

Supporting information

Fate and Transport of Pharmaceuticals in Iron and Manganese Binary Oxide Coated Sand Columns

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11 pages, 10 Figures, 3 Tables

Synthesis of acid birnessite and goethite

Acid birnessite used in this study was prepared following the procedure of McKenzie¹. Briefly, 166 mL of concentrated HCl was added dropwise to 2.5 L of 0.4 M KMnO₄ using a burette. The temperature of the suspension was maintained at 90 °C while stirring vigorously during the HCl addition. The reaction was continued at 90 °C for a further 10 min. After that, the precipitate was collected by centrifugation and then washed with ultrapure water repeatedly until the conductivity was close to 0.6 µS/cm. The suspensions were stored at 4 °C in polypropylene bottles. Goethite (α -FeOOH) was prepared following Mazeina and Navrotsky's work². Briefly, 500 mL 2.5 M KOH was added to 120 ml 0.5 M Fe(NO₃)₃·9H₂O solution at a rate of 4 mL/min with stirring in Nalgene bottle. Nitrogen was purged before and during the synthesis procedure in order to remove dissolved carbon dioxide. The mixture was then aged for 98 h at 60°C. After precipitation, the solid were dialyzed for 2 weeks using Spectra/Por® Dialysis Tubing (MWCO: 1kD), water was change every day until water conductivity was < 5 µS/cm. The resulting goethite was stored as aqueous suspensions in a Nalgene bottle at ambient temperature in the dark.

Synthesis of goethite-coated sand (GCS) and Acid birnessite-coated sand (MCS)

The Fontainebleau quartz sand (150 – 200 µm) was cleaned following a previous laboratory procedure. Briefly, the uncleaned quartz sand was first refluxed in 1 M HCl for 48 h and then cleaned several times with ultrapure water. Then the sand was dried at 100 °C in an oven for 24 h and cleaned with ultrapure water. Finally, to remove any potential organic contamination, the quartz sand was soaked in H₂O₂ for 24 h and then

rinsed again with ultrapure water several times. Finally, the cleaned quartz sand was dried at 100°C in an oven. The clean, dried quartz was then mixed with a goethite suspension. The ionic strength of the suspension was adjusted to 10 mM using NaCl stock solution. The suspension was then placed in a shaker at 130 rpm for 48 h. The excess solution was decanted, and the solid was washed several times with 10 mM NaCl solution until the runoff was clear. Then the goethite-coated sand (GCS) was dried at room temperature. Similar process was taken for the synthesis of MCS.

pH dependent PIP and Mn(II) adsorption at GCS surface

In 15 mL polypropylene tubes, 0.25g of GCS was placed in a 10 mL of solution containing 10 mM NaCl and 10 μ M PIP at 5 different pH values (4, 5, 6, 7, and 8) using additions of 0.1 M HCl or 0.1 M NaOH solution. In experiments where the effect of dissolved Mn(II) was investigated, 10 μ M MnCl₂ solution was also added. The tubes were then placed in a shaker at 200 rpm for 24 hours. The pH was maintained throughout the course of the experiment. At the end of the experiments, aliquots were withdrawn and filtered (0.2 μ m) for PIP (using HPLC) and Mn(II) (using ICP/AES) analysis. To check the competitive sorption of PIP and Mn(II), only Mn(II) but no PIP existed in the GCS solution was also taken and other procedures kept same to the description before.

Kinetics of PIP removal with 0.05 MGCS

In 15 mL polypropylene tubes, 0.25 g of 0.05 MGCS was placed in a 10 mL of solution

containing 10 mM NaCl and 10 μ M PIP at pH 5.2 and maintained throughout the course of the experiment. The tubes were then placed in a shaker at 200 rpm for 24 hours. The batch experiment was stopped at various time intervals. Aliquots were withdrawn and filtered (0.2 μ m) for PIP and Mn(II) analysis. Then NaOH solution (at pH = 11) was added in the in the tubes containing unfiltered solution to desorb PIP. The amount of PIP adsorbed was determined as the difference between the total aqueous concentration (after NaOH desorption) and the residual concentration, and the oxidized amount was determined as the difference between the initial concentration and the total aqueous concentration.

Kinetic sorption of Mn(II) on MCS and 0.05 MGCS

To keep same Mn contents, 5 g of MGCS or 2.6 g of MCS was placed into 200 mL reaction solution containing 10 mM NaCl and 10 μ M Mn(II) at pH 5.2 and maintained throughout the course of the experiment. In case of destroying the structure of MGCS, the whole experiments were conducted under static condition without stirring. Because only sorption reaction happened on mineral surface, the dissolution of MnO₂ is negligible. Aliquots were withdrawn and filtered (0.2 μ m) for Mn(II) analysis.

PIP and PIPox detection by HPLC and UPLC-MS/MS

Pipemidic acid (PIP) and its primary byproduct (PIPox) were analyzed by highperformance liquid chromatography (HPLC) using a C18 column (L \times D: 250 mm \times 4.6 mm, 5 μ m pore size) and a UV detector at the wavelength 278 nm (Waters 2489). The mobile phase consists of mixture of water/acetonitrile (85:15 v/v)

containing 0.1% of formic acid. The flow-rate of the mobile phase was set at 1 mL/min. The mass-to-charge ratio of PIPox was detected by ultrahighperformance liquid chromatography (Waters Acquity UPLC) system using a Waters BEH C18 column (100 mm×2.1 mm, 1.7 μm) and a mass spectrometer. The mobile phase consisted of acetonitrile containing 0.1% of formic acid (eluant A) and mixture acetonitrile/water 10%/90% containing 0.1% of formic acid (eluant B) with gradient 0 min/0% A – 1 min/0% A – 9 min/100% A – 12 min/0% A, and a flow rate of 400 μL/min. An electrospray interface (ESI) was used for the MS measurements in positive ionisation mode and full scan acquisition.

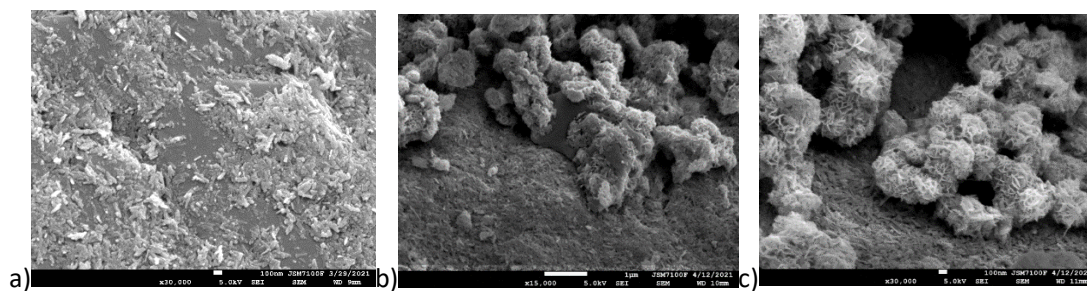


Fig. S1 SEM images of MGCS with different AB content a) GCS, b) 0.05 MGCS, c) 0.1 MGCS.

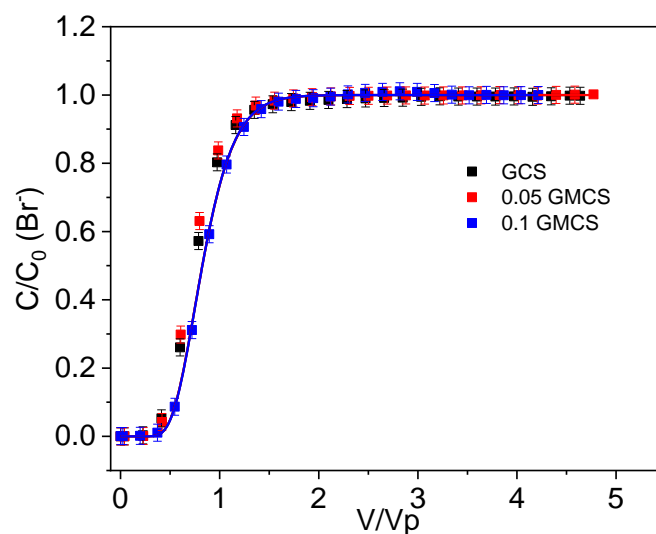


Fig. S2 Br⁻ transport experiments in different columns.

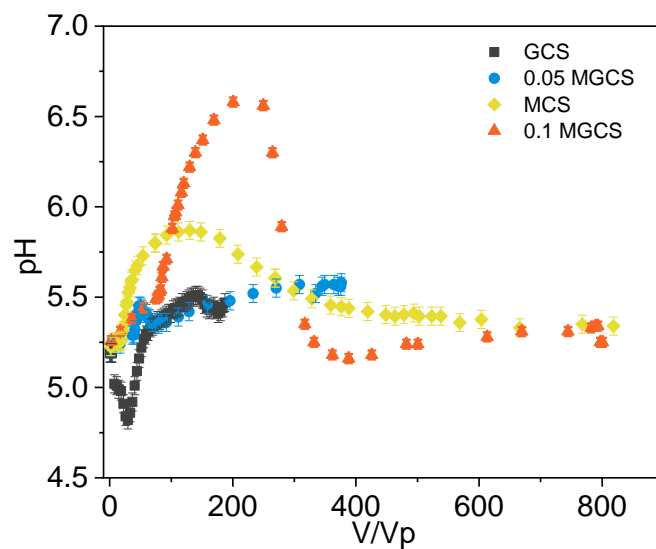


Fig. S3 Breakthrough curves of pH in the different MnO₂ content packed columns. Inflow conditions: 10 μM PIP; pH 5.2 ± 0.1; 10 mM NaCl; PV 4 mL; flow rate 0.5 mL/min.

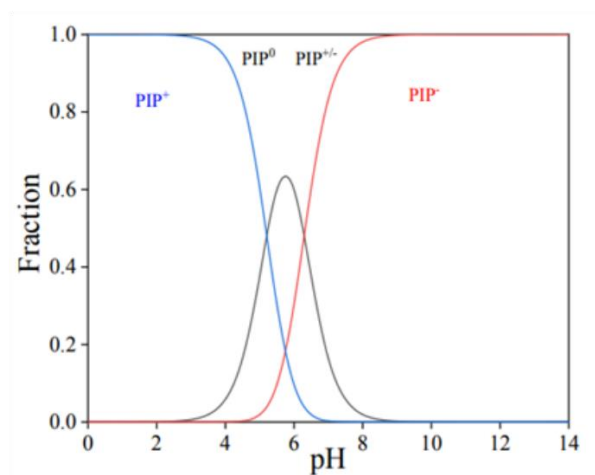


Fig. S4 Chemical speciation of PIP under different pH.

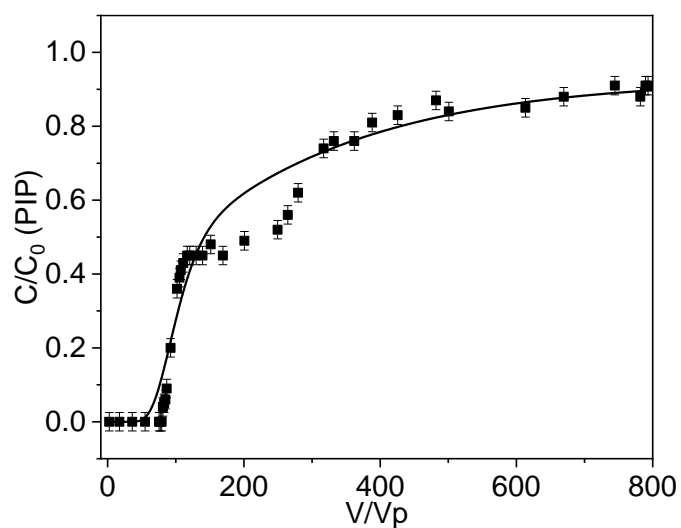


Fig.S5 Modeling of PIP transport in 0.1 MGCS using same parameters for whole process. Inflow conditions: 10 μ M PIP; pH 5.2 ± 0.1 ; 10 mM NaCl; PV 4 mL; flow rate 0.5 mL/min.

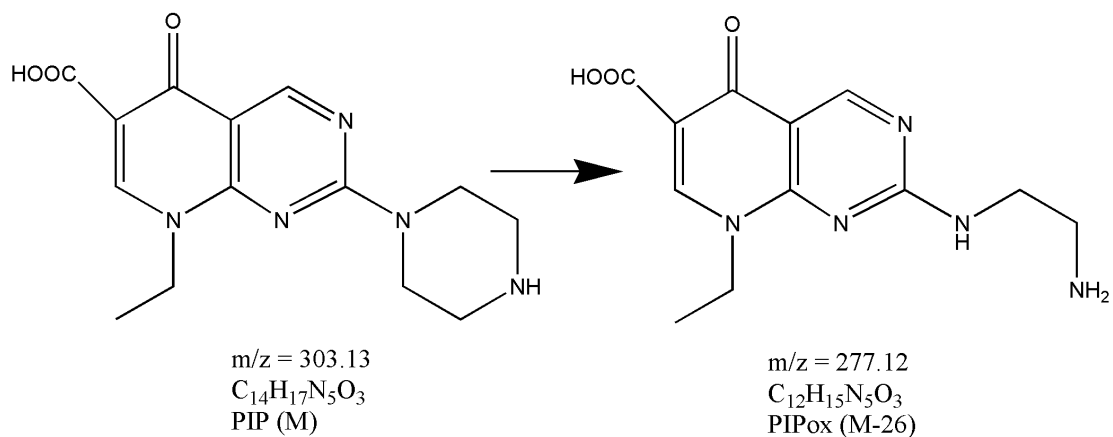


Fig. S6 Pipemidic acid (PIP) and identified oxidation by-product (PIPox) by LC/MS. M-26 indicates the net mass loss of PIP_{ox}.

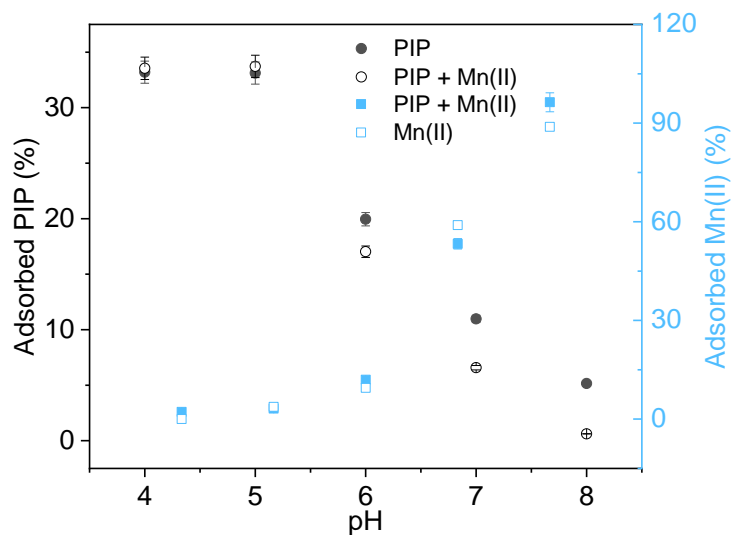


Fig. S7 PIP and Mn(II) removal under different pH in the GCS solution. Initial conditions: 25 g/L GCS, 10 μ M PIP, 10 mM NaCl, 10 μ M Mn(II), 24 h equilibrium time.

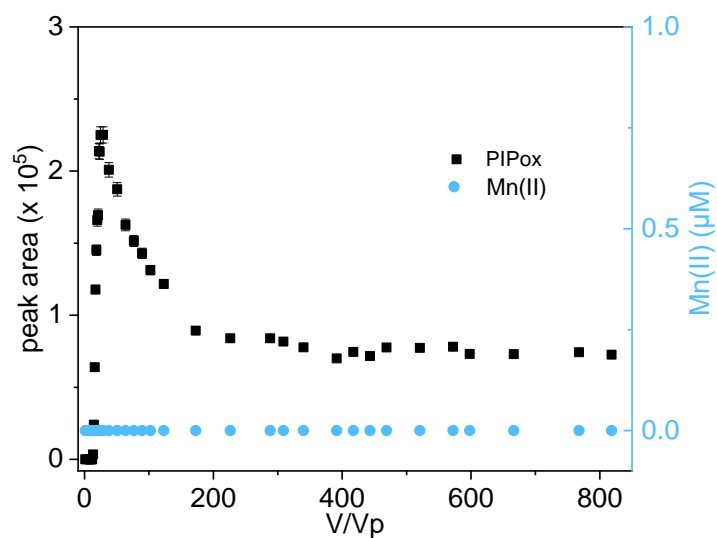


Fig. S8 Byproducts identification in the MCS column. Inflow conditions: 10 μ M PIP, pH 5.2 ± 0.1 , 10 mM NaCl, PV 4 mL, flow rate 0.5 mL/min.

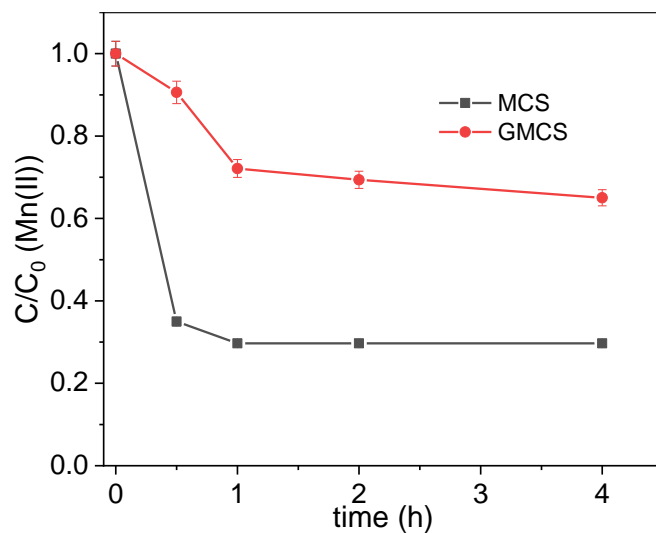


Fig. S9 Kinetic Mn(II) adsorption on MCS or MGCS at pH 5.2 under static condition. Initial conditions: 25 g/L 0.05 MGCS, 13 g/L MCS, 10 mM NaCl, 10 μ M Mn(II).

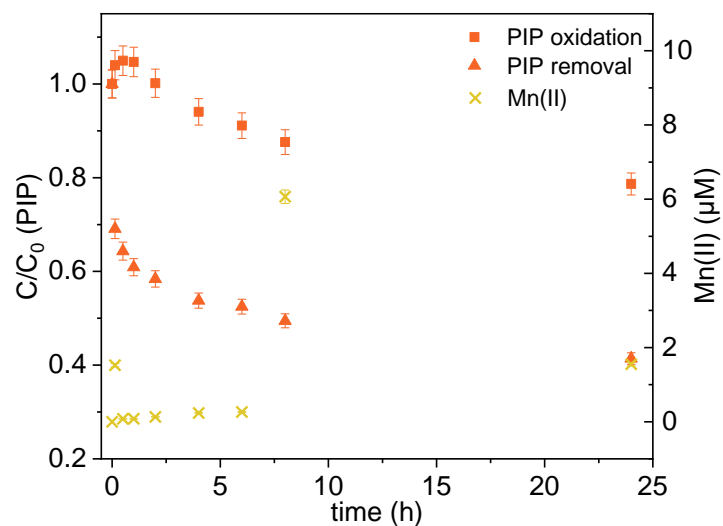


Fig. S10 Changes of PIP and Mn(II) concentration in 0.05 MGCS solution. Initial conditions: 25 g/L 0.05 MGCS, 10 μ M PIP, 10 mM NaCl, pH 5.2.

Table. S1 Experimental conditions and results for dynamic column breakthrough experiments

Geomedia	Flow rate	pH	Interruption time	PIP removal (μmol)
GCS	0.5 mL/min	5.2	-	1.5
MCS	0.5 mL/min	5.2	-	5.0
0.05 MGCS	0.5 mL/min	5.2	24 h	3.2
		7	24 h	1.8
0.1MGCS	0.5 mL/min	5.2	24 h	11.0

Table S2 Parameters of Pipemidic acid (PIP) transport under flow-through conditions

	GCS	MCS	0.05 MGCS-1		0.05 MGCS-2		0.1 MGCS		
pH	5.2	5.2	5.2		7		5.2		
			Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2	Stage 3
^a λ	0.241	0.189	0.241		0.241		0.241		
^b f	0.95	0.34	0.94	0.36	0.71	0.21	0.82	0.53	0.19
^c K	11.5	31.1	15.1	7.8	11.7	7.2	40.1	51.2	27.7
^d β	1	1	1	1	1	1	1	1	1
^e μ_s	0	1.1×10^{-4}	1.2×10^{-4}	5.5×10^{-6}	0	0	1.8×10^{-5}	7.5×10^{-5}	2.2×10^{-4}
^f α	8×10^{-6}	5.4×10^{-4}	8.8×10^{-3}	3×10^{-3}	8.6×10^{-4}	5.2×10^{-4}	1.2×10^{-6}	3.3×10^{-3}	1.1×10^{-3}
R ²	0.93	0.99	0.97	0.98	0.97	0.95	0.94	0.98	0.98

^a λ is the dispersivity. Units: cm.

^bf is the fraction of equilibrium sites.

^cK is the empirical distribution coefficient in freundlich isotherm. Units: cm^3/g .

^d β is the index of freundlich isotherm.

^e μ_s is the first-order degradation rate. Units: cm^{-1} .

^f α is the adsorption rate. Units: cm^{-1} .

The modeling range of 0.05 MGCS-1, stage 1 and stage 2: 0-376 PV and 376-554 PV, respectively.

The modeling range of 0.05 MGCS-2, stage 1 and stage 2: 0-319 PV and 319-347 PV, respectively.

The modeling range of 0.1 MGCS, stage 1, stage 2 and stage 3: 0-139 PV, 139-789 PV and 789-954 PV, respectively.

Table S3 Degradation rate coefficient (k , min^{-1}) calculated from flow-interruption events.

	0.05 MGCS, pH 5.2	0.05 MGCS, pH 7	0.1 MGCS, pH 5.2
k (min^{-1})	1.4×10^{-4}	3.5×10^{-4}	2.1×10^{-4}

References

- (1) McKenzie, R. M. The Synthesis of Birnessite, Cryptomelane, and Some Other Oxides and Hydroxides of Manganese. *Miner. Mag.* **1971**, *38*, 493–502.
- (2) Mazeina, L.; Navrotsky, A. Surface Enthalpy of Goethite. *Clays Clay Miner.* **2005**, *53* (2), 113–122.