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Water flow and dissolved Mn^{II} alter transformation of pipemidic acid by manganese oxide

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Abstract

Manganese oxides have been proposed as a promising geomedia to remove trace organic contaminants in both natural soils and artificial infiltration systems. Although MnO_x -based redox processes have been largely investigated, little is known on the effects of water flow and dissolved Mn^{II} on manganese-mediated redox reactions in saturated porous media. Here, we have demonstrated that the reactive transport of a widely used quinolone antibiotic, piperidic acid (PIP), in MnO_2 -coated sand (MCS) columns is altered by the presence of dissolved Mn^{II} , *in situ* generated as reduced ions or present in inflow solution. Decreasing flow rate or flow interruption facilitated oxidation reaction and generated redox byproducts (Mn^{II} and PIP_{ox}). However, preloading of MCS columns with dissolved Mn^{II} led to suppressed reactivity with PIP. When PIP and Mn^{II} are simultaneously injected, competition between PIP and Mn^{II} for binding at the edge sites takes place during the initial kinetic phase of reaction, while at later breakthrough time Mn^{II} will occupy both edge and vacancy sites due to continuous supply of Mn^{II} . We also developed a reactive transport model that accounts for adsorption kinetics to predict changes in transport behavior of antibiotics in presence of different doses of dissolved Mn^{II} . This work has strong implications for an accurate assessment of reactivity of manganese oxides used as an engineered geomedia for quinolones remediation and in developing transport models of antibiotics in natural systems.

TOC/Abstract art

1. Introduction

The widespread occurrence of pharmaceuticals (e.g. quinolone antibiotics) in nature is an emerging global threat with alarming consequences on public health (e.g. multiple antimicrobial resistance has emerged as one of the serious health threats of the 21st century)¹ and water resources quality.²⁻⁴ The use of recycled sewage sludge (which contain antibiotics up to several mg/L)⁵ by farmers globally as fertilizers for agricultural practices, further increases the chances of their re-entry to humans/animals through soil-groundwater route. As a result, antibiotics have been detected in food and different water reservoirs such as surface, ground and drinking water at concentration levels ranging from ng/L to mg/L.⁶

The fate and transport of quinolones in aquatic and terrestrial systems are strongly related to their interactions with environmental mineral surfaces. Among redox-sensitive minerals, manganese species can be found as oxides and/or hydroxides in the form of coatings on other particles and/or as nodules of various diameters.⁷ Manganese oxides are less abundant in comparison to Fe-oxyhydroxides but have higher redox potential.⁸ Studies have shown that layered manganese oxide (also known as birnessite), one of the most common manganese oxides mineral in both terrestrial and marine settings⁹, play an important role in the sorption and transformation of antibiotics.¹⁰⁻¹³ Few studies have proposed birnessite coated sand as a potential geomedia in engineered infiltration systems to prevent quinolone from percolating into the groundwater sources.¹⁴⁻¹⁶ Although manganese oxides are of great interest from both natural and engineering points of view, most of available studies were limited to static batch experiments.^{10-13, 17}, and little is known about the assessment of redox transformation of antibiotics under flow-through conditions. Only two recent column studies have demonstrated the high reactivity of birnessite coated sand towards organic contaminants together with a progressive loss of reactivity over

breakthrough time^{14,15}, but mechanistic insights on the competitive adsorption of Mn^{II} and organic compounds on MnO₂ surfaces and reactivity suppression under flow-through conditions is still missing. Furthermore, no data exist on how water flow variability influences the interactions of organic compounds and Mn^{II} with birnessite surfaces. This is particularly relevant when solutes and redox byproducts (e.g. dissolved Mn^{II}) concurrently affect surface reactivity and thus mobility of compounds in environmental settings. Indeed, dissolved Mn^{II} can interact with hexagonal birnessite (δ -MnO₂ and acid birnessite) and then transfer electron to lattice Mn^{IV} producing Mn^{III}, which induce changes in mineral structure and composition, e.g. conversion of birnessite into lower-valence Mn phases and/or modification of birnessite through adsorption or incorporation of Mn^{III} into the mineral sheets.¹⁸⁻²⁷ This reductive transformation of hexagonal birnessite depends on several factors, including pH and the ratio of dissolved Mn^{II} to structural Mn^{IV}.^{18,25}

In this study, we investigate the adsorption and redox transformation of a model quinolone antibiotic, pipemidic acid (PIP), in water saturated MnO₂-coated sand columns. Acid birnessite was used as it is structurally similar (layers with hexagonal sheet symmetry comprising of edge-sharing Mn^{IV}O₆ octahedra and nanoscale particle size distribution) to biogenic birnessite found in soils.^{19,28} Pipemidic acid, commonly used to treat urinary tract infections in humans and animals²⁹, was chosen as a model quinolone compound. In order to mimic natural conditions where water movement is discontinuous, we employed the 'intermittent flow/no-flow' method in the column experiments. This technique allowed also to assess changes in reactivity of manganese oxides upon modification of the residence time in column. Furthermore, we also examined the impact of two contrasting concentrations of dissolved Mn^{II} in the reactivity of MnO₂-coated sand with PIP. The dissolved Mn^{II} concentration range was chosen in order to cover a wide variety of relevant concentration found in shallow groundwater, soil pore waters and surface waters.³⁰⁻³² Finally, a

transport model that accounts for oxidation and adsorption kinetics was used to help us in understanding adsorption/oxidation changes of PIP in presence of dissolved Mn^{II} .

2. Materials and Methods

2.1. Preparation and characterization of acid birnessite and manganese oxide-coated quartz

Acid birnessite (AB) was prepared following the procedure of McKenzie (1971). More details are provided in the Supporting Information. The solid was characterized using X-ray powder diffraction (XRD) using the Bruker AXS D8 Advance diffractometer (θ -2 θ Bragg-Brentano geometry) using monochromatized $\text{CuK}\alpha 1$ radiation. X-ray diffraction (XRD) confirmed that the only product of the synthesis was poorly-crystalline hexagonal birnessite (Fig. S1). The Mn average oxidation state (AOS) was measured to be 3.98 ± 0.02 (SD) using the back-titration method with KMnO_4 solution.³⁴

Scanning electron microscope (SEM; JEOL JSM-7100F) and High-resolution transmission electron microscope (HRTEM; JEOL 2100 LaB₆) were used for the ultrastructure examination of AB. SEM images showed that acid birnessite exhibits sheet stacked nanoflower spheres with a diameter of ~ 400 nm (Fig. S2). HRTEM images showed aggregation of small crystalline domains surrounded by poorly-crystalline material. The surface area of AB was 57 ± 4.5 (SD) m^2/g measured by N_2 adsorption BET method.

The prepared birnessite was coated with Fontainebleau quartz sand ($150 - 200 \mu\text{m}$). Prior to coating, trace metal impurities from the pure quartz were removed (see the Supporting Information for details). The clean dried quartz was then mixed with AB suspension (quartz to AB ratio of 3). The ionic strength of the suspension was adjusted to 10mM 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 AB coated quartz, hereafter referred as MnO₂-coated sand (MCS), was dried at room temperature. Mn content in the MCS was determined by dissolving in 30 mM Ascorbic acid following the protocol of Charbonnet et al. (2018) and analyzed with Atomic absorption spectroscopy (AAS). The measured amount was 0.48 ± 0.02 (SD) mg Mn in one gram of MCS. The coating density was within the previously reported range.³⁵ Scanning electron microscope / Energy dispersive X-Ray spectroscopy (SEM/EDS) was applied to study the surface morphology and elemental composition of the MCS. Samples were examined with a JSM JEOL 7100 F with a field emission gun and OXFORD Genesis energy-dispersive X-ray spectrometer at 20kV at a working distance of 5-10 mm and magnifications from 10,000x to 20,000x. The SEM/EDAS imaging of MCS showed clusters/aggregates of AB inhomogeneously distributed over the surface of MCS (Fig. S2). Aggregates tend to accumulate in surface depressions and cracks of the quartz surface. Examination using the highest SEM magnification showed particles in AB aggregates in coated sand were similar in morphology as uncoated AB, suggesting no significant modification in morphology occurred during the coating process. The quantitative EDAS spectra of MCS showed Mn, Si, and O as the main constituents (Fig. S8). Due to extremely low Mn amount in the MCS, XRD and AOS techniques could not be used for MCS characterization.

2.2. Dynamic column breakthrough experiments

The experimental setup used for dynamic column tests is described in Zhou et al. (2019). Briefly, column experiments were conducted under ambient conditions and water-saturated conditions. Fifteen grams of MCS (containing 131 μmol MnO₂) was packed into a glass column with an internal diameter of 1.6 cm and a bed length of 4.7 cm. The uniform bulk density after packing was $(1.59 \pm 0.05 \text{ g/cm}^3)$. The pore volume (PV or V_p) of the column was $4 \pm 0.1 \text{ mL}$. The

column was saturated with a background solution of 10 mM NaCl (previously purged with N₂) at pH 6 with a constant flow-rate of 0.5 mL/min (residence time of 8 min). After saturation, bromide tracer experiments were performed to determine column transport properties using 10 mM sodium bromide (NaBr) solution at pH 6 as input solution and ionic chromatography to determine Br⁻ breakthrough curve (Fig. S3). Details on calculation and interpretation of hydrodynamic parameters obtained from the bromide tracer experiments are provided in the Supporting Information. During water saturation and tracer experiments, total dissolved Mn in outflow was below the detection limit (<0.02 μM), and therefore possibility of mobilization of Mn particles was excluded from the column. Blank tests conducted also confirmed no adsorption of Mn^{II} ions to the quartz sand ($\leq 0.06 \text{ m}^2/\text{g}$) used in this study.

Different column experiments were performed by injecting input solutions consisting of a constant amount of 10 mM NaCl and 10 μM pipemidic acid but with variable concentrations of Mn^{II}. All input solutions were adjusted to pH 6 ± 0.1 and injected with a constant flow-rate of 0.5 mL/min, conditions close to or within range of natural soil pore water.^{37,38} The input solution was purged with N₂ to avoid CO₂ contamination and maintain the experimental pH throughout the course of the experiment. Flow-interruption for 24 h (single or double) was done in some columns to assess the effect of residence time. After complete PIP breakthrough in some columns, desorption was done by injecting 10 mM NaCl at pH 6 at 0.5 mL/min. All effluent solutions were passed through a 0.2 μm filter and were collected in 7.5 mL – 15 mL increments using a fractional collector. The pH of the effluent solution was determined by using an online pH meter. The effluent solution was also analyzed for PIP and by-products with High performance liquid chromatography (HPLC) and Ultraperformance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) system. Details on experimental set-up for these techniques are provided in the Supporting Information. Because the adsorption of target compounds is negligible at pH higher than 10,

desorption tests were conducted at pH 11 as a means to check the mass balance. After the column experiment, the solid bed was freeze-dried. The total Mn content in MCS before and after flow experiments was determined by ascorbic acid reductive dissolution¹⁴ and AAS measurement. SEM-EDS microscopy was performed to monitor morphological changes in the reacted MCS. All experiments were conducted in duplicates and showed a good reproducibility within 5% of average standard deviation.

2.3. Model approach

The transport of PIP through MCS columns both in the presence and absence of Mn^{II} was simulated using a one-dimensional advection-dispersion model coupled with a two-site non-equilibrium adsorption model.³⁹ Hydrus-1D program was used to obtain the model parameters for the two-site non-equilibrium model. The modeling approach used is explained in detail in the Supporting Information.

3. Results and Discussion

3.1. Adsorption and oxidation of PIP in MCS column

The breakthrough curve (BTC) of PIP exhibited sigmoidal-like shape but with an extensive tailing when PIP was injected in pristine MCS column (Fig. 1a). The first breakthrough point of PIP was at around 20 PV (pore volume) and later achieved a steady state breakthrough at around $C/C_0 \sim 0.95$ after injection of 600 PV. This partial breakthrough continued to be observed until the end of the column experiment (more than 1000 PV). Increasing the residence time in the column by interrupting flow did not influence the incomplete breakthrough, as the same partial breakthrough ($C/C_0 \sim 0.95$) was still observed upon flow resumption (Fig. 1a). This flow interruption period allowed species to react over a longer period during flow-through conditions. Because the BTC of Br^- used as a tracer showed no change upon flow interruption, we conclude

that the PIP concentration drop cannot be caused by physical non-equilibrium or diffusive mass transfer between "mobile" and "immobile" regions.^{40, 41}

Fig. 1: Breakthrough curves of (a) PIP and PIP_{ox} (peak area of PIP byproduct; M-26) and (b) pH and Mn^{II}. The dashed lines indicate the theoretical complete breakthrough of PIP ($C/C_0 = 1$) in (a) and detection limit of Mn^{II} (0.02 μM) in (b). The arrow indicates the moment of flow-interruption (duration 24 h; $V/V_p = 876$). Inflow conditions: 10 μM PIP, pH: 6.1 ± 0.1 , 10 mM NaCl, PV: 4 mL, flowrate: 0.5 mL/min.

Over the course of the experiment, the pH of the output solution increased only slightly (~0.6 units), but regained the original value of the input solution (pH 6 ± 0.1) when steady state breakthrough was attained (Fig. 1b). At our experimental pH range, the PIP molecule exists in a zwitterionic form (pK_{a1} and pK_{a2} values are 5.20 and 6.38, respectively). It is previously observed that quinolones binding to negatively charged Mn-oxide surfaces possibly through a metal-bound complex may involve proton co-binding.¹³ This binding can be associated with a heterogeneous redox reaction where two one-electron transfer steps or a single two-electron step resulting in the concomitant oxidation of PIP and reduction of surface-bound metal. One electron is transferred from ligand to the surface-bound Mn^{IV} to yield radical intermediate and Mn^{III} that can be further reduced to give Mn^{II}. Subsequently, the formed radical intermediate may undergo several different reaction pathways to yield a range of by-products as shown by equation 1. A detailed step-wise reaction mechanism is provided in the Supporting Information.

To check the PIP heterogeneous reaction with MnO_2 , kinetic batch experiments were performed using 0.25 g MCS ($2.2 \mu\text{mol MnO}_2$) reacted with $10 \mu\text{M PIP}$ and 10mM NaCl solution at pH 6. As suggested by the mass balance, both adsorption and transformation processes may occur (Fig. 2). As an initial kinetic stage, the adsorbed amount increased to reach a maximum and then decreased. Once the PIP adsorbed reached a sufficient amount to trigger oxidation reaction, the oxidized amount increased to reach a steady-state (or plateau-like) (Fig. 2). However, Mn^{II} aqueous concentration was below the detection limit ($0.02 \mu\text{M}$), most likely due to strong binding of Mn^{II} to MCS surfaces at the working pH (i.e. pH 6). Indeed, adsorption isotherm determined at pH 6 showed great affinity of Mn^{II} to MCS at the first stage, followed by an almost linear increase of adsorbed amount with increasing equilibrated Mn^{II} concentration (Fig. S4). Since our experiments were performed under air ambient conditions, surface-catalyzed oxidation of Mn^{II} by molecular oxygen could enable more Mn^{II} sorption under oxic conditions relative to anoxic systems through the formation of new phases such as feitknechtite and/or manganite, as previously reported.¹⁸ However, it was also reported that formation of these lower valence Mn phases prevails at pH values higher than the working pH here (pH >7) and for high ratio of dissolved $\text{Mn}^{\text{II}}/\text{MnO}_2$.^{18,25} Only a disturbance of stacking of MnO_2 sheets with no mineralogical transformation has been observed at pH 6.¹⁸ We verified this by conducting Mn^{II} isotherm experiments with uncoated acid birnessite at pH 6 (± 0.1) under both oxic and anoxic conditions. Both isotherms overlapped at low range of $\text{Mn}^{\text{II}}/\text{MnO}_2$ ratio, indicating no influence of O_2 at the experimental conditions of column tests. Only at higher $\text{Mn}^{\text{II}}/\text{MnO}_2$ ratio (≥ 1.38), sharp removal in dissolved Mn^{II} was observed under oxic conditions relative to anoxic systems (Fig. S5a), yet no

new Mn-phase was detected by ATR-FTIR at pH 6 (Fig. S5b). The experimental setup as well as the results of all isotherm experiments is provided in the Supporting Information.

Fig. 2: Removal kinetics of PIP (aqueous residual PIP concentration, red circles in primary Y-axis) and evolution of PIP removed by adsorption and oxidation (black and white squares in secondary Y-axis) over reaction time. Adsorbed amount was determined as the difference between the total aqueous concentration after desorption and the residual concentration, and oxidized amount was determined as the difference between the initial concentration and the total aqueous concentration. Experimental conditions: 10 μM PIP; 10 mM NaCl; pH: 6 ± 0.1 ; MCS amount: 0.25 g ($\sim 2.2 \mu\text{mol MnO}_2$).

The incomplete PIP breakthrough observed here (Fig. 1) suggests that both adsorption and transformation of PIP may also occur in the column system. The drop in PIP concentration under no-flow condition can result from rate-limited sorption/redox processes. Redox byproducts were then monitored in column effluent throughout the whole breakthrough time. Dissolved Mn^{II} concentration was below the AAS detection limit ($<0.02 \mu\text{M}$), most likely because of the high tendency of manganese ions to be adsorbed at the oxide surface at the working pH. Dissolved Mn^{II} (up to $1.5 \mu\text{M}$) was only detected in column effluent after 24 h flow interruption and then flow resumption (Fig. 1b), probably because of generation of higher amount of Mn^{II} . Indeed, flow interruption provided additional time for the PIP oxidation reaction to occur (eq. 1), resulting in

accumulation of Mn^{II} as redox byproduct in the column. Sorption of Mn^{II} to MnO_2 surfaces may continue to proceed during the flow-interruption period, but was not able to entirely remove all accumulated Mn^{II} . When flow was recommenced, elution of the interrupt-period resident solution caused a decrease in PIP concentration and an increase in Mn^{II} concentration (Fig. 1b). Continuous injection of inflow solution led to an increase of PIP aqueous concentration up to reach the initial value and a decrease of Mn^{II} concentration below the detection limit.

In order to assess the PIP oxidation reaction, all possible byproducts previously detected for analogous quinolone compounds^{13,42} were searched by LC/MS. Consistently with past observations, PIP can be oxidized by MnO_2 through two one-electron transfers from the N atom of piperazine ring to Mn^{IV} , generating Mn^{II} and PIP cation radical. Further changes on the PIP cation radical can happen through C-hydroxylation and/or N-dealkylation that cause ring opening and subsequently forming several byproducts, as typically observed for other quinolones.^{11,13} However, only one predominant species of mass-to-charge ratio of $m/z=227$ can be detected using LC/MS (Fig. S6). The peak area of the LC/MS data of this species corresponding to M-26 (hereafter called PIP_{ox}) followed PIP breakthrough to reach a steady state (Fig. 1a). Because standards are not commercially available, an accurate quantification of formed species cannot be performed.

PIP_{ox} broke out at the same time as the mother compound, reached a maximum and then decreased after ~ 100 PV to have a plateau (Fig. 1a). When the flow is resumed after 24 h flow interruption period, PIP_{ox} concentration spiked up before reaching plateau again, suggesting the occurrence of kinetically limited redox process in the column system. Both sorption/desorption and oxidation reactions are expected during the flow interruption event, PIP concentration decreased and byproduct concentration increased, and then approached constant steady-state values. Because of a constant partial breakthrough (i.e. $C/C_0 < 1$) observed, ongoing oxidation and formation of

primary byproduct is highly expected. This primary byproduct reached a steady state concentration, thereby suggesting that a sorption/desorption equilibrium was reached.

The generation of redox byproducts (e.g. Mn^{II}) which in turn interact with MnO_2 surfaces may influence the ongoing oxidation reaction in the column, and thus affect the transport behavior of PIP in the column system. Furthermore, redox byproducts are flushing out of the column or moving up toward further zones, while they remained in contact with the reacted solid under static batch conditions. In order to test this hypothesis, the impact of dissolved Mn^{II} on the MnO_2 reactivity was investigated under two situations: (i) PIP injection in Mn^{II} -preloaded column and (ii) simultaneous injection of PIP and dissolved Mn^{II} in pristine columns.

3.2. Effects of dissolved Mn^{II} on the MnO_2 reactivity and PIP oxidation in column

In the Mn^{II} -preloaded column experiment, Mn^{II} and PIP were injected in column after injection of ~ 346 PV with Mn^{II} solution ($10\ \mu\text{M}$), i.e. $\sim 14\ \mu\text{mol}$ of Mn^{II} was reacted with $7.2\ \text{mg}$ ($131\ \mu\text{mol}$) of MnO_2 in the MCS column during preloading. Preloading of MCS column with $14\ \mu\text{mol}$ of Mn^{II} dramatically changed the transport behavior of PIP in terms of both retardation factor and breakthrough curve shape, as compared to no-preloading experiment (Fig. 3a and 1a). The BTC of PIP became more sigmoidal/steeper, with an early breakthrough occurring at ~ 10 PV and then a complete breakthrough at ~ 60 PV. No extensive tailing in both adsorption and desorption fronts (curve symmetry) was observed here relative to the BTC of PIP in no-preloading column. Furthermore, complete breakthrough (i.e. $C/C_0 = 1$) of PIP was achieved, suggesting very low to negligible oxidation extent under these experimental conditions. This was confirmed by the very low amount of PIP_{ox} detected in the column effluent (Fig. 3b). Since the oxidation was almost absent, the total removed amount of PIP in column should correspond to the adsorbed amount, determined as $\sim 0.65\ \mu\text{mol}$ of PIP bound to Mn^{II} preloaded MCS by integrating the breakthrough

curve. This amount was considerably lower than that of the total PIP removed (adsorbed + oxidized) in no-preloading column ($\sim 2.6 \mu\text{mol}$).

The complete PIP breakthrough and an incomplete Mn^{II} breakthrough suggested preferential adsorption of Mn^{II} over PIP in the Mn^{II} preloaded MCS (Fig. 3). A total of $\sim 22 \mu\text{mol}$ of Mn^{II} was injected over the whole course of experiment, but only $8.2 \mu\text{mol}$ of total Mn^{II} was removed (adsorbed + oxidized) as calculated by integrating breakthrough curve. This low $\text{Mn}^{\text{II}}/\text{MnO}_2$ ratio (0.17) may explain why complete breakthrough of Mn^{II} was never attained in the MCS column.

During Mn^{II} preloading the solution pH rapidly decreased by ~ 1.5 units, most likely because of release of H^+ in the solution upon binding of Mn^{II} ions to MnO_2 surfaces. Afterwards, outflow pH gradually increased to regain the inflow value, even after simultaneous injection of Mn^{II} and PIP. Desorption front suggests that not all Mn^{II} previously removed was released during desorption with 10 mM NaCl. Previous work indicates that monovalent cations like Na^+ cannot completely displace Mn^{II} from the MnO_2 structures.⁴³ Additional desorption tests in batch using 25 mM of Ca^{II} as a desorption agent of solid-bound Mn^{II} ¹⁶ did not allow more than 10% of previously adsorbed Mn^{II} . We cannot rule out the possibility that comproportionation of Mn^{II} to Mn^{III} might have occurred under our experimental conditions, even if adsorption of Ca^{II} on vacant sites is much weaker than Mn^{II} and only high pH favors comproportionation reaction forming Mn^{III} .⁴⁴ Indeed, infrared spectroscopic investigations (Fig. S5b) for uncoated MnO_2 in batch confirmed that transformation of hexagonal birnessite to manganite ($\gamma\text{-Mn}^{\text{III}}\text{OOH}$) only occurred at high pH (i.e. 8) and high ratio of Mn^{II} to MnO_2 (2.3).

Fig. 3: Breakthrough curves of (a) PIP and Mn^{II} and (b) pH and PIP_{ox} (peak area of PIP byproduct; M-26). The gray area represent Mn^{II} preloading period where an input solution consisting of $10\ \mu\text{M}$ Mn^{II} and $10\ \text{mM}$ NaCl was injected (up to $344\ V/V_p$), and the white area represent injection of $10\ \mu\text{M}$ Mn^{II} + $10\ \mu\text{M}$ PIP and $10\ \text{mM}$ NaCl. The dashed lines indicate the theoretical complete breakthrough of PIP ($C/C_0 = 1$). The arrow indicates point of injection of $10\ \text{mM}$ NaCl solution for desorption ($V/V_p = 530$). Inflow conditions: $10\ \mu\text{M}$ PIP, pH: 6.2 ± 0.1 , $10\ \text{mM}$ NaCl, PV: $4\ \text{mL}$, flowrate: $0.5\ \text{mL/min}$.

Simultaneous injection of Mn^{II} and PIP in pristine MCS column altered PIP mobility

relative to injection of PIP alone in pristine MCS column or in Mn^{II} -preloaded column. When low amount of Mn^{II} ($10\ \mu\text{M}$) was used, higher amount of PIP_{ox} was detected in the column effluent resulting in a partial breakthrough of PIP (Fig. 4a). Complete breakthrough of PIP was only achieved after two interruption events through generation of more redox byproducts and thus by complete passivation of MnO_2 (Fig. 4a). At each flow interruption event, PIP concentration decreased and PIP_{ox} and Mn^{II} concentration increased, and then approached constant steady-state value (Fig. 4a and 4b). The PIP_{ox} became negligible after the second interruption event, as complete breakthrough was achieved for PIP.

Higher Mn^{II} loading ($117\ \mu\text{M}$) led to a steeper BTC and earlier breakthrough as compared to the BTC of PIP injected alone or with $10\ \mu\text{M}$ of Mn^{II} (Fig. 4a, 4c, and 1a). The sharp decrease in pH during Mn^{II} adsorption followed by a gradual increase to regain the original input value was observed here for both Mn^{II} doses (Fig. 4b and 4d). However, the decrease in pH was more

pronounced during the high Mn^{II} dose, indicating more Mn^{II} adsorption. As expected, reacted Mn^{II} amount ($\sim 6.4 \mu\text{mol}$) estimated at the breakthrough point of PIP was higher than in the low Mn^{II} dose column ($\sim 0.7 \mu\text{mol}$). Furthermore, a complete PIP breakthrough was attained in the high Mn^{II} dose and very low amount of PIP_{ox} detected in column effluent, suggesting very low to negligible oxidation rate in this column. The desorption front of both PIP and Mn^{II} indicated no significant tailing and an incomplete Mn^{II} removal, similar to that observed in the Mn^{II} preloaded column.

When $10 \mu\text{M}$ of Mn^{II} was used as an inflow concentration, the amount of removed Mn^{II} estimated before PIP breakthrough point ($0.7 \mu\text{mol}$) was much lower than $8.2 \mu\text{mol}$ removed in the Mn^{II} preloaded column over the whole course of the experiment. This may explain why complete suppression of MnO_2 oxidative ability was only observed in the Mn^{II} preloaded column. However, injection of higher amount of Mn^{II} together with PIP, led to higher amount of removed Mn^{II} ($6.3 \mu\text{mol}$), and thus complete suppression of MnO_2 oxidative ability. This falls in line with the very low amount of PIP_{ox} observed in both high Mn^{II} dose and Mn^{II} preloading experiments.

A complete breakthrough of Mn^{II} was also achieved after the second flow interruption (Fig. 4b). The C/C_0 of Mn^{II} greater than 1 indicates the generation of dissolved Mn^{II} from reductive dissolution of MnO_2 . This reductive dissolution has been confirmed by measuring the total Mn amount in the reacted MCS column. Around 44% decrease in total Mn content was observed as compared to the unreacted MCS. For other column experiments, only 15 % decrease in total Mn content was measured in the reacted MCS after breakthrough experiment. Taken together, the results showed that injection of high amount of Mn^{II} or *in situ* generation of dissolved Mn^{II} , for instance through flow interruption, may suppress PIP oxidation in the MCS columns.

Fig. 4: Breakthrough curves of (a) PIP and PIP_{ox} (peak area of PIP byproduct; M-26) and (b) pH and Mn^{II} for experiment with low Mn^{II} loading (10 μ M). Breakthrough curves of (c) PIP and PIP_{ox} (peak area of PIP byproduct; M-26) and (d) pH and Mn^{II} for experiment with high Mn^{II} loading (117 μ M). All dashed lines indicate the theoretical complete breakthrough of PIP or Mn^{II} ($C/C_0 = 1$). Arrows in (a) and (b) indicate the moment of flow-interruption (duration 24 h each; $V/V_p = 139$ and 300), whereas arrows in (c) and (d) indicates point of injection of 10 mM NaCl solution for desorption ($V/V_p = 341$). Inflow conditions: low Mn^{II} column: 10 μ M Mn^{II}, 10 μ M PIP, pH: 5.8 ± 0.1 , 10 mM NaCl, PV: 4 mL, flowrate: 0.5 mL/min; high Mn^{II} column: 117 μ M; 10 μ M PIP, pH: 6.1 ± 0.1 , 10 mM NaCl, PV: 4 mL, flowrate: 0.5 mL/min.

3.3. PIP oxidation mechanisms in Mn^{II}/MnO₂ systems

The structure of acid birnessite consists of two adsorption sites within its Mn^{IV}O₆ octahedra layers: 1) edge sites at the edge of Mn^{IV} octahedral sheets and 2) vacancy sites within the Mn^{IV} octahedral sheets.⁴⁵ Because of their high density of negative charge, vacancies sites could be the primary location for cationic species (e.g. heavy metals), while high electronegative

species (e.g. anionic species) would prefer edges sites.⁴⁶ As observed for oxyanions (e.g. As^{III} and As^{V})⁴⁷⁻⁴⁹ or anionic ligands (e.g. phosphate)^{46,50}, it is likely that organic ligands such as pipemidic acid can be probably sorbed at edge sites. On the other hand, numerous studies reported that binding of cationic metals (e.g. Ni^{II} , Zn^{II} , Mn^{II}) likely occurs on edge sites as well as vacancy sites of hexagonal birnessite.^{51,52} For example, some reports showed that Mn^{II} is preferentially sorbed at vacancy sites (higher thermodynamic stability forming triple corner-sharing complexes by sharing corners of its octahedral shell with Mn^{IV} octahedral corners) until they are all occupied, and when all vacancy sites are occupied, Mn^{II} will bind for the edge sites.^{47,49,53} However, a recent work reported that binding mechanisms of some cations (e.g. Co^{II}) are time dependent, i.e. they react first with edge sites within the first 10 min, and then diffuse to the vacancy sites at longer reaction times.^{54,55} Collectively, we can assume that vacancies sites are the long-term adsorption and oxidation sites for cationic metals (e.g. Mn^{II}), whereas edges sites tend to interact with anionic species (e.g. PIP). At the first kinetic phase, competition between PIP and Mn^{II} to edges sites can be expected.

When PIP is injected in pristine MCS column, PIP molecule will preferentially bind at the edge sites of MnO_2 , followed by electron-transfer reactions from ligand to surface-bound Mn^{IV} resulting in the concomitant generation of PIP_{ox} and Mn^{II} , which can in turn interact with MnO_2 surfaces. The suppression of the oxidative ability of MnO_2 or the decrease in oxidation rate observed in the PIP/ MnO_2 system under both batch and flow-through conditions, may result from competition of PIP and Mn^{II} to interact with reactive surface sites and/or aqueous complexation of PIP with Mn^{II} . The latter can be easily excluded because of weaker aqueous complexation of quinolones with divalent cations such as Mn^{II} .⁵⁶ However, more favorable electrostatic interactions exist between cationic metals and the negatively charged MnO_2 surface, thereby suggesting competition of PIP and Mn^{II} for surface sites. Furthermore, the generated Mn^{II} can exchange

electrons with Mn^{IV} to form two Mn^{III} centers and, conversely, two Mn^{III} centers can disproportionate to form Mn^{II} and Mn^{IV} centers.¹⁶

When Mn^{II} is first injected in MCS column (i.e. preloading experiment), Mn^{II} will interact first with edge sites and later diffuse to the vacancy sites (if we assume a similar behavior like Co^{II}). The vacancy content ranges from 6% (lowest) to 20 % (highest) of total Mn content (131 μmol here), corresponds to 8 and 26 μmol of vacancies, respectively.^{28,57} In Mn^{II} preloading, 14 μmol of Mn^{II} was reacted before PIP injection, being within the range of the estimated vacancy content. If the diffusion-limited transport to vacancy sites makes the edges sites free again (potential binding sites for PIP), no competition between PIP and Mn^{II} is expected here. However, the total adsorbed amount of PIP ($\sim 0.65 \mu\text{mol}$) was much lower in the preloaded column than in other columns (e.g. pristine column). This observation can be explained if Mn^{II} still occupied edges sites and compete with PIP, which could also depend on the amount of dissolved Mn^{II} . Indeed, previous spectroscopic investigations of Co binding at hexagonal birnessite ($\delta\text{-MnO}_2$) surfaces suggested that at longer time scale ($t > 10 \text{ min}$) the adsorbed amount at vacancy sites keep increasing, while the amount at particle edges remained constant or decreased depending on the absence or presence of aqueous Co^{II} .⁵⁵ Unlike static batch reactors where the aqueous concentration of species tend to deplete, continuous supply of Mn^{II} into MCS column enabled more competition for both edge and vacancy sites. This observation was supported by our batch data (Fig. S7 and 2) where adsorption of PIP remained constant with or without adding Mn^{II} at longer reaction times i.e. 24 h, but lower oxidation rate was observed in presence of dissolved Mn^{II} . Since all Mn^{II} was removed within the first 10 minutes in batch, PIP may compete with Mn^{II} as a first step (Fig. S7). When diffusion of Mn^{II} to vacancy sites take place, edge sites became free because of depleted aqueous Mn^{II} in batch and thus competition became less pronounced.

When PIP and Mn^{II} are simultaneously injected, PIP and Mn^{II} will compete to bind at the edge sites as a first kinetic stage. Later when the edge sites are filled, Mn^{II} will diffuse to the vacancy sites. Since most of PIP adsorption takes place in the first injected PV, there is probably competition between PIP and Mn^{II} to bind at the edge sites, particularly for a short residence time in the column (i.e. 8 min). The amount of PIP removed was higher than in the preloading experiment where edges sites were mostly pre-occupied by Mn^{II} . On the other hand, the amount of PIP removed (adsorbed + oxidized) determined by integrating the BTC decreased with increasing in Mn^{II} dose (1.65 μmol at 10 μM of Mn^{II} vs 0.78 μmol for 117 μM of Mn^{II}). When Mn^{II} is *in situ* generated through flow interruption events, the binding and oxidative abilities of MnO_2 are further suppressed. Since high amount of Mn^{II} is required to completely passivate MCS, several flow-interruptions events are needed to achieve complete breakthrough of PIP. This is also the case when low amount of Mn^{II} was used (Fig 4a).

As mentioned previously, the incomplete desorption of adsorbed Mn^{II} in column could also suggest the formation of Mn^{III} species through comproportionation reaction of bound Mn^{II} with structural Mn^{IV} . However, no further adsorption of PIP is observed throughout all breakthrough experiment (i.e. C/C_0 remained constant), unlike As^{III} and As^{V} binding to newly formed Mn^{III} species previously reported.^{47,49} Additionally, both ATR-FTIR and SEM/EDAS results showed no substantial differences in terms of composition or morphology between unreacted and reacted solids (Fig. S8), further ruling out significant mineral transformation under our experimental conditions.

The impact of dissolved Mn^{II} on MCS reactivity and PIP mobility was further evaluated using a two-site non-equilibrium model in order to describe the breakthrough curves of PIP in non-preloaded and preloaded columns. Lower values for adsorption and oxidation parameters (R_f or K_d

and μ_s respectively; Table S1; Fig. 5) are required to accurately fit the experimental BTC in presence of Mn^{II} . In simultaneous injection experiments, high dose of Mn^{II} led to lower adsorption extent (K_d or R_f), as expected from the experimental BTC. It is worth noting that fitted values of K_d and μ_s in Mn^{II} preloaded and high Mn^{II} dose column are close, confirming extensive suppression of MnO_2 reactivity in these columns. Indeed, complete breakthrough of PIP was observed upon adsorption of high amount of Mn^{II} in MCS through preloading or injection of higher amount of dissolved Mn^{II} .

Fig. 5: Experimental and modeling BTCs of PIP for all experiments. Solid line represents the calculated BTCs. Dashed line indicate theoretical complete breakthrough ($C/C_0 = 1$).

4. Environmental Implications

Manganese oxides have the potential to be applied as a geomedia to prevent organic contaminants from percolating into the groundwater sources in both natural soils and artificial

infiltration systems. We notably demonstrated that the reactivity of MCS can be strongly affected through reductive dissolution of birnessite and binding of reduced ions to MnO_2 surfaces. The presence of dissolved Mn^{II} frequently found in shallow groundwater, soil pore waters and surface waters, can also alter surface reactivity and ultimately suppress the oxidative ability of birnessite. The amount of dissolved Mn^{II} available to compete with PIP for binding at the edge sites is the driving factor, but this effect depends on the experimental setup (static batch vs continuous dynamic flow). When a high amount of Mn^{II} is contacted with MnO_2 surfaces through preloading or by increasing the inflow concentration, Mn^{II} will interact first with edge sites and later diffuse to the vacancy sites, but both sites will be occupied due to continuous supply of Mn^{II} in column experiments. Under these dynamic flow conditions, competition between PIP and Mn^{II} to edges sites take place over the whole reaction time. However, under static batch conditions where the aqueous concentration of species depletes over time, competition between PIP and Mn^{II} to edges sites is supposed to take place only during the first kinetic stage. Using reactive transport modeling, the estimated parameters are changed when column is previously loaded with Mn^{II} , suggesting the modification of adsorption/oxidation mechanisms of PIP. Taken together, this work sheds light on an overlooked aspect of manganese-mediated redox reactions in presence of reduced ions and under flow-through conditions.

The implication of this work for environmental processes is twofold. First, the outcomes of this investigation will help in developing fate and transport models of quinolones in natural systems (e.g. groundwater and subsurface environments). Second, they are also pertinent for applications of MCS in engineered infiltration systems of contaminated waters (wastewater, stormwater, agricultural runoff, etc.). Our efforts aid to show various scenarios on how the feasibility and longevity of using MCS as a geomedia in such systems may fail. For example, contacting a high amount of Mn^{II} with MCS before or simultaneously with target compound leads

to faster suppression of the MCS oxidative ability. Furthermore, flow interruption (or extremely low pore-water velocities and low Péclet number where diffusion dominates over advection) could trigger accelerated heterogeneous redox reactions to transform quinolones with MCS, but simultaneously generate large amounts of Mn^{II} to progressively diminish MCS reactivity. These observations could help to design MCS based treatment systems with great longevity. For instance, (electro)coagulation or oxidation and filtration systems prior to treatment with the MCS geomedia could be proposed as a potential solution to remove the dissolved Mn^{II} . Second, coupling water flow interruption with an *in situ* regeneration (e.g. using chlorine based oxidant or manganese-oxidizing microbes) of passivated MCS geomedia could increase both efficiency and longevity of manganese oxides based treatment systems. Finally, increasing the number of available reactive sites of MCS by increasing the coating density could further aid in developing effective systems for remediation of organic contamination.

Supporting Information

Methods: Synthesis of acid birnessite, procedure to clean quartz sand, bromide tracer experiments, oxalic acid-permanganate back-titration method, detection of pipemidic acid and byproducts by chromatographic analysis, batch experiments, isotherm experiments, model approach, and reaction mechanism of PIP and MnO_2 . Figures: XRD of AB, SEM and TEM images of AB and MCS, experimental and calculated bromide tracer breakthrough curve, sorption isotherm with MCS, sorption isotherm and ATR-FTIR with acid birnessite, PIP and PIP_{ox} molecular structure, batch kinetic study, and SEM/EDAS imaging of MCS. Table: Parameters of PIP transport under step-injection conditions.

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