

Spectroscopic Investigation of Interfacial Interaction of Manganese Oxide with Triclosan, Aniline, and Phenol

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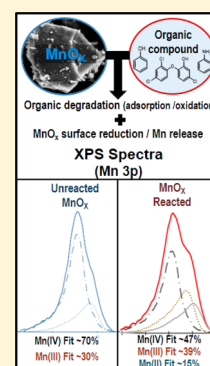
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S Supporting Information

ABSTRACT: We investigated the reaction of manganese oxide [MnO_x(s)] with phenol, aniline, and triclosan in batch experiments using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and aqueous chemistry measurements. Analyses of XPS high-resolution spectra suggest that the Mn(III) content increased 8–10% and the content of Mn(II) increased 12–15% in the surface of reacted MnO_x(s) compared to the control, indicating that the oxidation of organic compounds causes the reduction of MnO_x(s). Fitting of C 1s XPS spectra suggests an increase in the number of aromatic and aliphatic bonds for MnO_x(s) reacted with organic compounds. The presence of 2.7% Cl in the MnO_x(s) surface after reaction with triclosan was detected by XPS survey scans, while no Cl was detected in MnO_x-phenol, MnO_x-aniline, and MnO_x-control. Raman spectra confirm the increased intensity of carbon features in MnO_x(s) samples that reacted with organic compounds compared to unreacted MnO_x(s). These spectroscopy results indicate that phenol, aniline, triclosan, and related byproducts are associated with the surface of MnO_x(s)-reacted samples. The results from this research contribute to a better understanding of interactions between MnO_x(s) and organic compounds that are relevant to natural and engineered environments.



INTRODUCTION

The presence of emerging organic micropollutants (e.g., hormones, pharmaceuticals, and endocrine-disrupting compounds) has been increasingly scrutinized in natural waters, wastewater, and reused water in recent decades.^{1,2} Water reuse has become a necessary practice in semiarid regions experiencing extended dry seasons because of the effects of climate change and increasing population. Despite these organic micropollutants occurring in trace concentrations in the environment,^{3,4} new advances in analytical techniques have permitted the detection and quantification of these chemicals.^{5,6} Detrimental effects of increasing concentrations of these micropollutants on the ecosystem have been reported, especially effects on aquatic life.^{7,8} Olfactory disruption leading to loss of homing behavior, retarded growth, and mutation of reproductive organs are examples of negative impacts caused by these organic micropollutants.^{8–12}

Some examples of organic micropollutants are phenol, aniline, and triclosan. Phenol and aniline are widely used in manufacturing of chemicals such as plastics (polycarbonates and polyurethane), pesticides (phenoxy herbicides and diphenylamine), and pharmaceuticals (aspirin and acetanilide).^{13–15} Because of their toxicity, they have been listed as high-priority pollutants by the U.S. Environmental Protection

Agency (EPA).¹⁶ Triclosan [5-chloro-2-(2,4-dichlorophenoxy)-phenol] is another chemical widely used as an antimicrobial^{17,18} that can cause the development of bacterial resistance¹⁹ and can inhibit lipid synthesis.²⁰ Additionally, heat and light can cause degradation of triclosan, forming chloro-dioxins, which are highly toxic.²¹ Despite the existing evidence of the detrimental effects of these emerging contaminants, only 25% of wastewater treatment plants in the United States manage to exceed 90% removal of these micropollutants.²²

The reaction mechanism of phenolic compounds (ArOH) or aniline (ArNH₂) with manganese oxides has been studied as a surface-limited two-electron overall transfer redox reaction. The proposed step-by-step mechanism can be summarized as follows: (i) adsorption of ArO[•]/ArNH₂ to the MnO_x(s) surface,^{23–26} (ii) formation of radical ArO[•]/ArNH₂[•] and reduction of Mn(IV) to Mn(III) on the surface of MnO_x(s),^{24,25,27,28} (iii) release of a fraction of radicals followed by their resonance and formation of polymeric products,^{24,25,29} (iv) oxidation of adsorbed radicals to oxidized products and

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reduction of Mn(III) to Mn(II),^{24–26,29,30} (v) release of the redox reaction products from the surface,^{27,29} and (vi) adsorption and reoxidation of Mn(II) on the surface of MnO_x(s).^{29,31} Studies have shown that the reaction of phenols with MnO_x(s) produces a phenoxy radical that resonates and polymerizes to give polymeric products like phenol dimers, para-substituted benzoquinones, and hydroquinones.^{24,29} A major product of triclosan oxidation is 2,4-dichlorophenol along with some *p*-quinones.²⁶ Aniline reacts with MnO_x(s) to produce hydrazobenzene because of head-to-head coupling of the aniline radical, which is further oxidized to form azobenzene as the primary reaction product.²⁵

Although the oxidation of organic compounds by reaction with manganese oxide [MnO_x(s)] has been widely studied,^{28,29,32–34} little is known about the changes in the chemical composition of the reacted MnO_x(s) surfaces.²⁹ Several studies have shown the importance of MnO_x(s) in abiotic degradation of various phenolic^{24,26,35} and aromatic amines,^{25,36} which results in the reductive dissolution of MnO_x(s) and an increase in the level of soluble Mn²⁺. Abiotic reduction of MnO_x(s) by light and metals can result in varying amounts of stable Mn(III)–(oxyhydro)oxide solids.^{37–39} A recent study showed that the microbial reduction of MnO_x(s) under anaerobic conditions resulted in long-lived Mn(III)OOH, Mn(II) phosphate, and Mn(II) carbonate.⁴⁰ Although soluble Mn(III) is considered unstable, chelating agents such as pyrophosphate and DFOB (desferrioxamine B) can stabilize aqueous Mn(III).^{41–45} Given that Mn(III) is a relevant intermediate in the reduction of Mn(IV) to Mn(II), the fate and role of Mn(III) must be further investigated after the reaction of MnO_x(s) with organic compounds. The changes in chemical composition on the MnO_x(s) surface after reaction with organic compounds are not yet completely understood.^{26,29}

The objective of this study is to determine changes in the Mn oxidation state and chemical composition of MnO_x(s) after reaction with synthetic organic compounds under controlled laboratory conditions. We have integrated solution chemistry, X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy measurements to investigate the interfacial reaction of MnO_x(s) with aniline, triclosan, and phenol. The use of spectroscopic techniques in this study seeks to identify the increased presence of reduced Mn [e.g., Mn(III) and Mn(II)] on the surface of MnO_x(s) and surface association of organic compounds after these interfacial reactions. Findings from this study contribute to a better understanding of the reactivity of MnO_x(s) with organic compounds, which is relevant for naturally occurring biogeochemical processes. The knowledge of these interfacial interactions is also fundamental for the development of water treatment technologies that use MnO_x(s) to remove emerging organic micropollutants.

MATERIALS AND METHODS

Materials. Phenol, aniline, and triclosan (>99% pure) were purchased from Sigma-Aldrich (St. Louis, MO). All other chemicals were bought from VWR or Thermo Fisher with >90% purity and used without further purification. Delta manganese dioxide [δ -MnO_x(s)] was used in this study, as it is considered analogous to birnessite.^{43,46} Birnessite is the naturally abundant form of manganese oxide⁴⁶ arranged as edge-sharing MnO₆ octahedra with mixed valent manganese centers.³¹ The δ -MnO_x(s) was synthesized as described by Taujale and Zhang⁴⁷ by reacting KMnO₄ and MnCl₂ under basic conditions. Additional details about the synthesis of

MnO_x(s) are provided in the [Supporting Information \(text S1\)](#). The scanning electron microscopy (SEM) images, energy dispersive X-ray spectroscopy (EDX) spectra, and X-ray diffraction patterns for the synthesized MnO_x(s) are also provided in [Figure S1](#). A specific surface area of 168 m² g^{−1} was measured for the synthesized MnO_x(s) using multipoint N₂-BET.

Experimental Setup. The experiments were performed in triplicate in 200 mL amber glass bottles so that the conditions resembled those used in previous studies.^{26,47,48} Briefly, reactors with 10 mM MnO_x(s) were prepared and labeled as “MnO_x-control”, “MnO_x-aniline”, “MnO_x-phenol”, and “MnO_x-triclosan” (we will refer to these samples using these labels hereafter) to represent the experimental conditions tested ([Figure S2](#)). The addition of 0.01 M NaCl to each reactor provided background ionic strength, and the solution pH was constantly monitored and adjusted to 5.0 using hydrochloric acid and sodium hydroxide. The reactors were continuously stirred using a magnetic stirrer at 22 ± 2 °C. Aniline, phenol, and triclosan were added at a concentration of 1.0 mM to each reactor. Some reactors contained MnO_x(s) in a solution with a background ionic strength but no organic compounds and were used as the MnO_x-control. Samples of 1 and 10 mL aliquots were collected at different reaction time points (5, 10, 20, 30, 40, 60, 120, and 1440 min) for all reactors. A volume of 25 μL of 1 M NaOH was added to all 1 mL aliquots to quench the reaction and desorb all unreacted organics so that the measured loss of the organics was due to only oxidation.²⁶ After filtration through 0.22 μm membranes, the samples were analyzed by high-performance liquid chromatography (HPLC) coupled with diode array detection (DAD) for the concentrations of aniline, phenol, and triclosan. The 10 mL samples were filtered through 0.22 μm membranes and acidified with HNO₃, and total Mn was measured using a PerkinElmer NexION 300D (Dynamic Reaction Cell) inductively coupled plasma mass spectrometer (ICP-MS), with a detection limit of <0.5 μg L^{−1}. At the end of the reaction, the reactors were not stirred and left overnight to settle. After the supernatant had been decanted and discarded, the remaining suspensions were centrifuged at 12000g for 20 min. The supernatant was discarded, and the settled particles were collected for solid analysis.

Kinetics. Pseudo-first-order kinetic analyses were performed to represent mathematically the reaction of organic compounds with MnO_x(s) using the following equations:

$$\frac{dC_{\text{org}}}{dt} = -kC_{\text{org}} \quad (1)$$

where C_{org} is the molar concentration of the organic compound in the reactor, t is the time in minutes, and k is the pseudo-first-order rate constant.

Then the solution to eq 1 is

$$\ln\left(\frac{C_{\text{org}}}{C_0}\right) = -kt \quad (2)$$

where C_0 is the initial organic concentration. Note that, because the concentration of MnO_x(s) (10 mM) used in the batch experiments was in excess compared to the concentration of the organic compounds (1 mM), we considered a pseudo-first-order analysis to be appropriate; a similar approach and similar concentrations have been reported in other studies.^{24,25,35,49}

X-ray Photoelectron Spectroscopy (XPS). XPS was used to identify the surface composition and oxidation state of

Table 1. XPS Survey Scans for MnO_x Control and Reacted Samples

	C 1s (%)	O 1s (%)	Mn 2p (%)	N 1s (%)	Cl 2p (%)
MnO _x -control	26.2 ± 6	47.9 ± 2	25.4 ± 6	BDL ^a	BDL ^a
MnO _x -aniline	40.9 ± 3	38.6 ± 1	18.7 ± 3	1.4 ± 1.3	BDL ^a
MnO _x -phenol	39.4 ± 6	40.0 ± 3	19.9 ± 4	0.1 ± 0.6	BDL ^a
MnO _x -triclosan	39.6 ± 5	37.1 ± 2	19.5 ± 5	0.1 ± 0.6	2.7 ± 0.2

^aBelow the detection limit (<0.1%).

elements in the near surface of MnO_x(s) samples. XPS spectra were recorded on a Kratos Axis DLD Ultra X-ray photoelectron spectrometer using a monochromatic Al K α source operating at 225W with no charge compensation. Spectra were recorded from three different areas on each sample; triplicate samples were analyzed for each of the conditions tested in the laboratory experiments (e.g., “MnO_x-control”, “MnO_x-aniline”, “MnO_x-phenol”, and “MnO_x-triclosan”). Pure (>99%) manganese oxides [MnO, Mn₂O₃, MnO₂, and Mn(III,IV) oxide] were purchased from Strem Chemicals (Newburyport, MA) and Sigma-Aldrich (St. Louis, MO). Spectra from reference manganese oxide samples were recorded under the same instrumental conditions but with a charge neutralizer for charge compensation (shown in Figure S3). Elemental survey spectra were recorded at 80 eV and high resolution at a 20 eV pass energy. Data analysis, curve fitting, and quantification were performed using CasaXPS software. High-resolution XPS spectra were processed using Shirley background subtraction and a Gaussian–Lorentzian line shape for the curve fitting of spectra.^{50,51} Calibration of spectra of reference manganese oxide samples was performed using gold powder deposited on each sample with respect to the position of the Au 4f_{7/2} peak (at 84.0 eV). Oxidation states of Mn were determined using the Mn 3s multiplet splitting method and by examination of the shape and position of the Mn 3p region as described by Cerrato et al.^{50,52} Analyses of C 1s and O 1s peaks were conducted on the basis of the results obtained from other studies.^{53–55} The limits of detection for survey scans were 0.1%, and the precision of XPS was ± 0.1 eV.

Raman Spectroscopy. Raman spectroscopy analyses were performed on the samples MnO_x-control, MnO_x-phenol, MnO_x-aniline, and MnO_x-triclosan. All Raman spectra were recorded on a WITec Alpha 300R confocal Raman microscope with 532 nm laser excitation. Samples were prepared as powders on a glass slide, with the excitation laser focused through 10 $\times$ and 50 $\times$ microscope objective lenses for a total spot size of ~ 0.1 μ m. The excitation power was held constant at ~ 150 μ W for all samples. A grating of 600 mm^{−1} was used with a spectral resolution of 0.5 cm^{−1}. Each spectrum has 50 accumulations with an integration time of 0.63894 s. Spectra were fit using Project Four software. The spot size was calculated as $NA \times \lambda/2$, where NA is the numerical aperture and λ is the laser wavelength; 10 $\times$ and 50 $\times$ microscope objective lenses have NA values of 0.24 and 0.75, respectively, so the sampling depths were 64 and 200 nm, respectively.

RESULTS AND DISCUSSION

Surface Elemental Composition. The near surface (top 5–10 nm) elemental composition was quantified using XPS survey scan mode (Table 1). The carbon (C) content for the unreacted sample (MnO_x-control) was 26.2%, with the main peak located ~ 285 eV from C 1s XPS spectra, and is likely due to the contribution of adventitious carbon as reported by other studies.^{56–58} For the reacted samples, there is an increase in the

percentage of C for MnO_x-aniline (40.9%), MnO_x-phenol (39.4%), and MnO_x-triclosan (39.6%), suggesting that organic compounds are associated with the MnO_x(s) surface. Comparable Mn contents were measured for MnO_x-aniline (18.7%), MnO_x-phenol (19.9%), and MnO_x-triclosan (19.5%), which are within 1.3% of each other. In contrast, the Mn content for the unreacted MnO_x-control sample was 25.4%, greater than for all the reacted samples. A similar increase in C content and a decrease in Mn content observed for all the MnO_x(s) reacted samples suggest that the surface sites of MnO_x(s) are occupied by organic compounds. Chlorine is detected only on the surface of MnO_x-triclosan, at 2.7%, suggesting that triclosan reaction products are associated with the surface of MnO_x(s). For aniline-reacted samples, a slight increase in nitrogen content (1.3%) also indicates the presence of aniline and its products on the surface of the medium. Analyses of high-resolution XPS spectra were conducted to determine changes in Mn oxidation states in the unreacted and reacted MnO_x(s).

Analyses of Mn Oxidation States. XPS analyses suggest that Mn reduction in MnO_x(s) occurred given that an increase in the level of Mn(III) and Mn(II) was detected in all reacted MnO_x samples (MnO_x-phenol, MnO_x-aniline, and MnO_x-triclosan) compared to the initial content detected for unreacted MnO_x-control. Reduction of Mn in the reacted samples was confirmed with the XPS Mn 3s multiplet splitting analyses (Table 2). The MnO_x-control sample had a multiplet

Table 2. Results for XPS Mn 3s Multiplet Splitting for (a) Reference Mn Oxides and (b) Control and Reacted Samples^a

sample	curve 1, Mn ⁵ S (eV)	curve 2, Mn ⁷ S (eV)	multiplet splitting (eV)
(a) reference			
MnO; Mn(II)	89.10	83.40	5.69
Mn ₂ O ₃ ; Mn(III)	88.52	83.20	5.33
Li Mn(III,IV)O	88.94	84.05	4.90
MnO ₂ ; Mn(IV)	88.89	84.52	4.38
(b) sample			
MnO _x -control	88.99	84.36	4.63
MnO _x -aniline	88.94	84.00	4.94
MnO _x -phenol	88.77	83.99	4.78
MnO _x -triclosan	88.93	84.12	4.81

^aCurve 1 and curve 2 correspond to the position/binding energy of ⁵S and ⁷S, respectively, for each sample.

splitting of 4.63 eV, indicating the predominance of Mn(IV) given that the multiplet splitting obtained for the Mn(IV) reference is 4.38 eV. On the basis of the Mn 3s multiplet splitting analyses in this study (Figure S4), the Mn in the unreacted MnO_x(s) has an average oxidation state of 3.7, which is consistent with other studies.^{24,31,59} For example, the average oxidation state of Mn in birnessite is 3.6–3.8 due to the

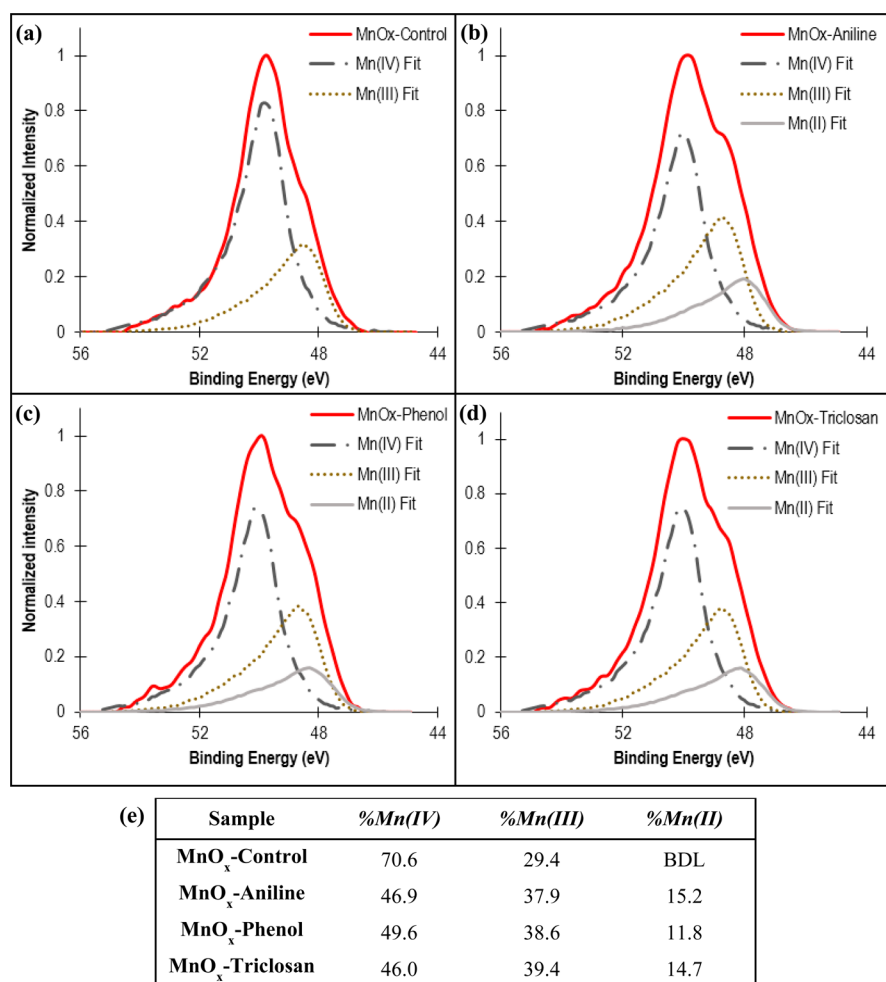


Figure 1. Mn 3p photopeak for (a) MnO_x-control (unreacted), (b) MnO_x-aniline, (c) MnO_x-phenol, and (d) MnO_x-triclosan and (e) percent compositions of Mn 3p spectra by fitting Mn(II), Mn(III), and Mn(IV) reference spectra. Note that the spectra for unknown samples are colored red and for the Mn(II), Mn(III), and Mn(IV) references are shown in grayscale.

presence of Mn(III) among the dominant Mn(IV) species.^{24,59} Hence, the unreacted MnO_x is likely not pure Mn dioxide, with the molecular formula being around MnO_{1.8}–MnO_{1.94} as reported in another study.³¹ The multiplet splitting of the aniline samples (4.94 eV) coincides with the Mn(III,IV) reference. Additionally, similar values for the multiplet splitting were obtained for the phenol-reacted (4.78 eV) and triclosan-reacted (4.81 eV) samples, which are close to the Mn(III,IV) reference (4.9 eV). The average Mn oxidation states for the MnO_x(s) reacted with aniline, phenol, and triclosan are 3.2, 3.4, and 3.3, respectively.

Analysis of XPS Mn 3p high-resolution spectra confirmed a shift toward a lower binding energy (BE) for the reacted MnO_x(s) samples compared to that of MnO_x-control, indicating the presence of Mn(III) and Mn(II) in the surface (Figure 1a–d and Figure S5). The XPS Mn 3p spectra for MnO_x-control closely match up with the Mn(IV) reference, with the exception of a slight shoulder indicative of Mn(III) features around 48.5 eV (Figure 1a). The percent contribution of Mn(IV), Mn(III), and Mn(II) in the Mn 3p spectra of the unreacted and reacted samples (Figure 1e) was determined on the basis of curve fitting and quantification of the Mn 3p high-resolution XPS spectra (shown in Figure 1a–d and Figure S5). An increase in the percent Mn(II) can be observed from fitting the Mn 3p spectra of the samples, with MnO_x-aniline (15.2%),

MnO_x-phenol (11.8%), and MnO_x-triclosan (14.7%) as compared to an undetectable amount of Mn(II) in MnO_x-control. The average oxidation state from the curve fitting was calculated for MnO_x-control (3.7), MnO_x-aniline (3.3), MnO_x-phenol (3.4), and MnO_x-triclosan (3.3). The data obtained from XPS analyses of Mn 3p high-resolution spectra for the average surface oxidation state of MnO_x-control and reacted species are consistent with the Mn 2s multiplet data. Thus, these results suggest that Mn reduction takes place, with reduced Mn(III) and Mn(II) associated with reacted MnO_x(s). Although Mn(IV) was predominant in unreacted MnO_x-control, it had an oxidation state of 3.7 and not 4 because of the presence of 29.4% Mn(III). Other studies have reported that the structural defect caused by the presence of Mn(III) can help to facilitate electron exchange and increase the reactivity of MnO_x(s).^{29,38,46} The observation that Mn was reduced after the reaction with organic compounds in this study indicates that MnO_x(s) acted as an oxidant (that is, it was reduced during these reactions). Additional C 1s and O 1s high-resolution XPS spectra were analyzed (shown below) to improve our understanding of the C and O bonding at the surface of MnO_x-reacted and unreacted samples.

Analyses of Carbon (C 1s) and Oxygen (O 1s) XPS Spectra. Fitting of the C 1s and O 1s high-resolution XPS spectra was performed to analyze the bonding of C and O in

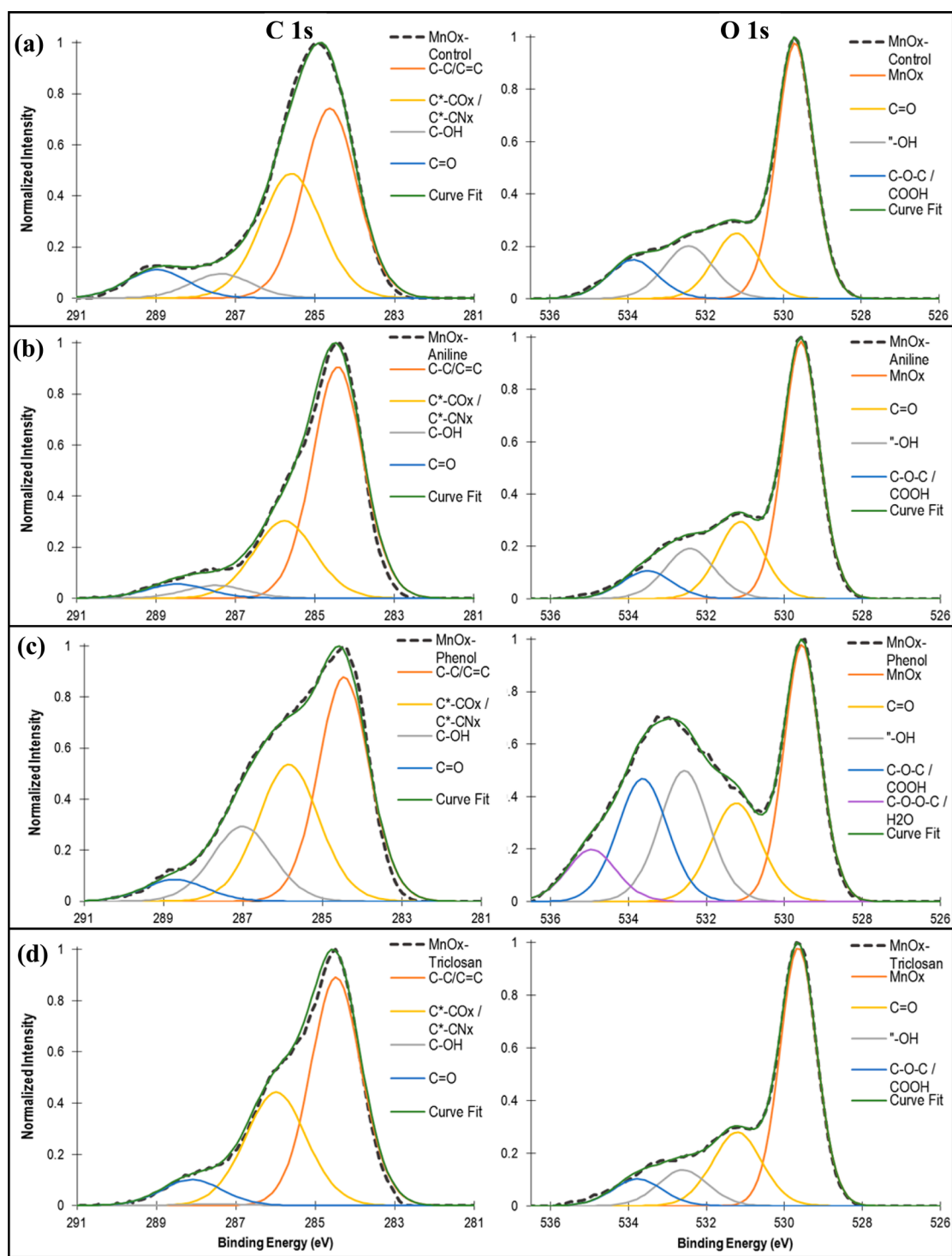


Figure 2. Fitting of XPS C 1s (left) and O 1s (right) spectra with corresponding types of carbon and oxygen bonds based on their signature binding energy for (a) MnO_x -control, (b) MnO_x -aniline, (c) MnO_x -phenol, and (d) MnO_x -triclosan. Black dotted lines correspond to XPS data for unknown samples, solid lines to data for the different types of carbon or oxygen bonds, and solid green lines to the composite curves of these bonds.

the near surface of the reacted and unreacted MnO_x (s) samples (Figure 2 and Figures S6 and S7). The percent compositions of C and O bonding types obtained from the fits of the C 1s and O 1s high-resolution XPS spectra are listed in Tables S1 and S2, respectively. The BE positions for the corresponding C and O bonds observed in this study are based on other studies,^{53–55} which are shown in the column headers of Tables S1 and S2, respectively. The BE positions for all the samples for C=O

bonds (peak at 288.5 eV) were within 1.5% of each other, indicating the lack of ketones and/or aldehydes on the surface.

The unreacted (MnO_x -control) sample had the highest percentage of secondary carbon $\text{C}^*-\text{CO}_x/\text{C}^*-\text{CN}_x$ (peak at 285.6 eV) on the surface that could be due to adventitious carbon with a maximum peak at 285 eV as reported in other studies.^{57,58} All of the reacted samples showed an increase in aliphatic/aromatic carbon C–C/C=C (peak at 284.7 eV), with MnO_x -phenol having the highest (70%) followed by

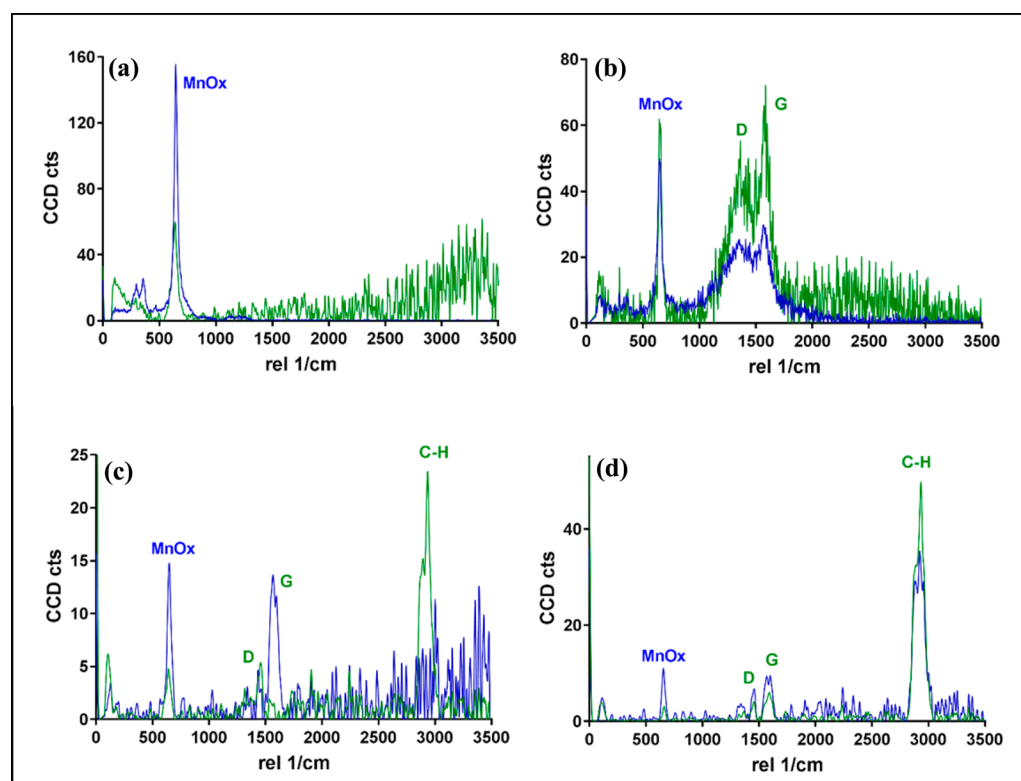


Figure 3. Raman spectra of (a) MnO_x -control (unreacted) and (b) MnO_x -phenol, (c) MnO_x -aniline, and (d) MnO_x -triclosan samples.

MnO_x -aniline (65.4%) and MnO_x -triclosan (62.1%), suggesting the increased level of organic compounds on the surface of MnO_x (s). Analyses of the C 1s high-resolution XPS spectra indicate that both MnO_x -phenol and MnO_x -triclosan have comparable features, suggesting similar binding characteristics (all fits for different carbon bonds were within 10% of each other).

The MnO_x -triclosan and MnO_x -phenol samples had percentages of C–OH bonds (peak at 287.2 eV) detected in the near surface region higher than those of the other samples, 12.5 and 14.2%, respectively, while MnO_x -control and MnO_x -aniline had 6.7 and 3.6% C–OH bonds, respectively. This suggests that phenolic compounds (reaction products such as hydroquinone and catechol^{24,26,60}) are present on the surface of MnO_x , most likely through the ortho or para position of the phenol ring ($>\text{MnO}_x\text{--C}_6\text{H}_4\text{--C--OH}$).³⁵ However, MnO_x -phenol shows a 25% decrease in the level of C*–CO bonds, while MnO_x -triclosan shows a 15% decrease and MnO_x -aniline a 12% decrease in the level of C*–CO bonds when compared to that of MnO_x -control (11, 21, 24, and 36% for MnO_x -phenol, MnO_x -triclosan, MnO_x -aniline, and MnO_x -control, respectively), indicating their different reactivities and surface affinities. Additional XPS analyses were performed on the O 1s high-resolution XPS spectra to improve our understanding of oxygen binding characteristics.

The XPS O 1s high-resolution XPS spectra (illustrated in Table S2 and Figure S7) for MnO_x -control showed a surface composition of metal-bound oxygen (MnO_x) at 55.5%. In contrast, we observed a decrease in the level of metal-bound oxygen on the surface of all the reacted samples, with the lowest being that for MnO_x -phenol at 44%, followed by that of MnO_x -triclosan at 48.6% and that of MnO_x -aniline at 50.6%. This trend is consistent with the decrease in the percent Mn surface composition on reacted MnO_x observed in the survey scans,

suggesting the association of organic compounds in the surface of MnO_x (s). The shape of O 1s spectra is similar for MnO_x -aniline and MnO_x -triclosan. Fitting of these high-resolution XPS O 1s spectra suggests that there was a comparable amount of oxygen double bonded to N or C ($\text{O}=\text{N--C/O}=\text{C}$) in MnO_x -aniline (29.7%) and MnO_x -triclosan (28.4%), with respect to a value of 30.2% in the unreacted control. There was an increase in the level of C–OH bonds for MnO_x -triclosan (15.0%) compared to that of MnO_x -control (10.3%), consistent with the increase in the level of C–OH bonds seen in C 1s high-resolution XPS spectra.

The shape of the O 1s XPS high-resolution spectra for MnO_x -phenol is unique compared to those of all other samples (Figure 2 and Figure S7), given that it has noticeable shoulders at a BE range from 530.6 to 535.4 eV. These shoulders result from the contributions of the C–O–O–C bonds (peak 535 eV) on the surface. Additionally, MnO_x -phenol had the highest composition of C–O–C/COOH bonds (13.4%, compared to 4% in control, 8.4% in aniline, and 8.0% in triclosan) and C–OH bonds (15.9%, compared to 10.3% in control, 11.3% in aniline, and 15.0% in triclosan). This finding in the O 1s high-resolution XPS spectra is consistent with the observed increase in the level of C–OH bonds observed in C 1s high-resolution XPS spectra. Additional Raman spectroscopy analyses were conducted to further analyze the surface of unreacted and MnO_x -reacted samples.

Raman Spectroscopy Analyses. Typical spectra from multiple locations on MnO_x (s) media for the unreacted control and reacted samples are illustrated in Figure 3. In MnO_x -control, the presence of a peak around 600 cm^{-1} is characteristic of manganese oxides.⁶¹ In addition to the peak due to MnO_x (600 cm^{-1}), the MnO_x -phenol-, MnO_x -aniline-, and MnO_x -triclosan-reacted samples have two peaks at 1350 cm^{-1} (D band) and 1580 cm^{-1} (G band). The G band peak at

1580 cm^{-1} is a result of in-plane vibrations of sp^2 -bonded carbon ($\text{sp}^2 \text{C}=\text{C}$ stretch vibrations), while the D band peak at 1350 cm^{-1} is the result of out-of-plane vibrations due to defects in the sp^2 carbon lattice (C–C stretching).^{62,63} MnO_x -aniline and MnO_x -triclosan have a peak at $\sim 2900 \text{ cm}^{-1}$ that is representative of C–H stretching. Poor separation between peaks and peak shapes is representative of highly defective structures such as graphene oxide in which carbon–oxygen species are abundant. This observation of organic groups present in the reacted $\text{MnO}_x(\text{s})$ surface is consistent with the XPS data discussed in the previous subsection. Note that Raman spectra originate from a much greater depth of up to 200 nm, suggesting the possible association of phenol or its oxidation products⁶⁴ within the bulk of reacted MnO_x . Analysis of the solution chemistry data from the batch experiments was then performed to assess the removal of organic compounds and the increase in soluble Mn concentrations in solution to complement these spectroscopic results.

Solution Chemistry Analyses. Increases in the total concentration of Mn in solution were observed for the duration of the batch experiments conducted for this study, confirming the reductive dissolution of $\text{MnO}_x(\text{s})$. This result is consistent with the increased level of Mn(III) and Mn(II) detected in XPS analyses indicating chemical reduction of Mn in $\text{MnO}_x(\text{s})$. The total concentrations of Mn released into solution measured using ICP-MS for the different batch reactors are presented in Figure 4a. The highest concentrations of Mn released in solution were observed for the experiments with $\text{MnO}_x(\text{s})$ reacted with aniline ($17.9 \pm 2.0 \mu\text{M}$), which could be due to the cationic competition for surface sites between aniline cations ($\text{pK}_a = 4.6$)³⁶ (or its oxidation products) and reduced Mn (Mn^{2+} and Mn^{3+}), resulting in a decrease in the extent of sorption of Mn from solution onto $\text{MnO}_x(\text{s})$. This finding is consistent with the Mn surface oxidation state being the lowest for MnO_x -aniline and the decrease in the percent Mn in the survey scans. MnO_x -phenol ($13.4 \pm 2.7 \mu\text{M}$) and MnO_x -triclosan ($11.9 \pm 0.8 \mu\text{M}$) had comparable Mn release concentrations. It is possible that the total concentration of Mn released into solution is predominantly Mn(II) given the absence of complexing agents that could stabilize soluble Mn(III), as suggested in other studies.^{42,65–67} In addition to the occupation of $\text{MnO}_x(\text{s})$ surface sites caused by the association of organic compounds as discussed in the previous paragraphs, the re-adsorption of soluble Mn(II) to the $\text{MnO}_x(\text{s})$ surface can also contribute to surface passivation of $\text{MnO}_x(\text{s})$.^{32,33,68} Assuming one-electron transfer between $\text{MnO}_x(\text{s})$ and the organic compounds, we found more than 90% of the organic compounds were oxidized in the initial 5 min of reaction, yet only a small fraction of soluble Mn was released to solution at this time. By the end of the experiment, the total concentration of Mn increased in solution as well as the percentage of Mn(II) associated with the surface, as suggested by the analyses of Mn high-resolution XPS spectra. It is also worth noting that Mn dissolution was observed for all reactors, consistent with the XPS analyses showing the increase in the level of Mn(III) and Mn(II) and the decrease in percent Mn in the survey scans for MnO_x -aniline, MnO_x -phenol, and MnO_x -triclosan as compared to that of the MnO_x -control samples.

The concentrations of organic compounds remaining in solution after reaction with $\text{MnO}_x(\text{s})$ media were measured (Figure 4b). Triplicate reactors were operated with organic compounds and the background solution in the absence of $\text{MnO}_x(\text{s})$ (organic control). The final measured concentrations

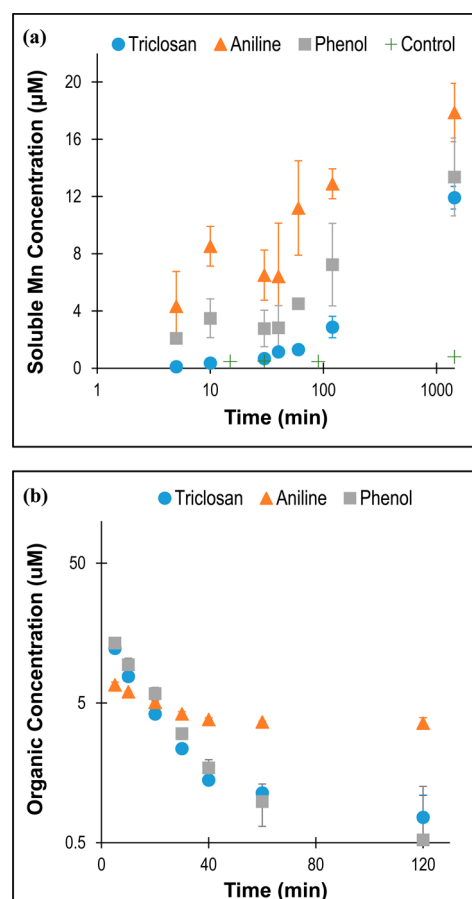


Figure 4. Results from batch reaction experiments ($n = 3$, at sampling times of 5, 10, 20, 30, 40, 60, and 120 min) conducted with 10 mM MnO_x , 1 mM organic reactant (aniline, phenol, or triclosan), and 10 mM NaCl, at pH 5. (a) Concentrations of Mn released into solution measured via ICP-MS, over time (log scale used for time on the X-axis). (b) Oxidation of triclosan, aniline, and phenol measured with HPLC coupled with DAD (log scale used for concentration on the Y-axis).

of these organic compounds were within 2.5% of the initial concentration (1000 μM) after reaction for 1440 min. This control experiment suggests that the degradation of these organic compounds was negligible in the absence of $\text{MnO}_x(\text{s})$. The remaining concentration in solution for the three organic compounds measured after reaction for 5 min is comparable, suggesting that all three compounds have similar initial reactivity. This result agrees with the observed similar C and Mn contents (from XPS scans) on the surface of the reacted $\text{MnO}_x(\text{s})$ samples (within 1.5% of each other). Differences in the pseudo-first-order rate constants of removal of phenol, aniline, and triclosan, however, were observed after the initial rapid phase of reaction. For instance, the pseudo-first-order rate constants between the 5 and 40 min reaction time points for the reaction of $\text{MnO}_x(\text{s})$ with triclosan ($k_{\text{triclosan}} = 0.061 \text{ min}^{-1}$) and phenol ($k_{\text{phenol}} = 0.058 \text{ min}^{-1}$) are similar (within 5% of each other), while the rate constant for the reaction with aniline is >3 -fold lower ($k_{\text{aniline}} = 0.017 \text{ min}^{-1}$). We observed more than 90% removal in the first 5 min, consistent with other studies reporting that the initial removal of organic compounds occurs due to rapid sorption onto unhindered surface sites and subsequent faster oxidation.⁶⁹ At later stages (after reaction for 5 min), much less removal of organic compounds from solution

was observed, likely caused by the occupation of reaction sites in the $\text{MnO}_x(\text{s})$ surface due to the association of organic compounds (causing surface passivation), as has also been observed in other studies.^{26,69} Thus, after 5 min, the organic removal slows and is accompanied by Mn release, likely due to association of Mn(II) on the $\text{MnO}_x(\text{s})$ surface (as seen in Mn 3p XPS fittings). The differences in the rate constants obtained in this study compared to others^{26,69} exist mainly because we did not consider the initial fast reaction and could also be due to the use of higher initial concentrations of organic compounds (1 mM) and $\text{MnO}_x(\text{s})$ (10 mM) to facilitate the spectroscopic analyses that were conducted in this study.

The pseudo-first-order kinetic analyses during the later stage of reaction (Figure S8) suggest that phenol and triclosan have similar oxidation rate constants upon reaction with $\text{MnO}_x(\text{s})$, but the oxidation of aniline is slower. If only the properties of the organic compounds determine the reaction kinetics, different kinetic behaviors should be observed. For example, the pK_a of triclosan ($\text{pK}_a = 7.9$) is lower than that of phenol ($\text{pK}_a = 9.9$), so both compounds are mostly neutral at pH 5. With a larger $\log K_{ow}$ value of 4.76, triclosan is more hydrophobic than phenol ($\log K_{ow} = 1.47$), resulting in stronger surface binding and hence likely higher reactivity.^{26,35} Phenol and aniline have similar reduction potentials (1.16 and 1.02 V vs NHE, respectively),^{70,71} while aniline has a slightly lower $\log K_{ow}$ of 0.90; therefore, their oxidative reactivity should be comparable. Therefore, the observed similar reaction rates for all compounds within 5 min and for phenol and triclosan between 5 and 40 min suggest that the availability of surface sites is more influential than the chemical properties of organic compounds associated with the solids.

Mechanistic Insights. The spectroscopic and kinetic analyses performed in this study identify the relevance of surface-controlled processes with respect to the reactivity of organic compounds with $\text{MnO}_x(\text{s})$. These interfacial interactions caused an increase in the level of Mn(III) and Mn(II) on reacted $\text{MnO}_x(\text{s})$. High-resolution XPS analyses for $\text{MnO}_x(\text{s})$ reacted with triclosan identified the association of organic C–OH and C–O–C functional groups in the near surface region that can be present in dioxins, quinones, and triclosan dimers formed after oxidative reaction of $\text{MnO}_x(\text{s})$ with triclosan as reported in other studies.^{17,21,26} These XPS results also confirmed the presence of C–OH, C–O–O–C, and C–O–C functional groups, which can be attributed to phenol polymerization products associated with the surface after the reaction of phenol with $\text{MnO}_x(\text{s})$. The observed kinetic trend of triclosan $\approx$ phenol > aniline thus suggests that the available surface sites, not the properties of the organic compounds, are important for oxidation kinetics and, subsequently, for resorption and/or reoxidation of aqueous Mn onto $\text{MnO}_x(\text{s})$, as suggested in other studies.^{24,30}

Environmental Implications. This work shows the increased levels of Mn(III), Mn(II), and organic groups on the surface of MnO_x after reaction with organic micro-pollutants, which affects the available reactive surface sites in the solid. These interfacial interactions among $\text{MnO}_x(\text{s})$, organics, and soluble Mn could affect the long-term reactivity of manganese oxides, which could be relevant to the biogeochemistry of $\text{MnO}_x(\text{s})$ in natural and engineered systems. The results of this study reveal relevant information about the changes in Mn oxidation state and chemical composition of $\text{MnO}_x(\text{s})$ after reaction with phenol, aniline, and triclosan. The oxidation of these organic compounds in the

laboratory experiments performed in this study resulted in the reduction of Mn, causing the increased level of Mn(III) and Mn(II) in the surface of reacted $\text{MnO}_x(\text{s})$. The spectroscopic detection of Mn(III) as a stable oxidation state in our experiments is a relevant finding, but more information is necessary to identify whether a phase change occurs and how Mn(III) facilitates the electron transfer process during the oxidation of organic compounds by $\text{MnO}_x(\text{s})$. The increases in soluble Mn concentrations detected by solution chemistry analyses confirm the reductive dissolution of $\text{MnO}_x(\text{s})$ after reaction with phenol, aniline, and triclosan. Although more than 90% of these organic compounds were removed in the first 5 min portion of the reaction in our experiments, a steady concentration of these compounds remained in solution after reaction for 60 min. The decrease in the rate of removal of these organics at later stages of the experiments was likely caused by surface passivation of the $\text{MnO}_x(\text{s})$ surface due to the occupation of surface sites by organic compounds (parent and reaction products) and soluble Mn(II)/Mn(III) associated with the surface, as detected by spectroscopic analyses. This result emphasizes the importance of surface regeneration of saturated $\text{MnO}_x(\text{s})$ media as a limiting factor for the application of $\text{MnO}_x(\text{s})$ to the successful treatment of organic micro-pollutants. Although spectroscopic data from this study provide information about C and O bonding in the reacted $\text{MnO}_x(\text{s})$ surfaces, the identification of specific organic reaction products and how these are associated with $\text{MnO}_x(\text{s})$ is a necessary task for future research. Resolving this gap could aid in the identification of mechanisms or pathways of surface reactions that could explain the difference in the removal rates and product patterns observed for phenol, triclosan, and aniline.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02673.

Additional information about the synthesis of $\delta\text{-MnO}_2$ (Text S1), two additional tables (Tables S1 and S2), and seven additional figures (Figures S1–S7) (PDF)

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Notes

Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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