

Supporting Information
for
“TiO₂-photocatalyzed As(III) oxidation in a fixed-bed,
flow-through reactor”

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SECTION S.1. ADDENDUM TO MATERIALS AND METHODS

SEM sample preparation. In preparation for examining coating thickness, beads were immobilized in epoxy, ground down to expose cross sections (Buehler Ecomet 3, 1 μM grinding size), and coated with a 9 nm layer of carbon (Cressington Turbo Carbon Evaporater 208c). To assess surface morphology, beads were immobilized with carbon tape and coated with a 4 nm iridium layer (Cressington Sputter Coater 208 HR).

Sample preparation for LC-ICP-MS analysis. Samples collected from runs with influent As(III) concentrations of 2.6 μM and 8.3 μM were diluted 3-fold and 10-fold in water. Standards (0.033–1.33 μM , PlasmaCal) were prepared in the same matrix as the samples being analyzed (i.e. 5 mM NaNO_3 or synthetic groundwater). The LC injection volume was 50 μL . An anion exchange column (Agilent speciation column with guard column) with an eluent solution of 3.4 mM phosphate, 0.26 mM EDTA, and 2% methanol (pH 6.0) was used to separate As(III) and As(V) peaks, resulting in respective retention times of 2.4 and 7.3 min at a flow rate of 0.9 mL min^{-1} .

Table S.1. Salts used for preparation of influent solutions and/or synthetic groundwater. All chemicals were analytical reagent grade. All solutions were prepared using 18.2 MΩ MilliQ water (Millipore).

| Salt | Manufacturer |
|---------------------------------------|---------------------|
| NaAsO ₂ | J.T. Baker |
| NaNO ₃ | Mallinckrodt |
| CaCO ₃ | Merck |
| NaHCO ₃ | Mallinckrodt |
| MgSO ₄ •7 H ₂ O | Mallinckrodt |
| SiO ₂ •xH ₂ O | Mallinckrodt |
| CuCl | Mallinckrodt |
| NaF | Sigma |
| FeSO ₄ •7 H ₂ O | Mallinckrodt |
| MnCl ₂ •4 H ₂ O | Fisher Scientific |
| KH ₂ PO ₄ | Mallinckrodt |
| SrCl ₂ •6 H ₂ O | Mallinckrodt |
| ZnSO ₄ •7 H ₂ O | Sigma |
| KOH | J.T. Baker |

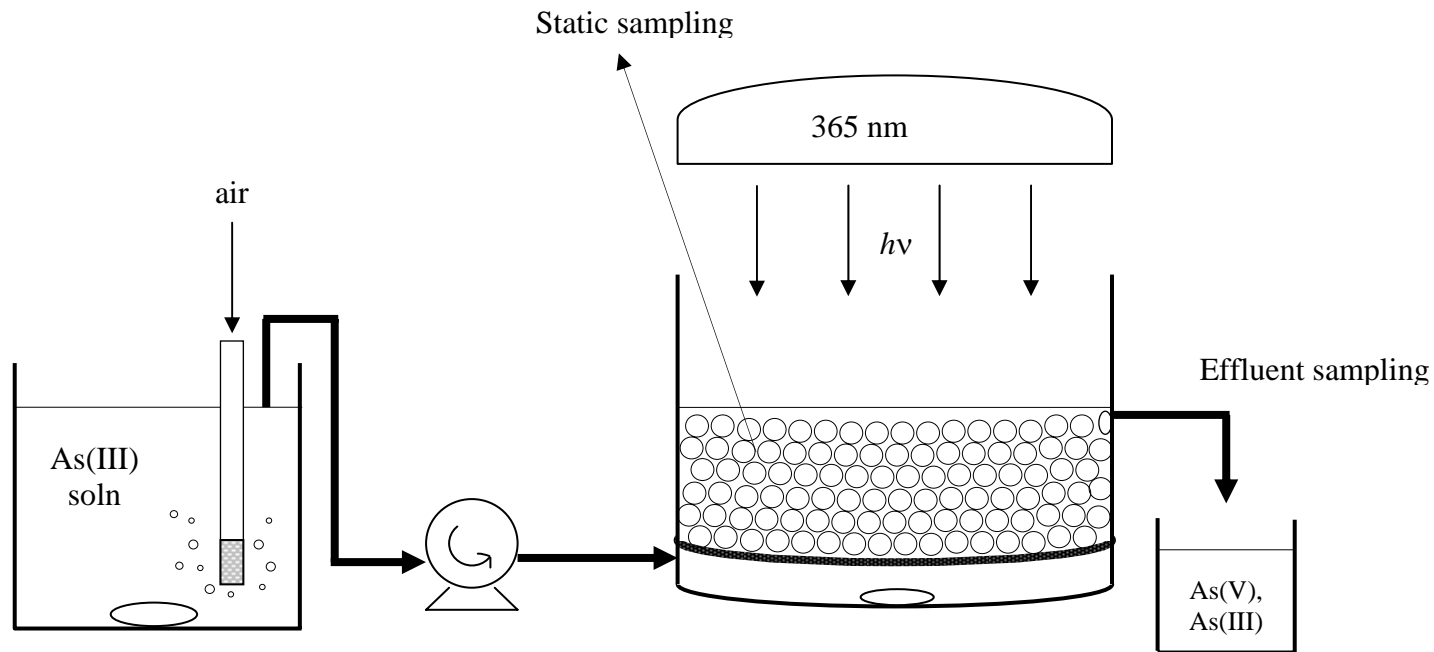


Figure S.1. Schematic of the reactor. Each bead layer contained 149 beads, and the pore volume of the bead-filled chamber was 42 mL.

Table S.2. Conditions for modeling (Geochemist's Workbench 6.0, X1t). Inlet composition was identical to initial composition for the first model, whereas the inlet composition for the lateral flow model was defined as the output of the upward flow model. Porosity = 0.42, run time = 100 min, specific discharge = 0.0007928–0.00357 cm s⁻¹ (corresponding to average residence times ranging from 26.25–5.85 min). For upward flow model: length = 2.5 cm, width = height = 5.8 cm. For lateral flow model: length = 0.75 – 5.95 cm, width = 5.8 cm, height = 0.5 cm.

| Component | Initial Composition |
|----------------------------------|--------------------------------------|
| H ₂ O | 1 kg (solvent) |
| As(OH) ₄ ⁻ | 2.64 μmolar |
| NO ₃ ⁻ | 5 mmolar, used for charge balance |
| Na ⁺ | 5 mmolar |
| H ⁺ | pH = 6.4 |
| O _{2(aq)} | 0.26 mM |
| AsO ₄ ⁻⁻ | 1 e-20 μmolar |

Table S.3. Contributing fraction of the six nodes to the total rate constant used in the model. Each node represents one bead layer, where influent solution progresses upward from node 1 to node 6. Fractional values for nodes 4–6 were assigned according to the fraction of incident light passing through each bead layer; fractions for nodes 1–3 were set arbitrarily because transmitted light was below the limit of quantitation.

| Node, <i>i</i> | Fraction of total rate constant, <i>f(i)</i> |
|-------------------|---|
| 1 | 0.00352 |
| 2 | 0.00469 |
| 3 | 0.00916 |
| 4 | 0.0194 |
| 5 | 0.0918 |
| 6 | 0.872 |

The default rate law in Geochemist's Workbench (GWB) was overridden using scripts which assigned the first-order rate law as a function of node i :

$$\text{Rate} = \text{Wmass} * \text{rate_con} * \text{molality}(\text{"As(OH)3"}) * f(i) * 6,$$

Where Wmass is the mass of water (i.e., it adjusts for node volume) and rate_con is the overall reactor rate constant inputted into the GWB interface. The rate was multiplied by a factor of 6 to adjust for the 6 nodes.

The variable length of the second GWB model was designed to incorporate 0.1 cm of upward flow through the top bead layer in addition to a variable distance representing lateral flow toward the reactor outlet. Since the top bead layer was cylindrical, the lateral flow took place across a circular cross section. This cross section was segmented into 5 circular arc sections of equal length on the diameter, and the midpoint of each section was taken to represent all effluent issuing from that section (Figure S.2). Model outputs were calculated for each of the 5 path lengths and multiplied by the percent area contribution values to get a weighted average $[\text{As(III)}]_{\text{out}}$.

Experimental flow was determined to be laminar based on Reynolds numbers ranging from 0.21–0.94.

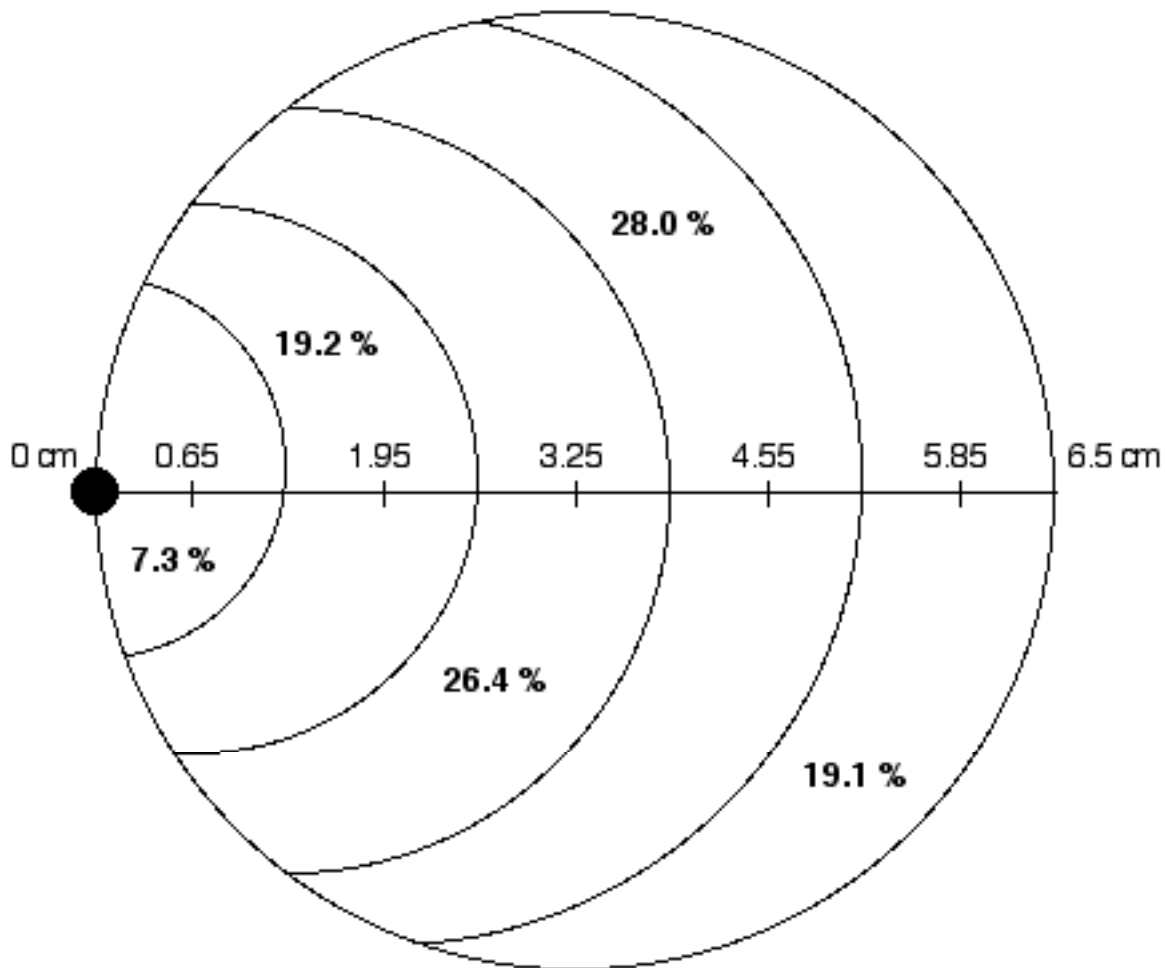


Figure S.2. The five sections of the top bead layer used in modeling reactor output and their corresponding contributions to total area. Path length used in the model is equal to the distance from the outlet (0) plus 0.1 cm for upward flow. Model outputs for each section were multiplied by the percent section area to calculate a weighted average $[\text{As(III)}]_{\text{out}}$.

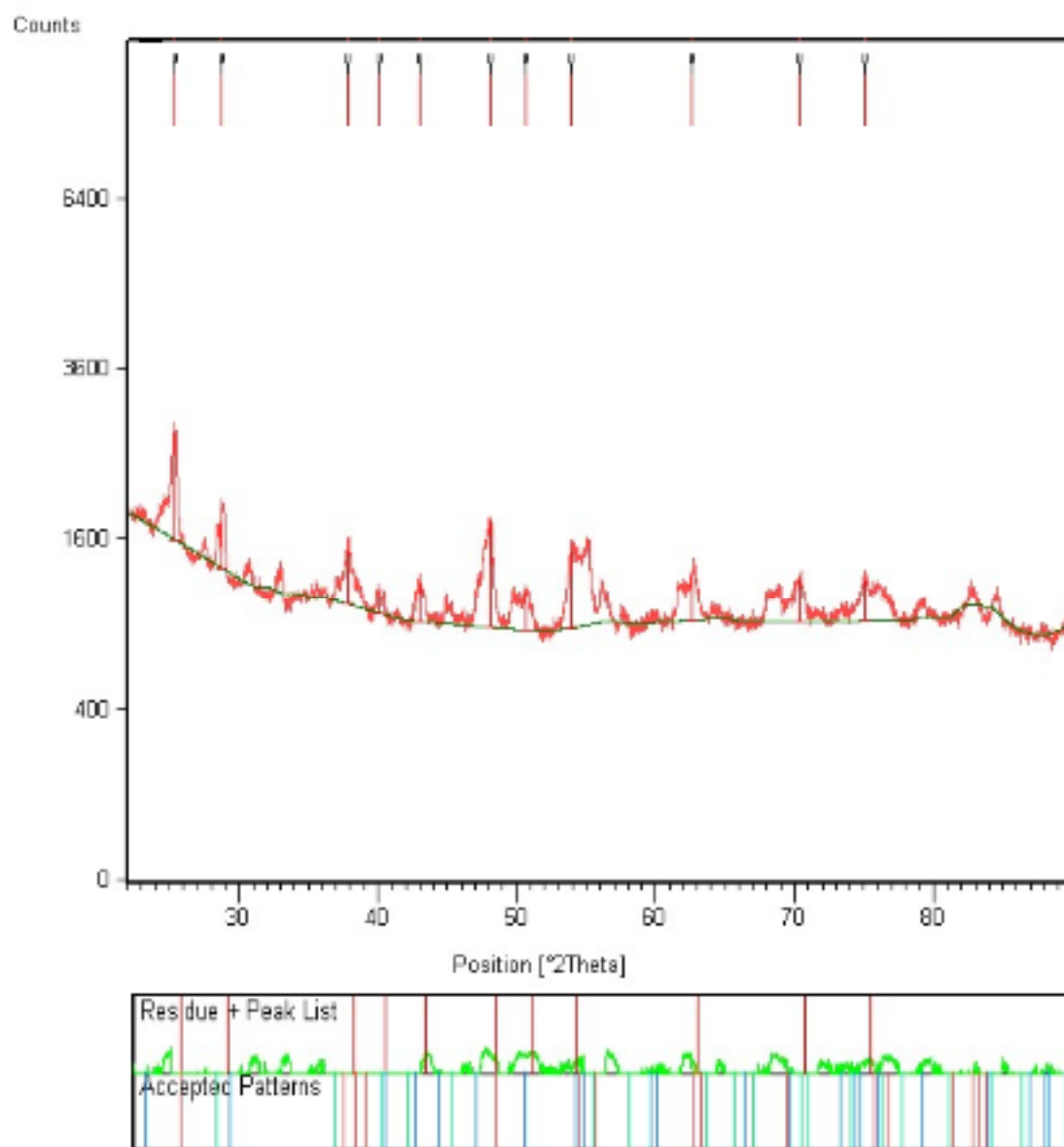


Figure S.3. X-ray diffractogram for a bead coated 8 times with P25/sol-gel. Conditions: step size = 0.0167, time per step = 240. Accepted patterns correspond to anatase (red), rutile (green), and the quartz bead support (blue).

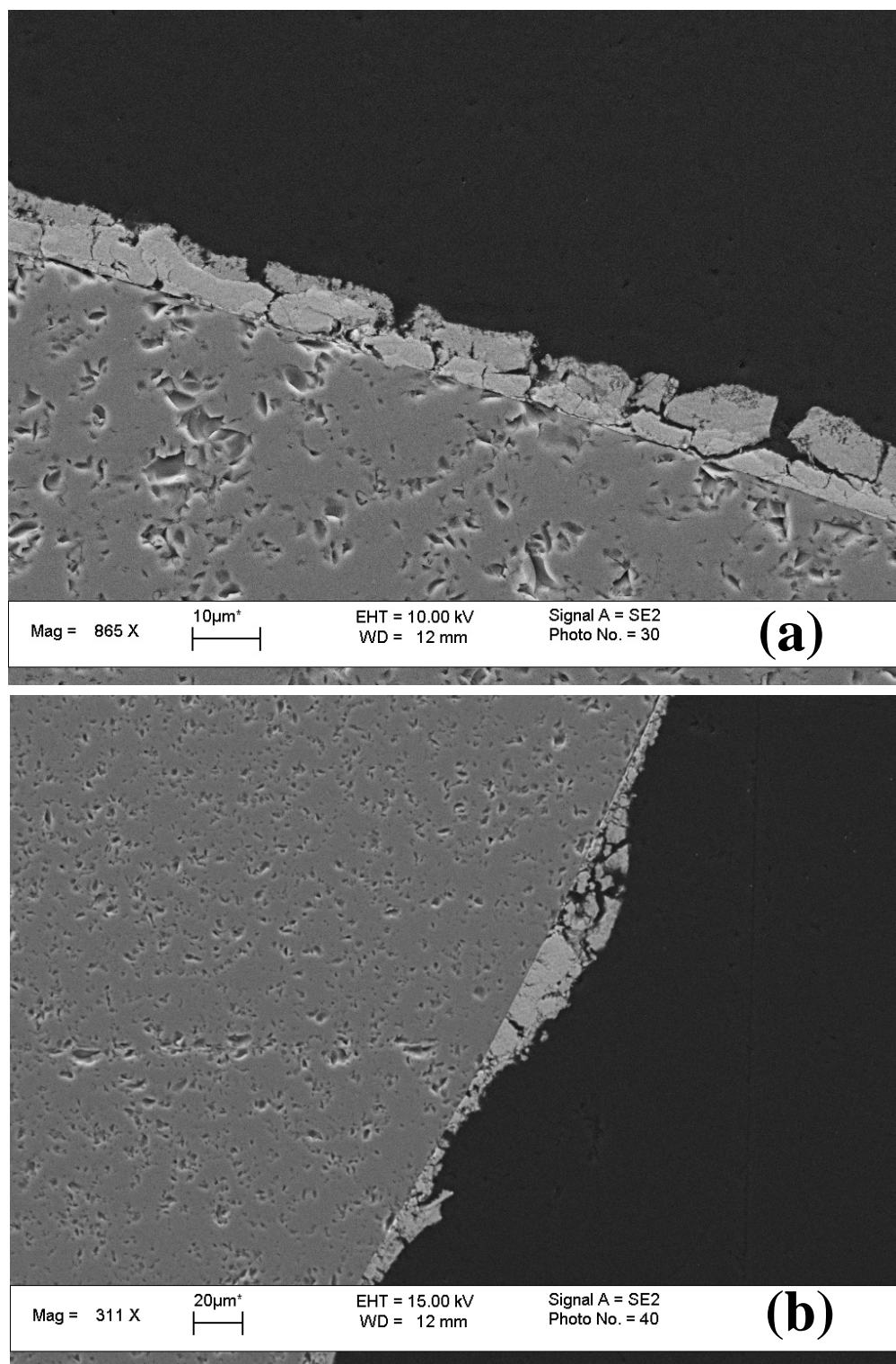


Figure S.4. SEM micrographs of cross-sections of beads coated 8 times (a) and 4 times (b). Conditions: electron high tension = 10 kV (a) or 15 kV (b); working distance = 12 mm, SE2 detector, 865x (a) or 311x (b) magnification.

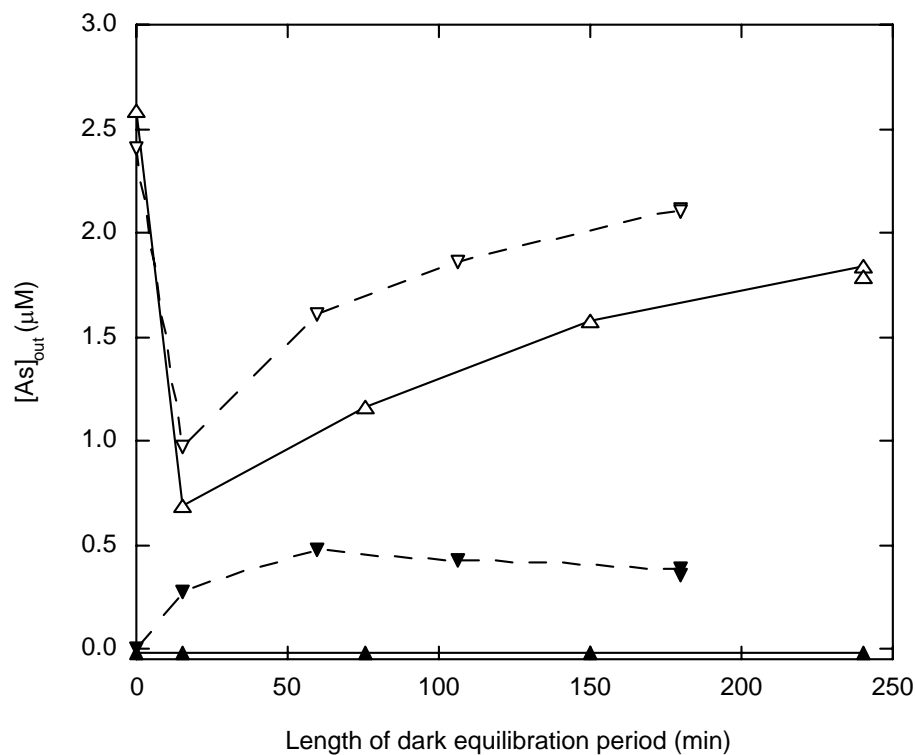


Figure S.5. Effluent As(III) (open symbols) and As(V) (closed symbols) concentrations during the dark sorption equilibration period for new beads (\triangle , \blacktriangle) and beads used 3 times previously (∇ , \blacktriangledown). Influent concentrations are plotted at $t = 0$. Conditions: pH 6.4, $[\text{As(III)}]_{\text{in}} = 2.6 \mu\text{M}$, $[\text{NaNO}_3] = 5 \text{ mM}$, average residence time = 10 min, 4x coated beads.

Table S.4. Conditions and values of steady-state $[\text{As(III)}]_{\text{out}}$ and $[\text{As(V)}]_{\text{out, } t = 180 \text{ min}}$ for all experiments. Groundwater is abbreviated by GW.

| Matrix | Flow rate (mL min^{-1}) | Number of TiO_2 coatings | $[\text{As(III)}]_0$ (μM) | Number of times beads used previously | Steady-state $[\text{As(III)}]_{\text{out}}$ (μM) | $[\text{As(V)}]_{\text{out}}$ at 180 min (μM) |
|---------------------------|---------------------------------------|---|---|---|--|--|
| 5 mM NaNO_3 | 7.2 | 4 | 2.6 | 2 | 0.76 | 1.8 |
| 5 mM NaNO_3 | 7.2 | 4 | 2.6 | 4 | 0.75 | 2.0 |
| 5 mM NaNO_3 | 7.2 | 4 | 2.6 | 4 | 0.61 | 2.1 |
| 5 mM NaNO_3 | 7.2 | 4 | 2.6 | 6 | 0.65 | 1.8 |
| 5 mM NaNO_3 | 4.2 | 4 | 2.6 | 0 | 0.29 | 0.72 |
| 5 mM NaNO_3 | 4.2 | 4 | 2.6 | 0 | 0.39 | 0.82 |
| 5 mM NaNO_3 | 4.2 | 4 | 2.6 | 1 | 0.29 | 1.1 |
| 5 mM NaNO_3 | 4.2 | 4 | 2.6 | 3 | 0.32 | 1.9 |
| 5 mM NaNO_3 | 4.2 | 4 | 2.6 | 5 | 0.42 | 2.3 |
| 5 mM NaNO_3 | 2.7 | 4 | 2.6 | 5 | 0.26 | 2.2 |
| 5 mM NaNO_3 | 2.7 | 4 | 2.6 | 6 | 0.22 | 2.6 |
| 5 mM NaNO_3 | 2.7 | 4 | 2.6 | 7 | 0.30 | 2.0 |
| 5 mM NaNO_3 | 1.6 | 4 | 2.6 | 1 | 0.20 | 0.95 |
| 5 mM NaNO_3 | 1.6 | 4 | 2.6 | 2 | 0.32 | 1.4 |
| 5 mM NaNO_3 | 7.2 | 4 | 8.3 | 3 | 3.0 | 5.3 |
| 5 mM NaNO_3 | 7.2 | 4 | 8.3 | 5 | 2.8 | 5.5 |
| 5 mM NaNO_3 | 7.2 | 4 | 8.3 | 6 | 3.2 | 4.5 |
| 5 mM NaNO_3 | 7.2 | 4 | 0.56 | 4 | 0.13 | 0.56 |
| 5 mM NaNO_3 | 7.2 | 4 | 0.56 | 6 | 0.13 | 0.54 |
| 5 mM NaNO_3 | 7.2 | 4 | 0.56 | 7 | 0.13 | 0.55 |
| 5 mM NaNO_3 | 7.2 | 8 | 2.6 | 3 | 0.85 | 1.0 |
| 5 mM NaNO_3 | 7.2 | 8 | 2.6 | 4 | 0.88 | 1.2 |
| 5 mM NaNO_3 | 7.2 | 8 | 2.6 | 5 | 0.75 | 1.7 |
| 5 mM NaNO_3 | 7.2 | 1 | 2.6 | 0 ^a | 1.1 | 1.6 |
| 5 mM NaNO_3 | 7.2 | 1 | 2.6 | 1 ^a | 0.77 | 1.9 |
| 5 mM NaNO_3 | 7.2 | 1 | 2.6 | 2 ^a | 0.65 | 1.8 |
| synthetic GW | 4.2 | 4 | 2.6 | 0 ^a | 0.86 | 1.6 |
| synthetic GW | 4.2 | 4 | 2.6 | 1 ^a | 0.68 | 1.8 |
| synthetic GW | 4.2 | 4 | 2.6 | 2 ^a | 0.51 | 2.0 |
| high F/PO_4 GW | 4.2 | 4 | 2.6 | 0 ^a | 0.74 | 1.5 |
| high F/PO_4 GW | 4.2 | 4 | 2.6 | 1 ^a | 0.75 | 1.7 |
| synthetic GW ^b | 4.2 | 4 | 2.6 | 2 ^a | 0.22 | 2.0 |

a. Beads were equilibrated with As(III) / As(V) solution overnight and rinsed several times with water prior to their first use.

b. Natural sunlight was used for irradiation rather than a 365 nm UV lamp.

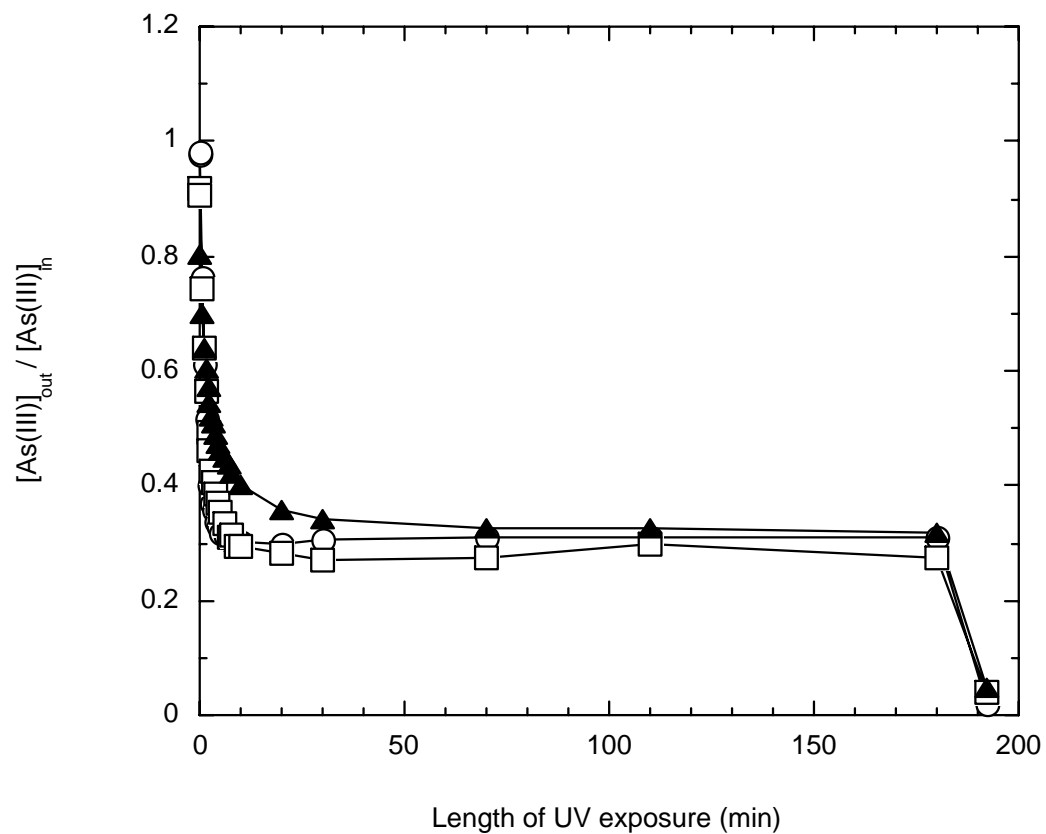


Figure S.6. As(III) oxidation performance for beads coated 1 (○), 4 (□), and 8 (▲), times with mixed P25/sol-gel TiO₂. Conditions: pH 6.4, [As(III)]_{in} = 2.6 μM, [NaNO₃] = 5 mM, average residence time = 5.85 min.

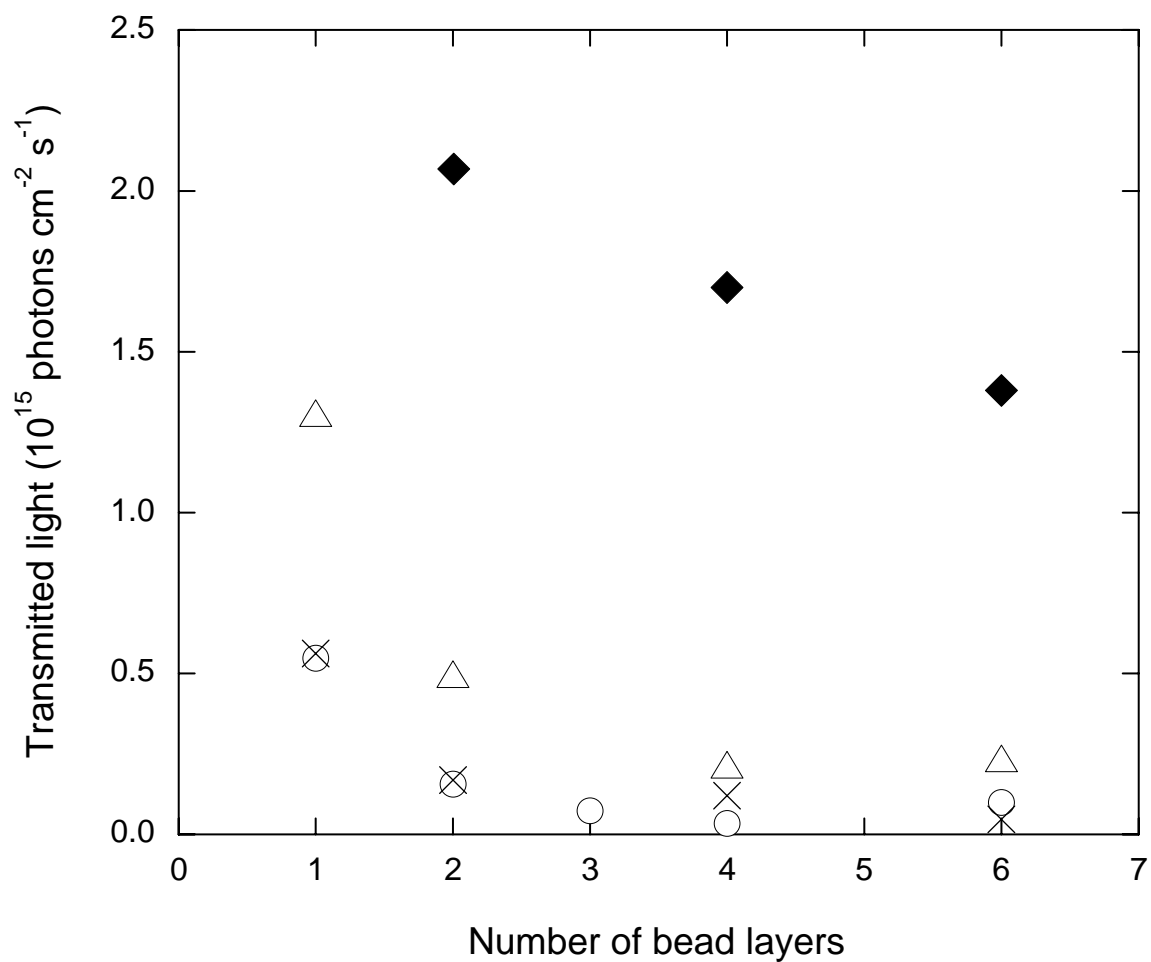


Figure S.7. Transmitted photon flux through successive layers of uncoated glass beads (\blacklozenge) and beads with 1 (\triangle), 4 (\circ), and 8 (\times) TiO_2 coatings. Incident photon flux = 4.3×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$.

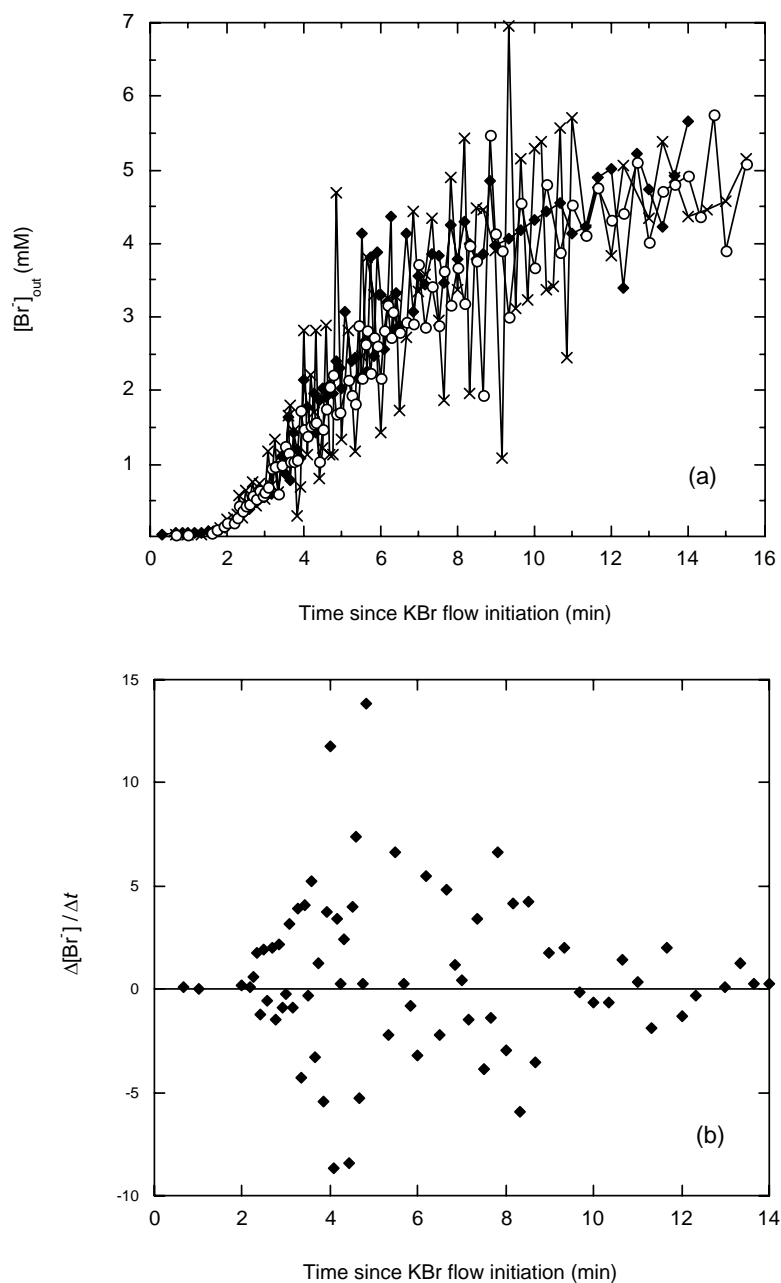


Figure S.8. Flow characterization of the reactor using a bromine-sensitive electrode (Orion) to measure $[\text{Br}^-]_{\text{out}}$. Reactor was first equilibrated with 0.05 mM KBr solution which was substituted by a 5 mM KBr influent solution at time = 0. The Br-sensitive electrode could not measure the effluent directly; instead it was placed in 50 mL of 0.05 mM KBr solution into which effluent dripped, and the change in $[\text{Br}^-]$ was used along with the reactor flow rate to calculate effluent $[\text{Br}^-]$. Three replicate experiments were conducted (a) and averaged. Average values of $\Delta[\text{Br}^-] / \Delta t$ are plotted in (b).