**Coupled effects of Mn(II), pH and anionic ligands on the reactivity
of nanostructured birnessite**

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21 Abstract

22 While the oxidative capacity of nanostructured birnessite-type manganese oxide has been
23 widely investigated, no comprehensive work exists on the combined effects of dissolved Mn(II),
24 pH and inorganic anions on sorption and redox reactions of organic contaminants with MnO₂.
25 Herein, we have showed how molecular interactions of two contrasting organic contaminants,
26 Pipemidic acid (PIP) and Bisphenol A (BPA), with MnO₂ surfaces controlled on the removal
27 kinetic behavior, which depended on contaminant type and co-existing anions. Competition
28 between contaminant and Mn(II) for binding at the edge sites determined the initial kinetic step,
29 while buildup of Mn(II) at both edge and vacancy sites continuously decreased adsorption and
30 subsequent oxidation over time. Redox interactions of Mn(II) to MnO₂ surfaces was a pH
31 dependent process, and high pH favored Mn(II) removal and comproportionation reaction, thus
32 decreasing adsorption and oxidation processes. At low Mn(II)/MnO₂ ratio, MnO₂ adsorbed more
33 effectively anions such as phosphate or silicate, thus reducing interactions with organic
34 compounds. These results highlight the combined suppressive effects of Mn(II), pH and naturally
35 occurring anions on the reactivity of nanostructured birnessite, and have strong implications on the
36 fate of organic contaminants in terrestrial and aquatic environments.

37 **Keywords:** nanostructured birnessite; redox; emerging contaminants; adsorption; oxidation.

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39 Dissolved Mn(II) , pH and naturally occurring anions exhibit combined suppressive effects on the
40 reactivity of nanostructured birnessite.

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1. Introduction

Manganese oxide / hydroxide (referred here as Mn oxide) are ubiquitous in a wide range of environmental settings, such as soils, sediments, rock dendrites, desert varnishes, ocean floor, and fresh-water bodies.^{1, 2} Because they are powerful oxidants and sorbents, they play a key role in the biogeochemical cycle of many elements.¹ Based on the mineral structure, manganese oxides can be divided into two types: layer and tunnel structure.¹ Layered structure manganese oxides (e.g. birnessite) has gathered interest because it is structurally similar to biogenically precipitated natural manganese oxides.³⁻⁶ The structure of layered birnessite consists of mineral sheets of hexagonal symmetry comprising of edge-sharing MnO_6 octahedra, accompanied by interlayer charge-neutralizing cations.^{3, 7-10} Because of the existence of Mn(III) and possibly Mn(II) within the MnO_2 layers, it has a manganese average oxidation state (AOS) lower than 4.¹¹ Typically, birnessite have high affinity for cations sorption because of high content of vacancy sites, with up to one out of six Mn absent from MnO_6 octahedral sites,^{12, 13} but they also exhibit non-negligible anion adsorption capacity.¹⁴⁻¹⁸ Another important feature of birnessite is the easy switching of the oxidation state, which imparts a good catalytic activity.^{10, 19} Therefore, nanostructured birnessite-type manganese oxides take part in redox-based and cation-exchange reactions with potential for various energy and environmental applications.^{1, 20-25}

Generally, binding of redox-active compounds to birnessite is followed by an electron transfer process resulting in the concomitant oxidation of sorbed compound and reduction of surface-bound metal. Typically, one electron is transferred from ligand to the surface-bound Mn(IV) to yield Mn(III) that can be further reduced to give Mn(II).^{17, 23, 24, 26, 27} This reactivity is mainly affected by solution pH, oxide surface properties, and structural characteristics of target compound.^{23, 24, 28-30} Some studies have shown that the presence of dissolved Mn(II) induces

changes in mineral structure and reactivity of MnO_2 , but this effect depends on the Mn(II)/MnO_2 ratio and pH value. A high Mn(II)/MnO_2 ratio and $\text{pH} > 7.5$, birnessite can be converted into lower-valence Mn phases, while only slight disturbance in the stacking of MnO_2 sheets caused by incorporation of Mn(III) can be observed at low Mn(II)/MnO_2 ratio and at acidic to neutral pH.^{31, 32} Although the effects of dissolved Mn(II) on the structure and AOS of birnessite have been well investigated,^{5, 17, 31-34} knowledge is limited on how co-existing anions and dissolved Mn(II) affect the dynamic changes of birnessite reactivity towards adsorption and oxidation of organic compounds. In addition, surface interactions of organic ligands with MnO_2 in the presence of dissolved Mn(II) and naturally occurring anions during birnessite partial reduction under a wide range of pH have been scarcely investigated.

In this study, we examined how dissolved Mn(II) , which is commonly found in groundwater from μM to mM concentration ranges^{35, 36} affects the interactions of organic compounds with MnO_2 surfaces and the reactivity of birnessite under different experimental conditions. For this purpose, two contrasting organic contaminants, Pipemidic acid (PIP) and Bisphenol A (BPA), frequently detected in aquatic environments such as surface water and groundwater³⁷⁻³⁹ were selected as environmentally relevant model compounds. PIP is a synthetic broad-spectrum antibacterial belonging to quinolone antibiotics, and widely used to treat various infections in human and veterinary medicine.²⁵ Quinolones are electron donor-acceptor compounds with the piperazinyl group serving as the electron donor and carboxylic group as the electron acceptor in the neutral and zwitterion forms.^{27, 40} Bisphenol A is an important endocrine-disrupting compound, and contains two hydroxyphenyl functionalities. Nanoflower-shaped birnessite, a poorly crystalline Mn oxide and ubiquitous in nature, was chosen as a representative manganese oxide mineral. The surface interactions of PIP or BPA including adsorption and

oxidation with birnessite have been investigated in presence of variable amounts of Mn(II) and under a wide range of pH (4-8). Total removal rates including the rate-determining step have been determined using different kinetic models. The oxidation byproducts of BPA and PIP were identified using Ultraperformance Liquid Chromatography-tandem Mass Spectrometry (UPLC-MS/MS) system. The impact of Mn(II) was also studied in presence of commonly found natural anions, phosphate and silicate. The possible transformation of solid has been monitored using XRD and ATR-FTIR under different conditions (Mn(II)/MnO₂ ratio and pH value). Finally, the reactivity changes of birnessite due to the combined effects of Mn(II), pH and anionic ligands and underlying mechanisms were discussed.

2. Materials and Methods

2.1. Materials

All reagents were purchased from Sigma-Aldrich and used without further purification. All solutions were prepared with ultrapure water (specific resistivity, 18.2 MΩ cm⁻¹, Milli-Q, Millipore).

2.2. Acid birnessite synthesis and characterization

Acid birnessite was prepared following the procedures of McKenzie.⁴¹ 166 mL of concentrated HCl was added dropwise to 2.5 L of 0.4 M KMnO₄. The suspension was stirred vigorously and kept at 90°C during the HCl addition. The reaction was continued at 90 °C for a further 10 min. Then, the obtained slurry was stirred vigorously at room temperature for 15 h. The precipitate was collected by centrifugation, washed with ultrapure water repeatedly until the conductivity was close to 0.6 μS cm⁻¹. The suspensions were stored in polypropylene containers at 4 °C for further use.

The purity of acid birnessite was confirmed by powder X-ray diffraction (XRD) (Figure S1). The XRD data were recorded with the monochromatized CuK α radiation on a Bruker AXS D8 Advance diffractometer (θ -2 θ Bragg-Brentano geometry) over the range of 10°-100° 2 θ at a step size of 0.02°. The N₂ Brunauer–Emmett–Teller (BET) specific surface area of the synthetic acid birnessite was $65 \pm 1 \text{ m}^2 \text{ g}^{-1}$. The Average Oxidation State (AOS= 3.98 (± 0.02)) of synthetic birnessite was measured using the oxalic acid-permanganate back-titration method (more details are provided in the Supporting Information (SI)). Scanning Electron Microscope (SEM; JEOL JSM-7100F) and High-resolution Transmission Electron Microscope (HRTEM; JEOL 2100 LaB₆) images showed a nanoflower-shaped birnessite consisting of nanoflakes aggregations (see Figures S2 and S3).

2.3. Adsorption/oxidation batch experiments

For all experiments, NaCl concentration was set to 10 mM. The pH was adjusted to the desired values using additions of 0.1M HCl or 0.1M NaOH solution and maintained constant throughout the experiments. Before experiments, acid birnessite was sonicated 5 min for better dispersion.

Batch experiments were carried out under ambient conditions. Solutions were spiked with aliquots of 1 mM PIP or BPA to achieve initial concentration of 20 μM . An Aqueous suspension of acid birnessite (870 μM) was employed, and the effect of dissolved Mn(II) was investigated by adding small amounts of 0.05 M MnCl₂ solution. In the simultaneous experiments, PIP or BPA, acid birnessite and MnCl₂ solution were mixed at the same time. In the pre-equilibrium or sequential experiments, suspensions containing manganese oxides and MnCl₂ were stirred for a certain time (2 h or 24 h) before adding PIP. The agitation speed of the mixture was stirred at 300 rpm during the experiments at room temperature. Aliquots of solution were periodically withdrawn

and filtered (0.2 μm) for compound analysis. Other aliquots without filtration were immediately mixed with NaOH or ascorbic acid to quench the reaction and release eventual sorbed compounds. The same procedure was applied to test the effect of Mn(II) in the presence of anions (silicate or phosphate) on PIP oxidation.

Mn(II)-birnessite isotherm experiments were performed at pH 4, 5.5, 7.5, 8 (± 0.1) under oxic conditions. The experiments were employed in 50 mL polyethylene tubes at a total volume of 50 mL solution using the same acid birnessite suspension density (870 μM) and initial aqueous Mn(II) concentrations in the range of 0 to 2000 μM . The tubes were sealed by caps and then shaken continuously at 200 rpm. During the equilibration time, the pH was adjusted to maintain the initial value. After 2 days of equilibration, the samples were centrifuged for 30 min at 4500 rpm. The supernatants were filtered through 0.2 μm membranes, while the centrifuged wet pastes of the acid birnessite obtained were analyzed by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) (more details are given in the SI). Mn(II) removal was calculated as the difference between the initial and final Mn(II) solution concentrations. To examine the impact of dissolved O_2 on the Mn(II) sorption, parallel experiments with the same process at pH 4 and 5.5 (± 0.1) were conducted in glovebox under N_2 atmosphere. All experiments were conducted in triplicates and the standard deviation was calculated for all experimental series.

2.4. Analytical procedures

Aqueous concentrations of PIP or BPA were determined using High Performance Liquid Chromatography analysis with UV-vis detection (HPLC-UV) equipped with a reversed-phase C18 column (250 mm $\times$ 4.6 mm i.d., 5 μm) and an UV-vis detector (Waters 2489). The mobile phase was a mixture of acetonitrile/water (15/85 v/v, PIP; 65/35 v/v, BPA) containing 0.1% formic acid. The flow rate of mobile phase was set at 0.5 mL/min (PIP) or 0.6 mL/min (BPA). The UV detector

was set to 278 nm for PIP and BPA. Silicate concentrations were determined by the molybdenum-blue colorimetric method.⁴² Dissolved Mn(II) concentrations in supernatants were determined by Atomic Absorption Spectroscopy (AAS, AA140, Varian, Shimadzu). The byproducts of BPA and PIP oxidation were identified using Ultraperformance Liquid Chromatography-tandem Mass Spectrometry (UPLC-MS/MS) system. An electrospray interface was used for the MS measurements in positive ionisation mode and full scan acquisition. No quantification has been made by LC/MS because the identified byproducts are not commercially available. ATR-FTIR and XRD were performed to determine the possible transformation of solids upon Mn(II) sorption. More details of these analytical methods are given in the SI.

3. Results and Discussion

3.1. Removal kinetics of PIP and BPA with birnessite

Kinetic batch experiments conducted at pH 5.5 showed complete removal of BPA within 1 h of reaction time (Figure 1a). A delay in complete removal was observed when Mn(II) was added to MnO₂ suspension, *e.g.* 25 h was needed for complete removal with the highest Mn(II) loading (Mn(II)/MnO₂ = 0.23). Slower removal kinetics were observed for PIP when compared to BPA (Figure 1b). Mass balance showed that adsorption and oxidation are involved in the removal of BPA or PIP in presence of MnO₂ (Figures 1 and S5), even though the adsorption appears to be relatively low under our experimental conditions. The overall removal rate can be dominated by either the rate of intrinsic chemical reactions on the surface (adsorption following by oxidation) or the rate of diffusion of the solute to the surface.

Pseudo-first-order and pseudo-second-order models were used to describe the removal of BPA and PIP, respectively, after an extensive search for best-fitting kinetic models accounting for these experimental concentration profiles. The pseudo-first-order rate equation is given as:

$$\ln \frac{[BPA]_{tot}}{[BPA]_0} = -k_1 t \quad (1)$$

The pseudo-second-order equation is expressed as:

$$\frac{1}{[PIP]_{tot}} = \frac{1}{[PIP]_0} + 2k_2 t \quad (2)$$

The pseudo-first-order apparent rate constant k_1 (h^{-1}) obtained by linear regression of $\ln([BPA]_{tot}/[BPA]_0)$ versus time were plotted against initial Mn(II) amount in Figure 1c. The pseudo-second-order rate constant, k_2 ($\text{L } \mu\text{mol}^{-1} \text{ h}^{-1}$), calculated from the slope of the plots of $1/[PIP]_{tot} - 1/[PIP]_0$ versus t , are given in Figure 1d (regression coefficients for all fitting is greater than 0.92). While a pseudo-first order may suppose no-chemical limiting step, the pseudo-second-order model suggests that the chemical reaction may be the rate-limiting step and the adsorption occurs probably via surface complexation reactions at specific sorption sites.⁴³ This falls in line with the PIP chemical structure where metal-bonded complexes with surface sites and/or directly hydrogen-bonded complexes with surface hydroxo groups involving both carboxylate and keto groups are expected based on previous investigations for analogous compounds.^{27, 44, 45} At pH 5.5, PIP exists under zwitterionic form (pK_a 5.20 and 6.38), whereas the BPA molecule is only in the protonated form (Figure S4). BPA containing only phenolic groups exhibits weaker sorption to metal surfaces through probably Van der Waals interactions and/or hydrogen bonds, but higher removal rate as compared to PIP (Figure 1). If the formation of the precursor complex is the rate-limiting step, our kinetic comparison let suppose that weaker binding of phenolic compounds are more energetically favorable than the surface complexation of polyfunctional carboxylated compounds. Afterwards, electron exchange of BPA with MnO_2 form a radical, followed by a series of reactions including radical coupling, fragmentation, substitution and elimination to form multiple byproducts (up to 11 byproducts have been reported).^{20, 22, 24} Our LC/MS analysis

202 identified one predominant species of mass-to-charge ratio of $m/z=135$ as the most dominant
 203 byproduct of BPA over the first reaction time (1 h), which likely corresponds to 4-hydroxycumy
 204 alcohol according to previous investigation.⁴⁶ For PIP, LC/MS analysis confirmed the formation
 205 of one predominant species of $m/z=227$ (M-26) through N-dealkylation of the piperazine ring of
 206 PIP. Indeed, the piperazine ring of PIP can be oxidized through two one-electron transfers from the
 207 N atom of piperazine ring to Mn(IV), and then N-dealkylation and/or C-hydroxylation cause ring
 208 opening, as typically observed for similar compounds.^{20,23,25}

Figure 1. Top: Removal kinetics of BPA and PIP ((aq) = aqueous residual concentration; (tot)= total concentration representing both residual concentration and adsorbed concentration obtained after desorption. The R number refers to Mn(II)/MnO₂ ratio. Bottom: kinetic rate constants at different Mn(II)/MnO₂ ratio. Experimental conditions: [BPA or PIP] = 20 μ M; [acid birnessite] = 870 μ M; [NaCl] = 10 mM; pH = 5.5 $\pm$ 0.1.

On the other hand, dissolved Mn(II) displayed suppressive effects on the removal rate of BPA and PIP (Figure 1). The rate constant for PIP sharply decreased with increasing in dissolved Mn(II) amount, whereas the rate constant for BPA did not significantly change between 0 and 50 μ M (the difference is statistically not significant given the relative standard deviation, Figure 1) but later decreased with increasing in Mn(II) amount as for PIP. The decrease in the oxidative ability of MnO₂ in the presence of dissolved Mn(II) may result from competition of compound and Mn(II) to interact with reactive surface sites and/or aqueous complexation of compound with Mn(II). However, the effect of aqueous complexation reaction should be of less importance due to weaker binding (low stability constant) of phenols or quinolones with divalent cations such as Mn(II).⁴⁷ It should be noted that the PIP adsorbed amount at low Mn(II) loading first increased, probably due to favorable electrostatic interactions with MnO₂ surfaces because of the adsorption of Mn(II) ions, and then decreased over reaction time (Figure S5). On the other hand, strong binding of Mn(II) to MnO₂ surfaces suggests competition of target compounds and Mn(II) for surface sites. Indeed, complete removal of dissolved Mn(II) was observed for initial [Mn(II)]_{aq} < 100 μ M, whereas at the highest Mn(II) supplied amount (200 μ M) more than 60 % of Mn(II) was removed (Figure S6).

Previous studies have determined two different types of adsorption sites at the MnO₆ octahedra layers of layered type birnessite, 1) edge sites and 2) vacancy sites.⁴⁸ Edge sites are present on the edge of Mn octahedral sheets and are usually the first sites to react with

contaminants, whereas vacancy sites are present within the Mn octahedral sheets, and are typically associated with long-term adsorption and oxidation sites of contaminants through diffusion from the edge sites.^{13,25,49} Previous reports^{25,50,51} predicted that anionic compounds are likely to bind only at the edge sites of MnO₂, whereas cationic Mn(II) could bind at both edge and vacancy sites. Wang et al.⁵⁰ reported that because of the highly negative charge of the vacancy sites, fulvic acid (negatively charged polycarboxylic compound) would bind preferentially to edges and not vacancies. Based on all these observations, we hypothesized that the total removal rate of PIP in our experimental scenario is controlled by the PIP adsorption onto surface sites (i.e. formation of the precursor complex) and/or the diffusion of Mn(II) from edge sites to vacancy sites, making the previously occupied edge sites available for further PIP binding. The latter diffusion process could explain the enhanced PIP adsorption during the initial kinetic phase, and subsequent oxidation of bound PIP as the reaction proceeded (Figure S5).

As an attempt to assess the time-dependent competition of PIP and Mn(II) towards MnO₂ surfaces, Mn(II) and MnO₂ (Mn(II)/MnO₂ ratio 0.11) were allowed for longer pre-equilibration times (2 h or 24 h pre-equilibration) before PIP addition instead of simultaneous mixing of all the three reactants. While the total removal rate of PIP is not significantly affected, the PIP adsorbed amount at the first kinetic stage decreased in pre-equilibrated tests, suggesting that adsorption sites for PIP may be pre-occupied with Mn(II) during the pre-equilibration period (Figure S7). When PIP and Mn(II) were reacted with MnO₂ at the same time, we speculate a competition between PIP and Mn(II) to bind at the edge sites of MnO₂ during the first kinetic phase. As a result, with increasing dissolved Mn(II) amounts, the competition for PIP binding to the edge sites also increases. Ultimately, the buildup of Mn(II) at the edge sites will continuously decrease PIP adsorption and the subsequent oxidation with time. A further kinetic modeling based on two types

of sorption sites (see details in the SI) confirmed that Mn(II) can alter both adsorption and oxidation reactions at MnO₂ surfaces. Taken together, our results showed that the amount of available dissolved Mn(II) considerably influenced organic contaminants interactions with MnO₂ surfaces. As pH may also affect Mn(II) redox reactions, the effect of pH on the PIP removal rate was investigated in the following section.

3.2. Effects of pH and Mn(II) on the removal rate of PIP

The removal kinetics of PIP at different initial concentrations of Mn(II) (0, 100, 200 µM) were compared at three pH values (4, 5.5 and 8). Figure 2 shows that pseudo-second-order rate constants of PIP removal were sensitive to solution pH. The rate constants for all investigated Mn(II) amounts (0, 100, and 200 µM) exhibited the same order, pH 4 > pH 5.5 > pH 8. This suggests that acidic conditions favored PIP removal, a trend also observed for analogous quinolones reacting with MnO₂.^{23,52} We attribute this to variability in two pH-dependent factors: 1) speciation of PIP that affects binding to MnO₂ surfaces and then oxidation (as described in section 3.1), and 2) redox-potential of MnO₂.^{23,52} PIP molecules were predominantly present in protonated (cationic), zwitterionic (neutral), and deprotonated (anionic) form at pH 4, 5.5, and 8 respectively (Figure S4). At relatively low pH, electrostatic interactions of positively charged PIP molecules are favored with the negatively charged surface of MnO₂ (PZC of MnO₂ is ~2.3-2.9).^{9,53}

Increasing the pH enables more negative surface charge, thereby limiting the interactions with the negatively charged PIP.⁵⁴ We verified this experimentally as the amount of PIP adsorbed at pH 8 was significantly less than that measured at pH 4 in all experiments (Figure S9). Second, a decrease in redox potential of MnO₂ from 0.99 V to 0.76 V has been reported when the pH increased from

4 to 8.⁵⁵ Indeed, reductive conversion of MnO₂ into Mn(II) is dependent on the amount of protons (Eq.3), which would result in increase in PIP removal rate when the pH decreases.

Figure 2. Kinetic rate constants of PIP, plotted as a function of pH at different initial concentrations of Mn(II) (0, 100, 200 μM). Experimental conditions: [PIP] = 20 μM; [acid birnessite] = 870 μM; [NaCl] = 10 mM.

As expected, Mn(II) formed by reductive dissolution of MnO₂ was completely removed by binding to MnO₂ irrespective of the solution pH (Figure S9). Mn(II) was below AAS detection limit (<0.02 μM) in all experiments when no dissolved Mn(II) was supplied in the input solution (Figure S9). When dissolved Mn(II) was supplied, Mn(II) removal was, however, dependent on the pH value. Lower pH enabled more dissolved Mn(II), while more Mn(II) removal was observed at pH 8. For the highest Mn(II) amount (200 μM), the final steady-state Mn(II) concentrations were ~120 μM, ~75 μM, and ~20 μM at pH 4, 5.5, and 8 respectively. Similarly, dissolved Mn(II) was below the detection limit at both pH 5.5 and 8 when 100 μM Mn(II) was used, while a concentration of ~25 μM was still measured at pH 4.

As an attempt to check whether pH can influence the structure of acid birnessite under our experimental conditions, sorption isotherms coupled to ATR-FTIR experiments were investigated at a wide range of Mn(II) concentration (10-2000 μM). First, sorption isotherms showed different shape depending on pH value across the Mn(II) concentration range (Figure 3). Two stages of Mn(II) removal were observed at pH higher than 5.5, while at pH 4 a typical L-shape with a plateau was observed. Indeed, substantial increase in Mn(II) removal amount was observed at higher residual Mn(II) concentration and at pH higher than 5.5, following by either a plateau or continuous increase in removal amount. This S-shaped isotherm of dissolved Mn(II) adsorption by birnessite has been already reported in literature but only at pH higher than 7.^{31,32} They have attributed this behavior to surface-catalyzed oxidation of Mn(II) by molecular oxygen enabling more Mn(II) sorption under oxic conditions relative to anoxic systems through the formation of low valence Mn oxides phases such as feitknechtite ($\beta\text{-MnOOH}$) and/or manganite ($\gamma\text{-MnOOH}$).

Figure 3. Mn(II) sorption isotherms at pH 4, 5.5, 7.5, 8 $\pm$ 0.1 under oxic conditions. Experimental conditions: [acid birnessite] = 870 μM ; [NaCl] = 10 mM; reaction time = 2 d.

To check whether this behavior may occur in our system at that pH range (i.e. lower than 7), we conducted sorption isotherms under anoxic conditions at pH 4 and 5.5, and compared to those determined under ambient conditions. While at pH 4 the oxic and anoxic isotherms overlapped (data not shown), there was significant influence of oxygen on Mn(II) removal at pH 5.5 (Figure S10). However, the ATR-FTIR spectra recorded for sample solids at pH 5.5 did not show any new Mn-phase over the Mn(II) concentration range (200 or 2000 μ M) and equilibration time (2 d or 10 d) (Figure S11), probably due to the low formation extent of Mn^{III}-bearing phase. Manganite was only detected at pH 8 and at high Mn(II) concentration (2000 μ M), at 2 d of equilibration time (as for sorption isotherms) and at longer equilibration time (10 d) (Figure S11). Collectively, these results suggested no phase transformation under the experimental conditions used for kinetic assessment (e.g. 200 μ M) over the investigated pH range. This was further confirmed by XRD analysis, where no notable transformation can be detected (Figure S12).

Despite no evident MnO₂ transformation, we cannot rule out the possibility of formation of Mn(III) species, via comproportionation reaction of adsorbed Mn(II) and structural Mn(IV) in birnessite especially at high pH.^{17,50,56} It is well known that Mn(III) centers are an important surface features of birnessite and are involved in redox reactions with various organic compounds.²⁹ First, the average oxidation state of samples reacted with PIP only slightly decreased from 3.98 to 3.92 (± 0.02) over the investigated pH range. However, partial reduction of MnO₂ upon addition of 200 μ M of dissolved Mn(II) dropped down the AOS to 3.68 (± 0.05) at pH 4 and 5.5, and 3.52 (± 0.05) at pH 8. This decrease suggests that percentages of Mn(III) or Mn(II) or both are relatively higher after 48 h of reaction time with respect to the initial sample. The formation of Mn(III) after 48 h of reaction time in kinetic experiments was further confirmed by the detection of Mn(III)-pyrophosphate complex at 480 nm, Mn(III) being stabilized through ligand-binding complexes.⁵⁷

As an attempt to check the mass balance of Mn(II), desorption tests with high amount of Ca(II) (25 mM) were conducted. This cation has been proposed as a desorption agent of solid bound Mn(II),⁵⁸ though adsorption of Ca(II) on vacant sites is much weaker than Mn(II).⁵⁹ It was also reported that Ca(II) may stabilize Mn(III) in the layers through stronger adsorption of Ca(II) in interlayer regions and then compensation of the charge deficiency caused by the presence of Mn(III).^{9,33,59} More recently, Wang et al.,⁵⁰ reported that Ca(II) could exchange adsorbed Mn(II) from vacancy sites, but not block the edge sites. Then, Mn(II) may be oxidized preferentially on edge sites in presence of Ca(II) favoring Mn(III) production and potential formation of MnOOH/Mn₃O₄ phases⁵⁰. Mn(II) desorbed amounts were determined in PIP/MnO₂ suspensions subject or not to Mn(II) supplying and at different pH values (Figures S13 and S14). As expected in no-input Mn(II) experiments, more Mn(II) was desorbed at low pH values, as more PIP oxidation and more Mn(II) formation were observed at this pH range (Figure S13). However, the desorbed Mn(II) amount was still lower than the stoichiometric amount corresponding to the oxidized PIP (Figure S9). When 200 μ M Mn(II) was present in the input solution, Ca(II) has almost no impact on the amount of dissolved Mn(II), yet a slight decrease in Mn(II) removal was observed at pH 4 and 5.5 (Figure S14). These results showed that Ca(II) failed to recover the removed Mn(II), thereby suggesting comproportionation reaction forming Mn(III), as previously reported in Wang et al.⁵⁰.

3.3. Combined effects of Mn(II) and anions on the oxidation capacity of birnessite

The effects of commonly found inorganic ligands, phosphate and silicate, on the oxidation of PIP with MnO₂ were investigated over the pH range (4-8). The two ligands exhibited similar effects on the PIP oxidation in presence or absence of dissolved Mn(II) (Figure 4). In no-input Mn(II)

experiments, the presence of silicate or phosphate did not significantly influence the kinetic rate constants for PIP removal over the whole pH range, only a small decrease in all experiments was observed (Figure 4). However, when Mn(II) was added in the reaction medium, more than 2-times decrease in kinetic rate constants was measured at pH 4 and 5.5 in presence of silicate or phosphate, and much more (~10 times) at pH 8. It is worth noting that similar behavior was observed in the presence of another type of anion, 100 μ M of NaHCO₃ (pK_a 6.3 and 10.5) at pH 8 (data not shown). Indeed, a significant effect on PIP oxidation was only observed in presence of Mn(II).

Sorption edges showed low affinity of silicate and phosphate (see speciation in Figure S16) to the negatively charged MnO₂ surfaces in absence of dissolved Mn(II). However, presence of Mn(II) relatively enhanced adsorption of silicate and phosphate into MnO₂ surfaces, particularly at high pH values (> 6) (Figure S17).

Figure 4. Kinetic rate constants of PIP vs pH in the absence or presence of silicate or phosphate: (a) no-input Mn(II) experiments, (b) $[Mn(II)]_0=100 \mu M$. Experimental conditions: $[PIP]=20 \mu M$; $[acid birnessite]=870 \mu M$; $[Na_2SiO_3]=100 \mu M$; $[NaH_2PO_4]=100 \mu M$.

These results indicate that the pH-dependence of phosphate or silicate sorption is relatively affected by the presence of Mn(II) ion, which may suppose an enhancement of adsorption of anionic ligands through the formation of a surface-Mn(II)-ligand ternary complex. Indeed, Mn(II) may act as a bridge ion to form a complex with the functional groups of ligand. The formation of aqueous complexes of phosphate with Mn(II) ions has been previously reported and different coordination modes have been proposed.^{60,61} However, there is a lack of information about the complexation of Mn(II) with dissolved silicate ions, but we may suppose that the aqueous

complexation of silicate with divalent cations such as Mn(II) is relatively weak, and lower than that with phosphate.⁶² Furthermore, according to the Irving-Williams series⁶³ and cation adsorption data⁵⁵ ternary surface complexation of cations such as Mn(II), Co(II) and Ni(II) with silicate are supposed to follow the order: Mn(II) < Co(II) < Ni(II). As a result, the stability constant value of Mn(II) should be lower than that previously determined for Ni(II), $\text{Ni(OSi(OH)}_3\text{)}^+$, $\log \beta = 6.34$ at $I = 0.00\text{M}$.⁶⁴ Because both ligands exhibited similar effects on removal kinetics, there are probably additional factors which may explain enhanced suppressive effects in presence of these ligands.

As dissolved Mn(II) was completely removed from solution at pH 5.5 and 8 over the first reaction time, enhancement in Mn(II) removal due to the presence of anions cannot be highlighted. At pH 4, no significant change in Mn(II) removal has been observed upon addition of ligands. On the other hand, possible formation of precipitates (*e.g.* phosphate or carbonate with manganese ions) is not expected under our experimental conditions due to the low degree of saturation. Indeed, the lower aqueous concentration of free Mn(II) (particularly after adsorption) or ligand exclude a possibility of such precipitation based on the mineral solubility, *i.e.* according to the solubility constant of Mn(II) phosphate ($\log K_s = -27.07$)⁶⁵ and MnCO_3 ($\log K_s = -10.58$).⁶⁶ In addition, FTIR analysis of reacted samples did not reveal any new precipitate (data not shown).

While interactions of silicate with MnO_2 is rarely investigated, adsorption of phosphate has been described by the formation of outer-sphere complexes with surface hydroxyl groups of $\delta\text{-MnO}_2$ at the same pH range (4-8).^{14,67} On the other hand, potential change of the surface charge from negative to positive by exchange of H^+ on the MnO_2 surface may occur during Mn(II) adsorption, a phenomenon also observed during the adsorption of arsenate in presence of Ca(II) or Mg(II).^{14,67} The Mn(II) adsorption should lead to a decrease in the negative surface charge, thereby enhancing ability to bind anions and ultimately competition with target compounds. Therefore,

positively charged MnO_2 surface may favor adsorption of anionic compounds like phosphate and silicate through electrostatic attraction. Indeed, in experiments with input Mn(II) , competition between PIP and silicate/phosphate to bind at the MnO_2 edge sites can be responsible for suppressed PIP oxidation. However, in experiments with no input Mn(II) , potential changes in surface charge of MnO_2 caused by the *in situ* generated Mn(II) was probably not sufficient to permit favorable electrostatic binding of silicate/phosphate. Hence, negligible influence in PIP adsorption and removal rates has been observed in this setup. Furthermore, possible stabilization of dissolved Mn(III) through ligand complexation with phosphate or silicate (as generally reported for pyrophosphate) cannot be verified because of the lack of data on complexation reactions. Nevertheless, this potential stabilization of Mn(III) could be excluded because no significant impact of phosphate or silicate has been observed in no-input Mn(II) experiments. Overall, the results suggest that the MnO_2 -bound Mn(II) system could adsorb more effectively anions such as phosphate or silicate and thus reducing interactions with organic compounds.⁵⁶

4. Conclusions

We have notably demonstrated that dissolved Mn(II) and anionic ligands, commonly found in terrestrial and aquatic environments, concurrently affect the adsorption and oxidation of organic compounds on nanostructured MnO_2 surfaces. In contrast to phenolic compounds where adsorption is mainly driven by weak van der Waals-type hydrophobic interactions, removal kinetics of carboxylated compounds (e.g. PIP) generally bound to MnO_2 through surface complexation reactions exhibited two-stage behavior. During the initial kinetic stage, there was competition between compound and Mn(II) for binding at edge sites, while accumulation of Mn(II) at both edge and vacancy sites continuously decreased adsorption and subsequent oxidation over time. Furthermore, pH affected redox interactions of Mn(II) on MnO_2 surfaces and Mn(II) - Mn(IV)

comproportionation reaction, thus decreasing adsorption and oxidation processes. Nanostructured birnessite, with a surface charge modified upon Mn(II) binding, adsorbed more effectively anionic ligands such as phosphate or silicate and thus reducing interactions with organic compounds at a range of environmentally relevant pH values. Therefore, co-existing anions and dissolved Mn(II) must be considered when examining the reactivity of nanostructured birnessite under environmentally relevant conditions. These findings call for consideration of the co-binding effects of cations and anions on the surface charge of birnessite-type manganese oxide nanoparticles, in contaminant fate and transport modeling studies.

Conflicts of interest

There are no conflicts to declare.

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Footnote

† Electronic supplementary information (ESI) associated with this article can be found in the online version: Additional information regarding analytical and characterization techniques, SEM/TEM images, additional data on removal kinetics and kinetic modeling, ATR-FTIR and XRD data, anions adsorption and speciation.

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