange of mercury between the fast and the slow reaction sites facilitates the spreading of mercury throughout the slow reaction sites. Equation (4) is also different from equation (3) in that the apparent diffusion rate is independent of the aqueous concentration, but uses a constant surface diffusion coefficient, D_s .

To describe the overall mercury adsorption efficiencies of PSR-AC, the kinetic sorption model invoked the sorption isotherm data fitted with a Langmuir equation (Figure 2) to calculate the solid phase mercury concentrations at the fast reaction sites. The solid phase

concentrations at the slow reaction sites were estimated by a forward Euler method analogous to equation (5), where the aqueous concentrations (C_{fast} and C_{slow}) were substituted with the solid concentrations ($\bar{C}_{fast}$ and $\bar{C}_{slow}$) respectively. Similar to the Langmuir model, the solid and liquid phase mercury concentrations within a particle, $\bar{C}_{fast}$, $\bar{C}_{slow}$, C_{fast} and C_{slow} , update the boundary condition according to equation (2). The values for the fitting parameters, f , D_s , and k_f were obtained from the best fit of the experimentally measured final aqueous concentration with the one that the model predicted. The fitting parameters of $f = 0.127$, $k_f = 9.25 \times 10^{-8} \text{ s}^{-1}$, and $D_s = 1.44 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ resulted in the least square residual value. The kinetic sorption model with these parameters (Figure 5) showed a somewhat faster diffusion of mercury into the particle compared to the μ -XRF data (Figure 4).

Figure 5-c summarizes the results of the Langmuir sorption isotherm and the kinetic sorption concept compared with the μ -XRF data, which are normalized by the total mass of mercury in a particle calculated from each distribution. Assuming the diminishing mercury concentrations near the edge of the cross-section as shown in Figure 4 is an artifact created during the sample preparation, the right shoulder of the graph was removed for the comparison with the modeling results. T-tests with $\alpha = 0.05$ determined the range of r in the right shoulder that could be treated as statistically equal to the mercury concentration at the peak (at $r = 0.758 \text{ mm}$). According to the t-test results, $0.758 \text{ mm} \leq r \leq 0.768 \text{ mm}$ is the region where the average intensity is statistically same as that at $r = 0.758 \text{ mm}$. As a result, the mercury concentrations at $r \leq 0.768 \text{ mm}$ shown in Figure 4 were regarded as the region where the mercury distribution was formed by an intra-particle solute transport, which is relevant to the modeling.

Therefore, the discrepancies between the two depth profiles are to some extent inevitable because the depth profile curve shape of the model (i.e., half bell shape) does not match with that of the experimental result (i.e., bell shape). The irregular shape of the PSR-AC resulted in the dilution of mercury near the particle exterior up to $30 \mu\text{m}$ deep, which was cut off from the original μ -XRF data (Figure 4) to match the shapes of the model depth profiles. Consequently, the experimental results in Figure 5-c) represent a slower overall mercury transfer rate and thus concentrating more toward the edge.

A faster diffusion rate obtained from the kinetic sorption model may also result from overestimating the diffusion rate in the fast reaction sites of PSR-AC or the exchange reaction rate between the fast and the slow reaction sites. The reason for this overestimation may come from the underlying assumption of equation (4) such that the retardation effect from the reaction between PSR and mercury ion in the fast reaction sites can be incorporated in a lumped parameter, D_s . However, the fitting result for D_s may underestimate the retardation effect especially at low mercury concentrations, which in turn procures a faster diffusion rate throughout the particle. The assumption that the exchange reaction linearly depends on the concentration gradients between the fast and slow reaction sites may also result in underestimating the retardation effect during the exchange reaction.

The observed depth profile falls closer to that for the kinetic sorption model than the Langmuir model, although the depths for 95% of the total mercury distribution are within the same order of magnitude (Langmuir: $24 \mu\text{m}$, μ -XRF: $64 \mu\text{m}$, kinetic sorption: $144 \mu\text{m}$). The discrepancies between the modeling results and the observation may be due to the assumptions used for the simplification of the models. The Langmuir model used a single reaction domain where mercuric ion is in equilibrium between water and the PSR-AC surface, and the kinetic sorption model assumes constant D_s and k_f that are independent of the aqueous concentrations throughout the whole transport processes. Conversely, the two models could complement each other by adapting the concept of non-equilibrium reaction

from a kinetic sorption model, and the concentration dependent retardation of mercuric ion from a Langmuir model. The slow reaction sites may represent the non-equilibrium reaction sites where the transport pathway can be regarded as a pure diffusion process without retardation, and the fast reaction sites may represent the equilibrium reaction sites where mercuric ions behave according to a Langmuir sorption model.

4. Conclusion

This study results indicated that reaction-mediated intra-particle diffusion was associated with the immobilization processes of mercuric ions with PSR-AC. The presence of a surface-mediated chemical reaction was supported by the μ -XANES analysis showing a large fraction of the total mercuric ions within the PSR-AC particle was in the HgS form. The mathematical modeling results provided rough estimates of the mercury depth profile in the PSR-AC particle, but revealed that the mercuric ion diffusion could not be described with a simple Langmuir model or entirely by a kinetic sorption model. The Langmuir model demonstrated the fate of mercuric ions at the maximum extents of retardation, which predicted a much slower mercury transport rate. The kinetic sorption model is a powerful tool for estimating the mercury depth profile without having experimental values of a fast to slow reaction site ratio, a diffusion coefficient, and a reaction constant. The kinetic sorption model in this study resulted in some differences from the observed mercury depth profile. This may be due to the changes in surface diffusion coefficient and solute exchange rate between the fast and slow reaction sites depending on aqueous concentrations that changed by three orders of magnitude over three months. Because natural waters have smaller extent of variation in aqueous mercury concentrations, a kinetic sorption model is expected to be more suitable for a natural water system. Therefore, it might be reasonable to utilize a kinetic sorption model to understand the micro-scale movement of other small neutral mercury species of unknown diffusion coefficients in nature with corresponding partition coefficients. This study results indicate that smaller particle size of PSR-AC should be used to fully utilize the PSR-coated surface when the practical reaction time is less than a few months.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors acknowledge the National Institute of Environmental Health Sciences (NIEHS), grant number R01 ES016143-02, for the financial support of this study. The authors would like to thank Prof. David Werner at Newcastle University, UK, for providing the Matlab codes for a Langmuir sorption-mediated diffusion transport model and a kinetic sorption model. We thank Sam Webb and Matthew Marcus for μ -XAS/XRF data collection and analysis. A portion of this research was conducted at ALS and SSRL, user facilities supported by the Department of Energy, Office of Basic Energy Sciences.

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HIGHLIGHTS

- Mercuric ions can migrate into the interior of a PSR-AC particle
- Intraparticle transport of mercuric ion within PSR-AC involves chemical reactions.
- The chemical reactions retard the intraparticle transport rate of mercuric ion.
- A kinetic sorption model approximates the overall mercury transport rate.

Figure 1.
 μ -XRF images of PSR-AC cross-sections. a) sulfur, b) mercury distribution, and c) overlay of the two images.

Figure 2.

Mercury adsorption isotherm fitted with a Langmuir sorption model. Each circle represents an averaged point for the duplicate, and the linear trend line is derived from the average data points. (C_{aq} : aqueous concentration of total mercury, Q_{ac} : solid concentration of total mercury in PSR-AC) The sulfur content of the granular PSR-AC particle was 12.5 wt%.

Figure 3. μ -XRF images of a PSR-AC particle. a) Overlay of mercury and sulfur maps as shown at the right side of Figure 1-c. b) High resolution μ -XRF images corresponding to boxes, X, Y, and Z.

Figure 4.

Mercury depth profile obtained from the high resolution μ -XRF images. (r: distance from the center of the particle, R: radius of the particle = 0.08 cm). The solid line represents the average concentrations of 35 depth profiles and the error bars represent the standard deviations.

Figure 5.

Intra-particle reactive diffusion modeling results. a) Langmuir sorption isotherm model, b) kinetic sorption model for three months of HgCl₂ transport in spherical PSR-AC ($R = 0.08$ cm). C_{ac} denotes solid mercury concentration at r in PSR-AC, and C_{acss} denotes a steady state solid mercury concentration in PSR-AC. c) comparison between the experimental data and the modeling results; here, the mercury concentrations were normalized by the total mercury across the particle to calculate the relative abundances (i.e., the area under each curve is one). The μ -XRF data represent the average mercury concentrations of 35 depth profiles along the radial axis.

Table 1

Particle properties of granular AC before and after the PSR coating

	AC	AC after PSR-coating
BET surface area ^a [m ² g ⁻¹]	600	168
Micropore surface area ^a [m ² g ⁻¹]	264	2.3
Average particle radius [cm]	0.08 ^b	0.08
Particle density [g cm ⁻³]	0.588 ^b	0.69 ^c
Porosity [-]	0.58 ^b	0.09 ^d
Sulfur content ^a [wt %]	0.79	12.5

^a BET surface area, micropore surface area, and sulfur content are measured values.

^b These values are calculated based on the data reported in the literature (Clark and Lykins, 1989).

^c Particle density of AC after PSR-coating was calculated assuming all polymer filled the inside of the AC and neglecting the portion of polymer covering the outer-surface of AC.

^d Porosity of AC after PSR-coating was estimated with the BET surface area assuming the relationship of pore volume/mass $\approx k \cdot (\text{surface area}/\text{mass})^{1.5}$, where k is a constant.

Table 2

Summary of variables and parameters used in the modeling equations

variables and parameters	Definition	unit
r	distance from the center of the particle	cm
R	radius of the particle	cm
t	reaction time	s
V_{AC}	total volume of PSR-AC in the system	cm ³
V_{aq}	total volume of water in the system	cm ³
C_l	porewater concentration of mercury in PSR-AC	g Hg cm ⁻³
$\overline{C}_1$	solid concentration of mercury in equilibrium with C_l	g Hg g ⁻¹ PSR-AC
ρ	solid density of PSR-AC	g PSR-AC cm ⁻³
ε	inner porosity of PSR-AC	-
τ	tortuosity of PSR-AC	-
D_{aq}	diffusion coefficient of HgCl ₂ in water	cm ² s ⁻¹
Q_{acmax}	maximum mercury concentration in PSR-AC	g Hg g ⁻¹ PSR-AC
K	Langmuir adsorption coefficient	cm ⁻³ g ⁻¹ Hg
C_{fast}	porewater concentration of mercury in fast reaction sites of PSR-AC	g Hg cm ⁻³
C_{slow}	porewater concentration of mercury in slow reaction sites of PSR-AC	g Hg cm ⁻³
f	fraction of fast reaction sites out of the total reaction sites in PSR-AC	-
D_s	surface diffusion coefficients of mercury in PSR-AC	cm ² s ⁻¹
k_f	exchange reaction constant	s ⁻¹