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**Acetaminophen and Caffeine Removal by $MnO_x(s)$ and GAC
Media in Column Experiments**

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Columns with $\text{MnO}_{x(s)}$ and GAC media operated in series can be used for the removal of organic compounds such as acetaminophen and caffeine in waters with low organic matter content. The $\text{MnO}_{x(s)}$ media can selectively remove acetaminophen, which would retard the exhaustion of available adsorption sites on the non-selective GAC media.

1 Acetaminophen and Caffeine Removal by $\text{MnO}_{x(s)}$
2 and GAC Media in Column Experiments

3 *Rachael Miera¹, Nabil Shaikh¹, Kateryna Artyushkova², Abdul-Mehdi Ali³, Carlo Santoro⁴,*
4 *Bruce M. Thomson¹, Kerry J. Howe¹, and José M. Cerrato^{1*}*

5 * Corresponding authors' email address: jcerrato@unm.edu

6 ¹ Department of Civil, Construction, and Environmental Engineering, MSC01 1070, University of New
7 Mexico, Albuquerque, New Mexico 87131, USA

8 ² Department of Chemical & Biological Engineering, MSC01 1120, 1 University of New Mexico
9 Albuquerque, NM 87131, USA

10 ³ Department of Earth and Planetary Sciences, MSC03 2040, University of New Mexico, Albuquerque,
11 New Mexico 87131, USA

12 ⁴ Department of Chemical Engineering and Analytical Science, The University of Manchester, The Mill,
13 Sackville Street, M13AL Manchester, UK

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22 Abstract

23 The objective of this study was to investigate the application of manganese oxide
24 $[\text{MnO}_{x(s)}]$ and granular activated carbon (GAC) media for the removal of caffeine and
25 acetaminophen from water. Organic contaminants of emerging concern represent a developing
26 issue due to their effects on human health and the environment. Manganese oxides are effective
27 for water treatment because of their ability to mediate adsorption and oxidation-reduction
28 reactions for many organic and inorganic constituents. Laboratory scale column experiments
29 were performed using different combinations of commercial $\text{MnO}_{x(s)}$ and GAC for assessing the
30 removal of caffeine and acetaminophen, and the subsequent release of soluble Mn due to the
31 reductive dissolution of $\text{MnO}_{x(s)}$. The removal of acetaminophen was detected for all media
32 combinations investigated. However, the removal of caffeine by adsorption only occurred in
33 columns containing GAC media. There was no removal of caffeine in columns containing only
34 $\text{MnO}_{x(s)}$ media. Manganese release occurred in columns containing $\text{MnO}_{x(s)}$ media, but
35 concentrations were below the secondary drinking water standard of $50 \mu\text{g L}^{-1}$ set by the US
36 Environmental Protection Agency. Soluble Mn released from a first process by $\text{MnO}_{x(s)}$ media
37 column was removed through adsorption into the GAC media used in a second process. The
38 results of this investigation are relevant for implementation of $\text{MnO}_{x(s)}$ and GAC media
39 combinations as an effective treatment process to remove organic contaminants from water.

40

41 1. Introduction

42 The presence of organic contaminants of emerging concern (CECs) in natural waters is
43 relevant to human health and the environment due to their persistence, accumulation and
44 bioactivity.¹⁻⁴ These CECs include pharmaceuticals and personal care products (PPCPs), synthetic
45 organic compounds (SOCs), endocrine disrupting compounds (EDCs) and industrial chemicals
46 that can occur in water supplies at very low concentrations ranging from nanograms per liter (ng
47 L⁻¹) to micrograms per liter ($\mu\text{g L}^{-1}$).⁵⁻⁸ Endocrine disrupting compounds may cause hormonal
48 imbalances in aquatic life, including feminization and decreased reproductive success of
49 organisms. These ecological impacts present the need for the development of water treatment
50 technologies that can target the selective and specific removal of CECs. Many of these compounds
51 may pose a threat to human health, however these risks are not well established.^{9, 10}

52 A variety of treatment processes have been studied for the removal of CECs applicable for
53 drinking water and wastewater. Successful removal depends on the chemical properties of each
54 compound, as well as the characteristics of the solution in which they are found. The most common
55 removal processes are activated carbon adsorption, membrane filtration, and oxidation processes
56 such as chlorination, ozonation, and ultra violet (UV) light.² Activated carbon adsorption has been
57 thoroughly studied because of its ability to remove a wide range of organic compounds. Activated
58 carbon removal of micropollutants can decrease if the water has a high concentration of dissolved
59 organic matter which competes for sorption sites on the carbon.^{6, 11-13} Similarly, high dissolved
60 organic carbon concentrations can consume oxidants, which decreases removal effectiveness.^{2, 6,}
61 ^{14, 15} Advanced oxidation processes (AOPs), involving combinations of UV light and oxidants such
62 as hydrogen peroxide (H₂O₂) or ozone (O₃),¹⁴⁻¹⁶ or silica-gel enhanced oxidation,¹⁷ have been
63 shown to remove acetaminophen, caffeine, and other organic contaminants. However, these

64 technologies have high capital and operating costs and are difficult to operate and maintain. Thus,
65 there remains a need for simpler yet effective technologies.

66 Acetaminophen and caffeine are common organic contaminants often detected in water
67 effluents which can cause adverse toxic effects on freshwater species and can be considered
68 surrogates for other CECs.¹⁶⁻²⁰ The chemical properties of acetaminophen and caffeine are
69 presented in Table 1. Acetaminophen (N-acetyl-para-aminophenol), also known as paracetamol,
70 is used as an active ingredient in pain relieving drugs such as Tylenol[®]. Acetaminophen has a
71 phenolic structure that can be oxidized by $\text{MnO}_{x(s)}$ ²¹⁻²³ into 1,4-benzoquinone.^{23, 24} Caffeine is a
72 naturally occurring central nervous stimulant that is the most consumed psychoactive drug by
73 humans. Caffeine is a purine alkaloid from the methylxanthine compound.^{16, 25, 26} Caffeine
74 scavenges highly reactive free radicals and has been shown to have antioxidant activity.^{25, 27} A
75 challenge for degrading caffeine is attacking the C4=C5 double bond in its ring structure.²⁵⁻²⁸

76 Manganese oxides [$\text{MnO}_{x(s)}$] have been commercialized for use in water treatment systems
77 as an adsorbent and oxidation catalyst for removal of inorganic and organic contaminants.^{22, 29-}
78 ³¹Various organic compounds including amines, anilines, phenols, antibacterial agents, atrazine,
79 aromatic N-oxides, and fluoroquinolones can react with $\text{MnO}_{x(s)}$ through adsorption and oxidation
80 .^{21, 32-39} Additionally, oxidation of organic compounds such as aromatic amines and phenols using
81 $\text{MnO}_{x(s)}$ has been researched,^{1, 22, 36} but fewer studies have focused on the investigation of $\text{MnO}_{x(s)}$
82 reactions with alkaloids such as caffeine. Full scale application of $\text{MnO}_{x(s)}$ for adsorption and
83 oxidation of organic compounds is limited and is an area that will benefit from additional research.
84 The use of $\text{MnO}_{x(s)}$ and GAC media in combination may provide an alternative technology for
85 treatment to remove organic compounds from drinking water. Addressing these gaps will aid in

86 providing a better understanding of the use and application of $\text{MnO}_{x(s)}$ media alone or in
87 combination with GAC as a treatment technology for micropollutants.

88 The objective of this study was to investigate the performance of $\text{MnO}_{x(s)}$ and GAC media
89 for removal of acetaminophen and caffeine for water treatment in de-ionized (DI) water and a real
90 water system using laboratory column experiments. The compounds acetaminophen and caffeine
91 were selected because they are: 1) common in water and have different chemical behavior in
92 solution; 2) relatively recalcitrant for biological oxidation; and 3) easy to detect and measure. The
93 experimental approach involved the use of column studies to contact contaminated water with
94 $\text{MnO}_{x(s)}$ and GAC media separately and in combination. The integration of aqueous chemistry,
95 microscopy, and spectroscopy analyses facilitated the investigation of processes for the removal
96 of acetaminophen and caffeine. The findings from this study provide insights into the combined
97 use of $\text{MnO}_{x(s)}$ and GAC for removal of organic contaminants from water.

98 **2. Materials and Methods**

99 **2.1 Materials**

100 Acetaminophen ($\geq 99\%$ purity) was purchased from Sigma Aldrich. Caffeine (99% purity) was
101 purchased from Alfa Aesar (Ward Hill, MA). Acetaminophen was selected because of its phenolic
102 structure since it is known to be adsorbed by GAC and can be oxidized and adsorbed by $\text{MnO}_{x(s)}$.
103 Caffeine was chosen because it has a purine alkaloid structure and limited studies have focused on
104 its removal by $\text{MnO}_{x(s)}$. Commercial manganese oxide (LayneOx) was purchased from Layne
105 (Woodlands, TX). The commercial manganese oxide has a Mn content of 70-80% by weight, as
106 reported in other studies that used the same media.^{37, 40} Granular activated carbon (Norit® PK 3-
107 5) was purchased from Sigma Aldrich. Manganese oxides and granular activated carbon media

108 were crushed, washed with 18 mΩ ultrapure water, dried and sieved to particle sizes of 0.250-
109 0.840 mm (US sieve 20x60 mesh) for use in the columns.

110 **2.2 Analytical Methods**

111 A PerkinElmer Flexar 400 HPLC was used to measure acetaminophen and caffeine.
112 Calibration of the HPLC-UV-VIS was done using stock solutions of acetaminophen and caffeine
113 measured at a wavelength of 254 nm. The HPLC column used was TSKgel ODS-80Tm C-18
114 (4.6×250 mm, 5 μm) with a mobile phase of 40% methanol, 60% 10 mM phosphate buffer at a
115 flow rate of 0.8 mL min⁻¹. The peak for acetaminophen occurred at 2.5 minutes retention time, and
116 the peak for caffeine occurred at 3 minutes retention time. Anion analyses were conducted using
117 ion chromatography (IC, ThermoFisher ICS-1100). Analyses of metals in solution were conducted
118 using a PerkinElmer Optima 5300DV inductively coupled plasma-optical emission spectrometer
119 (ICP-OES) for major elements, and a Perkin Elmer NexIon 300D inductively coupled plasma-
120 mass spectrometer (ICP-MS) for trace elements. Alkalinity was determined by the standardized
121 titration method.⁴¹ X-ray photoelectron spectroscopy (XPS) was used to characterize the surface
122 of unreacted and reacted MnO_x media. Spectra were collected from three different areas on each
123 sample using a Kratos Axis DLD Ultra XPS with a non-monochromatic Mg Kα source. XPS was
124 done for the experiments with samples taken from both the top and bottom of the columns. A
125 Tescan Vega3 XMU scanning electron microscope/energy dispersive X-ray spectroscope
126 SEM/EDX was used to determine the morphology and chemical composition of both the GAC and
127 MnO_{x(s)} media.

128 2.3 Experimental Set Up

129 2.3.1 Preliminary Experiments for Process Control

130 A batch experiment was performed using tap water from the University of New Mexico
131 (UNM) water system to determine whether the water is buffered well enough to maintain a stable
132 pH and measure alkalinity. This tap water comes from a well that supplies the university campus.
133 Chlorination is the only treatment provided before distribution to the campus. For the batch
134 experiment, 50 mL of tap water were placed in an open beaker and stored for 7 days prior to use
135 to allow residual chlorine to decay below the detection limit of 0.1 mg L⁻¹. Then the pH was
136 monitored for 72 hours. Samples of tap water were taken to measure alkalinity using the
137 standardized titration method.⁴¹ A second batch experiment was performed to investigate whether
138 the acetaminophen or caffeine decay naturally in tap water. This experiment was performed in
139 beakers using 50 mL of tap water spiked with 50 mg L⁻¹ of acetaminophen and caffeine, along
140 with an additional beaker of un-spiked tap water as a negative control. A calibrated portable meter
141 (Yellow Springs Instrument, Co., Model 63) was used to measure solution pH. Water samples and
142 pH measurements were taken at time intervals 0, 1, 4, 24, and 72 hours. The concentration of
143 caffeine and acetaminophen were determined using HPLC-UV-VIS. Samples were filtered
144 through 0.45 µm filters prior to ICP analyses. Cations (Ca, Mg, Al, Si) in the tap water were
145 analyzed using ICP-OES. Anions (SO₄²⁻, NO₃⁻, Cl⁻, PO₄³⁻) were analyzed using IC. All
146 experiments were performed in triplicate.

147 2.3.2 Removal from Spiked DI Water

148 The single-stage column experiments were conducted as an initial assessment of the
149 performance of MnO_{x(s)} and GAC single-media compared to 50% MnO_{x(s)}/50% GAC dual-media
150 in a spiked DI water solution. This experiment consisted of a setup of single packed columns.

151 Acrylic columns 15.2 cm long by 1.3 cm in diameter were packed with 13 cm of media. 1 cm of
152 glass wool was placed at the entrance and exit of each column to support the media and to
153 distribute flow across the column cross section. A volumetric flow rate of 2.0 ml min⁻¹ was used.
154 Each column was fully packed with the following media combinations: 100% GAC, 100%
155 MnO_{x(s)}, and 50% MnO_{x(s)}/50% GAC, and one Control column which contained no media
156 (empty column). The 100% MnO_{x(s)} columns were packed full with MnO_{x(s)} media, the 100%
157 GAC columns were packed full with GAC media, and the 50%/50% combination was packed
158 with MnO_{x(s)} media on the bottom and GAC media on top. A spiked DI water containing 50 mg
159 L⁻¹ of acetaminophen and caffeine was prepared by dissolving each constituent in 18 megaohm
160 (MΩ) water with 10 mM HEPES buffer which maintained the pH of the solution at 7.5. This
161 concentration was selected to ensure effluent concentrations would be within the detection limit
162 of the HPLC-UV-VIS. The empty bed contact time (EBCT) was 8.04 minutes, corresponding to
163 12.7 cm of media considering that the bottom and top of the column were packed with wool. A
164 Masterflex L/S cartridge peristaltic pump, model 7519-25 pumped water into the columns, which
165 were operated in up-flow configuration. Each column experiment was performed in triplicate,
166 except for the control. Effluent samples were collected at times 0.5, 1, 2, 4, 24, 48, 72, 96, 120,
167 144, 168, and 192 hours and reported as the number of bed volumes (BVs) of water treated.
168 Samples were analyzed with HPLC-UV-VIS for acetaminophen and caffeine, and filtered
169 through 0.45 μm filters prior to Mn analyses using ICP-MS.

170 **2.3.3 Removal from spiked Tap Water**

171 Another set of experiments was conducted operating MnO_{x(s)} and GAC columns in series which
172 has important implications for the application of a two-stage water treatment process to remove
173 organic compounds in tap water. These experiments consisted of two columns connected in

174 series with the first column containing $\text{MnO}_{x(s)}$ media and the second column containing GAC
175 media. Columns of the same dimensions of those for single column experiments were used.
176 Columns were operated in an up-flow configuration to minimize the presence of trapped bubbles
177 in the packed bed. These experiments were done to determine if the use of GAC media as the
178 second column would remove constituents not completely removed by the $\text{MnO}_{x(s)}$ media. Two
179 Control columns with no media (empty columns) were operated for the column experiments in
180 series. One column (Control 1) was operated in parallel with the $\text{MnO}_{x(s)}$ media column in a first
181 process, and another column (Control 2) was operated in parallel with the GAC media in a
182 second process.

183 The concentration of acetaminophen and caffeine in solution was 50 mg L^{-1} prepared using tap
184 water. The alkalinity of the tap water was sufficient so that an additional buffer was unnecessary.
185 Each of the series was performed in triplicate. Effluent samples were collected at the times 0,
186 0.5, 1, 2, 3, 4, 5, 24, 48, 72, 96, 120, 144, 192, 216, and 240 hours and reported as the number of
187 BVs of water treated. Samples were analyzed by HPLC-UV-VIS for acetaminophen and
188 caffeine, and filtered through $0.45 \mu\text{m}$ filters prior to Mn analyses using ICP-MS.

189 **3. Results and Discussion**

190 **3.1 Removal of Acetaminophen and Caffeine by $\text{MnO}_{x(s)}$ and GAC from Spiked DI Water**

191 Removal of both acetaminophen and caffeine from spiked DI water was observed in columns
192 reacted with 100% GAC and 50% $\text{MnO}_{x(s)}$ /50% GAC media combination (Figures 1a and 1b).
193 However, only acetaminophen was removed in columns containing 100% $\text{MnO}_{x(s)}$ (Figure 1a).
194 Minimal caffeine removal was observed in columns containing only $\text{MnO}_{x(s)}$ (Figure 1b). Each
195 column combination reached exhaustion after treating 1254 and 1433 bed volumes (BV) of water
196 after 168 – 192 hours of reaction. Limited change in concentrations was observed in columns

197 containing no media (control), indicating that the HEPES buffer (at pH 7.5) did not react with
198 acetaminophen or caffeine.

199 Acetaminophen was removed from solution by all combinations of media. The removal of
200 acetaminophen accomplished with the 50% $\text{MnO}_{x(s)}$ /50% GAC media column combination
201 motivated the column experiments with $\text{MnO}_{x(s)}$ and GAC columns in series presented in the next
202 sub-section. Acetaminophen has been shown to be removed by GAC.^{10,32} Other studies have
203 shown that the removal of phenolic compounds, such as acetaminophen, by $\text{MnO}_{x(s)}$ occurs by
204 adsorption followed by rapid oxidation.^{21, 22, 39} Oxidation of phenolic compounds such as
205 acetaminophen is triggered by reactions that take place on the surface of the $\text{MnO}_{x(s)}$ media and is
206 generally considered to occur in two steps: (i) surface complex formation and (ii) electron transfer.
207 These two steps occur at the $\text{MnO}_{x(s)}$ surface with subsequent desorption of by-products.²³

208 Caffeine was removed from solution by columns containing 100% GAC and 50%
209 $\text{MnO}_{x(s)}$ /50% GAC. The use of GAC alone or in combination with $\text{MnO}_{x(s)}$ provided the best
210 removal for both organic compounds. Granular activated carbon can adsorb a large variety of
211 compounds, including caffeine^{6, 12, 13, 42} due to its high specific surface area.^{11, 43} There was
212 negligible removal of caffeine by the 100% $\text{MnO}_{x(s)}$ column. It is possible that, due to the free
213 radical scavenging properties of caffeine,^{25, 44, 45} $\text{MnO}_{x(s)}$ is not capable of cleaving the C4=C5
214 double bond,²⁵ thus limiting removal of caffeine by reaction with $\text{MnO}_{x(s)}$.

215 Soluble Mn was found in effluent from the 50% $\text{MnO}_{x(s)}$ /50% GAC and 100% $\text{MnO}_{x(s)}$
216 columns at concentrations ranging from 3 to 5 $\mu\text{g L}^{-1}$, following an initial spike ranging from 20
217 to 35 $\mu\text{g L}^{-1}$ for the time zero samples (Supplementary Material- Figure S1 and S2). The reductive
218 dissolution of $\text{MnO}_{x(s)}$ has been observed after reaction with organic compounds; $\text{MnO}_{x(s)}$ is
219 reduced from a combined +3/+4 oxidation state to an oxidation state of +2.^{37, 39, 46} Dissolved Mn(II)

220 can be adsorbed onto the surface of both the GAC and the $\text{MnO}_{x(s)}$. Previous research has identified
221 the re-adsorption of Mn after reductive dissolution of $\text{MnO}_{x(s)}$.^{40, 47} All dissolved Mn
222 concentrations detected in the spiked DI water were below the secondary drinking water standard
223 of $50 \mu\text{g L}^{-1}$. Reductive dissolution of $\text{MnO}_{x(s)}$ after reaction with acetaminophen, aniline, triclosan,
224 BPA and other organic compounds has also been reported in other studies.^{21, 39, 46}

225 **3.2 Removal of Caffeine and Acetaminophen by $\text{MnO}_{x(s)}$ and GAC from spiked Tap Water**

226 **3.2.1. Preliminary tests.** The pH of the tap water ranged between 7.6 and 7.9 throughout the batch
227 control test (Supplementary Material- Figure S4). The circumneutral pH range observed
228 throughout the 72 hours of the experiment indicates that the tap water is well buffered with
229 bicarbonate as indicated by the measured alkalinity range of $105\text{-}160 \text{ mg L}^{-1}$ as CaCO_3 . The
230 chemistry of tap water is shown in Table 2. Total organic carbon of the tap water is low, as
231 evidenced by low DBP formation (maximum trihalomethanes are $9 \mu\text{g L}^{-1}$, maximum haloacetic
232 acids is $2 \mu\text{g L}^{-1}$).⁴⁸ A batch control experiment found no degradation of acetaminophen or caffeine
233 in tap water over 72 hours (Supplementary Material- Figure S3). No acetaminophen or caffeine
234 were detected in unspiked UNM tap water. Negligible changes in acetaminophen or caffeine
235 concentrations were detected in the spiked tap water indicating that the background ions have
236 limited effect on the degradation of these organic contaminants.

237 **3.2.2 Columns in-series.** The results from the column-in-series experiments indicate that $\text{MnO}_{x(s)}$
238 media will selectively react with phenolic compounds like acetaminophen, but not with caffeine.
239 Removal of acetaminophen was observed by $\text{MnO}_{x(s)}$ from spiked tap water in the column
240 experiments (Figure 2a). The pH of the tap water stayed at a comparable range to that reported in
241 the batch experiments in Figure S4. The outcomes with spiked tap water were similar to those
242 obtained in the single column experiments done with the spiked DI water, indicating negligible

243 effect of solution chemistry on adsorption/oxidation reactions of acetaminophen and caffeine. The
244 $\text{MnO}_{x(s)}$ media removed acetaminophen throughout the experiment, reaching a maximum C/C_0 in
245 the range of 0.8. As observed in the single column spiked DI water experiments, limited removal
246 of caffeine occurred after reaction with $\text{MnO}_{x(s)}$ media in the experiments conducted in series
247 (Figure 2b).

248 The occupation of surface adsorption sites by acetaminophen and reduced Mn can cause
249 gradual passivation of $\text{MnO}_{x(s)}$ (Figures 1 and 2). The results confirm that there is no adsorption
250 or oxidation of caffeine provided by the $\text{MnO}_{x(s)}$ media. Acetaminophen and caffeine were both
251 removed by GAC (Figure 2b). However, since the columns were operated in series with $\text{MnO}_{x(s)}$
252 followed by GAC media, the minimal removal of caffeine by $\text{MnO}_{x(s)}$ in the first stage caused
253 exhaustion of the GAC media within 1074 BV. In contrast, the contribution of acetaminophen
254 removal by the $\text{MnO}_{x(s)}$ media column in the first stage prior to reaction with the GAC column
255 contributed to the retardation of GAC exhaustion, obtaining a higher BV (after 1430 BV) for
256 acetaminophen compared to caffeine (after 1074 BV). Note that, due to analytical and
257 experimental error, some values for C/C_0 are higher than 1. The removal mechanism for GAC
258 media is by adsorption, as it is a non-selective adsorptive media.⁴⁹ Previous studies have described
259 measurements of Freundlich isotherm parameters for adsorption of acetaminophen and caffeine
260 by GAC.⁵⁰ Values of $K = 1.84$ and $n = 0.746$ have been reported for acetaminophen, and $K = 10.8$
261 and $n = 0.551$ have been reported for caffeine.⁴³ Using these values and a concentration of 50
262 mg/L, the adsorption capacity for acetaminophen based on the Polanyi equation and Freundlich
263 parameters was $34.06 \text{ mg g}^{-1}_{\text{GAC}}$ for acetaminophen and $93.23 \text{ mg g}^{-1}_{\text{GAC}}$ for caffeine, which are
264 consistent with those reported in another study.⁵⁰ In full scale operating treatment plants, the initial

265 concentrations of these CECs would be in the $\mu\text{g L}^{-1}$ range but the influence of competing water
266 constituents such as natural organic matter (NOM) and other ions should also be considered.

267 **3.3 $\text{MnO}_{x(s)}$ and GAC Media Solid Analyses**

268 Analyses were conducted to investigate the changes in chemical composition of unreacted
269 and reacted $\text{MnO}_{x(s)}$ and GAC media, and oxidation state of Mn for $\text{MnO}_{x(s)}$ to further assess
270 adsorption and oxidation removal processes. Scanning electron microscope (SEM) and energy
271 dispersive X-ray spectroscopy (EDX) analyses found that both unreacted and reacted $\text{MnO}_{x(s)}$ from
272 the column experiments operated in series have a similar morphology and chemical composition.
273 For example, both unreacted and reacted $\text{MnO}_{x(s)}$ media (Supplementary Material- Figure S5a and
274 S6a) have an average grain size ranging from 460-775 μm characterized by a porous surface. The
275 EDX results (Supplementary Material- Figure S5b and S6b) found that the chemical composition
276 of the virgin and reacted $\text{MnO}_{x(s)}$ media consisted primarily of Mn and O (Supplementary Material-
277 Table S1). Impurities included Al (5.69%), and Si (3.94%) (Supplementary Material- Table S1).
278 These results are similar to those reported in a previous study in which commercial $\text{MnO}_{x(s)}$
279 contained 29.1% impurities, including 10% Al, 9% Fe, and 7% Si.³⁷ The chemical composition
280 detected by EDX analyses for unreacted and reacted $\text{MnO}_{x(s)}$ media is similar which is why XPS
281 analyses are presented below to further investigate changes in Mn oxidation state after the reaction.
282 The SEM/EDX analyses for unreacted GAC media (Supplementary Material- Figure S7a) showed
283 a porous surface with grain sizes ranging from 600-800 μm . The EDX results found that the
284 chemical composition of the unreacted GAC was mostly C (94.17%) with a small amount of O
285 (5.22%) (Supplementary Material- Table S1). This is consistent with previous reports.⁵¹ As
286 expected, the SEM images for reacted GAC analysis looked similar to those obtained for unreacted
287 GAC (Supplementary Material- Figures S7a and S8a) with various pore and an average grain size

288 raining from 370-730 μ m. Although imaging looked similar, EDX spectra (Supplementary
289 Material- Figures S7b and S8b) indicated that there were other constituents adsorbed on the surface
290 of the GAC including Si (0.65%), Mg (0.43%), Al (0.35%), and Ca (0.26%), but Mn was below
291 detection (Supplementary Material- Table S1). The presence of these constituents on the reacted
292 GAC is likely due to the adsorption of ions from the tap water.

293 The detection of soluble Mn in the column effluent indicates that reductive dissolution of the
294 MnO_{x(s)} media occurred in these experiments (Figure 3), suggesting that the main mechanism for
295 acetaminophen removal was oxidation catalyzed by MnO_{x(s)}. The higher concentration of Mn in
296 columns in series compared to single columns could be due to background concentrations from
297 tap water and constituents in this tap water that undergo redox reactions with the MnO_{x(s)} media
298 which cause Mn dissolution. The Mn reduction in MnO_{x(s)} media was confirmed by XPS analyses
299 of the Mn3p high resolution scans (Figure 4). The fits of the XPS Mn3p high resolution spectra
300 indicate an increase of 28.4% Mn(III) and 8.8% Mn(II) for the MnO_{x(s)} media from the 50%
301 MnO_{x(s)}/50% GAC media combination column and increase of 33.3% Mn(III) and 8.5% Mn(II)
302 for the 100% MnO_{x(s)} media column compared to what was initially present in the unreacted
303 media. These results are consistent with previous research which reports the occupation of MnO_{x(s)}
304 surface by reduced Mn on MnO_{x(s)} media during reaction with phenolic organic compounds.^{37, 39,}
305 ⁴⁶ It should be noted that the effluent Mn concentration in the effluent of the GAC media is lower
306 than that of the MnO_{x(s)} media (Figure 3). This result indicates that soluble Mn is released from
307 the MnO_{x(s)} media column caused by acetaminophen removal catalyzed by MnO_{x(s)}. However,
308 some of this soluble Mn is adsorbed to the GAC media in the second process, resulting in the
309 decrease on soluble Mn in the effluent of the GAC media column compared to the effluent
310 concentration detected in the effluent of the MnO_{x(s)} media column (Figure 3).

311 3.4 Implications for Water Treatment

312 The results from this study suggest that the application of $\text{MnO}_{x(s)}$ and GAC in series can
313 remove organic compounds from water with minimal release of soluble Mn. Acetaminophen and
314 caffeine were effectively adsorbed by GAC confirming that the process could be used for water
315 treatment. The price by weight of the commercially available $\text{MnO}_{x(s)}$ was ten times less compared
316 to that of the GAC at the time this study was conducted. The use of $\text{MnO}_{x(s)}$ and GAC media may
317 be more affordable and applicable for treating a broader range of compounds than by either process
318 alone. Additionally, the performance of the columns in series with $\text{MnO}_{x(s)}$ and GAC was better
319 compared to that obtained for each media operated separately. This approach can facilitate the
320 selective removal of phenols, anilines, and other compounds that are removed by $\text{MnO}_{x(s)}$,^{21, 34, 35,}
321 ³⁹ slowing the exhaustion of available adsorption sites on GAC. Comparison of results from spiked
322 DI water and spiked tap water solutions suggest that co-occurring ions did not affect the removal
323 of acetaminophen and caffeine. This suggests that a treatment system using $\text{MnO}_{x(s)}$ and GAC
324 media for the removal of organic compounds is technically feasible in waters with low organic
325 matter content such as the tap water used in this study. Experiments with high concentrations of
326 NOM and other constituents are necessary to evaluate the removal of organic contaminants from
327 different water chemistry and media combinations. Also, identification of the oxidative byproducts
328 from $\text{MnO}_{x(s)}$ treatment and their presence after GAC treatment needs to be further studied due to
329 increased toxicity of some byproducts compared to the parent organic compounds. Addressing
330 these research gaps could provide further opportunities for the application of these media in
331 treatment systems and determine the removal of emerging organic contaminants under these
332 conditions.

333 4. Conclusions

- 334 • The removal of acetaminophen was observed by packed bed columns containing $\text{MnO}_{x(s)}$.
335 However, $\text{MnO}_{x(s)}$ did not remove caffeine. Columns packed with GAC provided removal
336 of both acetaminophen and caffeine.
- 337 • The results indicate that the combination of $\text{MnO}_{x(s)}$ and GAC resulted in the removal of
338 acetaminophen and caffeine in the spiked DI water and spiked tap water. The $\text{MnO}_{x(s)}$
339 media can selectively remove acetaminophen, which would retard the exhaustion of
340 available adsorption sites on the non-selective GAC media.
- 341 • Reaction of $\text{MnO}_{x(s)}$ with acetaminophen resulted in the reductive dissolution of $\text{MnO}_{x(s)}$,
342 causing the release of soluble Mn. However, soluble Mn can be adsorbed by GAC media
343 after operation in series with $\text{MnO}_{x(s)}$.

344

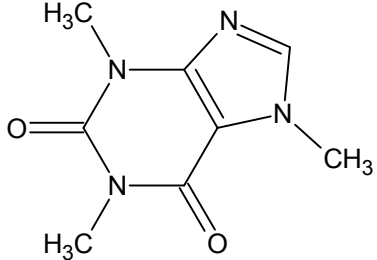
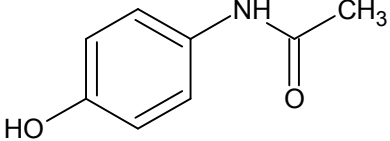
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350 expressed in this material are those of the authors(s) and do not necessarily reflect the views of the
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352

353 **Table 1.** Relevant chemical properties and structure for caffeine and acetaminophen.

354

Chemical	Structure	Molecular mass (g/mol)	Acid dissociation constant (pKa)
Caffeine		194.19	14 ^a 0.7 ^b
Acetaminophen		151.16	9.7

355 ^a Obtained from A.C. Moffatt et al.⁵²356 ^b Obtained from National Center for Biotechnology Information.⁵³

357

358 **Table 2.** Physicochemical Characteristics of tap water.

359

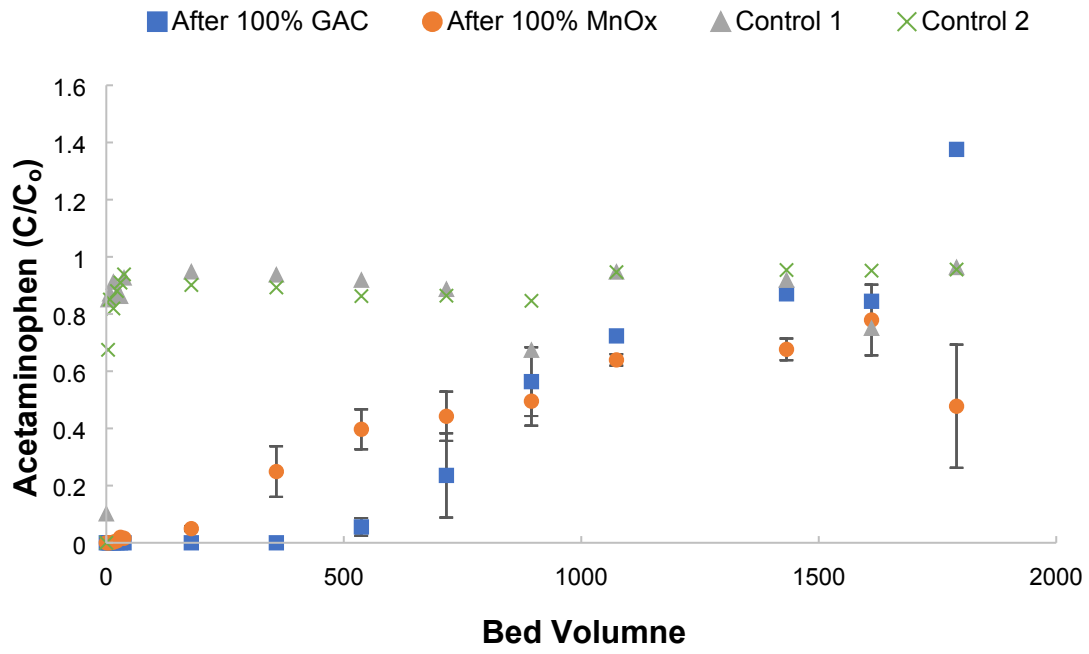
Analyte	Detected Concentration (mg L ⁻¹)
Calcium (Ca)	43.50
Magnesium (Mg)	8.01
Potassium (K)	5.22
Sodium (Na)	33.53
Silicon (Si)	27.9
Iron (Fe)	B.D.L. *
Manganese (Mn)	B.D.L. *
Sulfate (SO ₄ ²⁻)	58.50
Nitrate (NO ₃ ⁻)	2.42
Chloride (Cl ⁻)	30.50
Phosphate (PO ₄ ³⁻)	B.D.L. *
Alkalinity (mg L ⁻¹ as CaCO ₃)	105-160
pH	7.6 – 7.9

360

361 * B.D.L. = Below Detection Limit. Note that the lowest standard used for calibration of the ICP-OES (for Ca, Mg,

362 K, Na, Si, Fe, and Mn) and IC (SO₄²⁻, NO₃⁻, Cl⁻, and PO₄³⁻) for these analyses is 0.1 mg L⁻¹.

(a)



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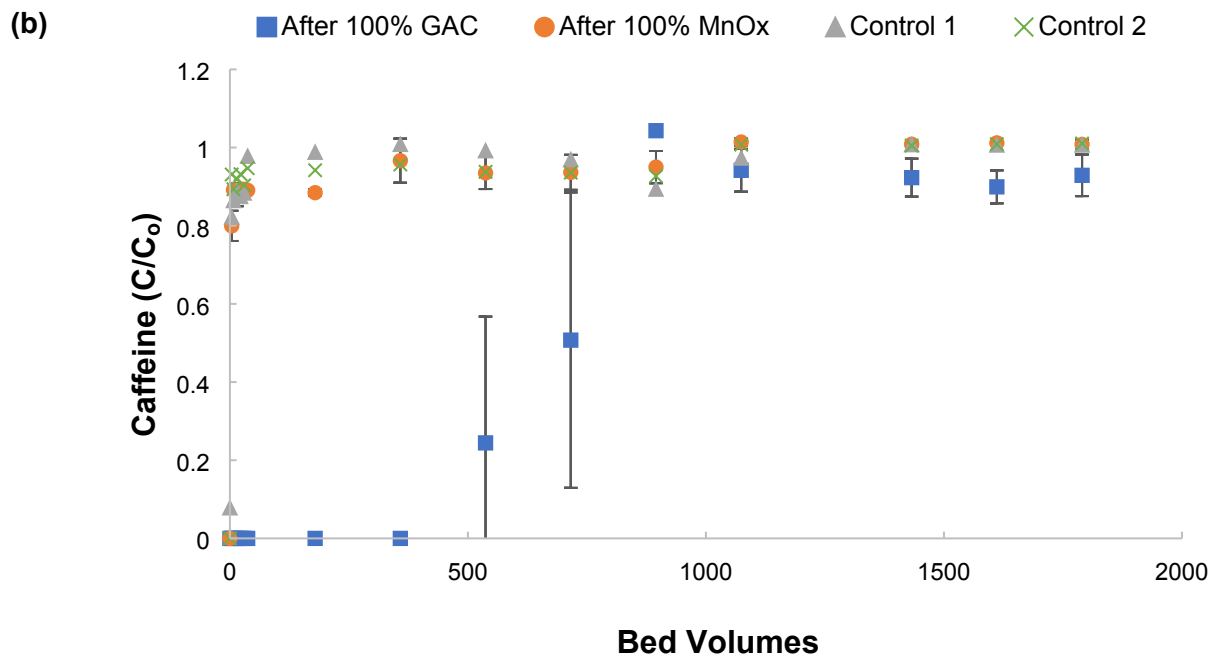
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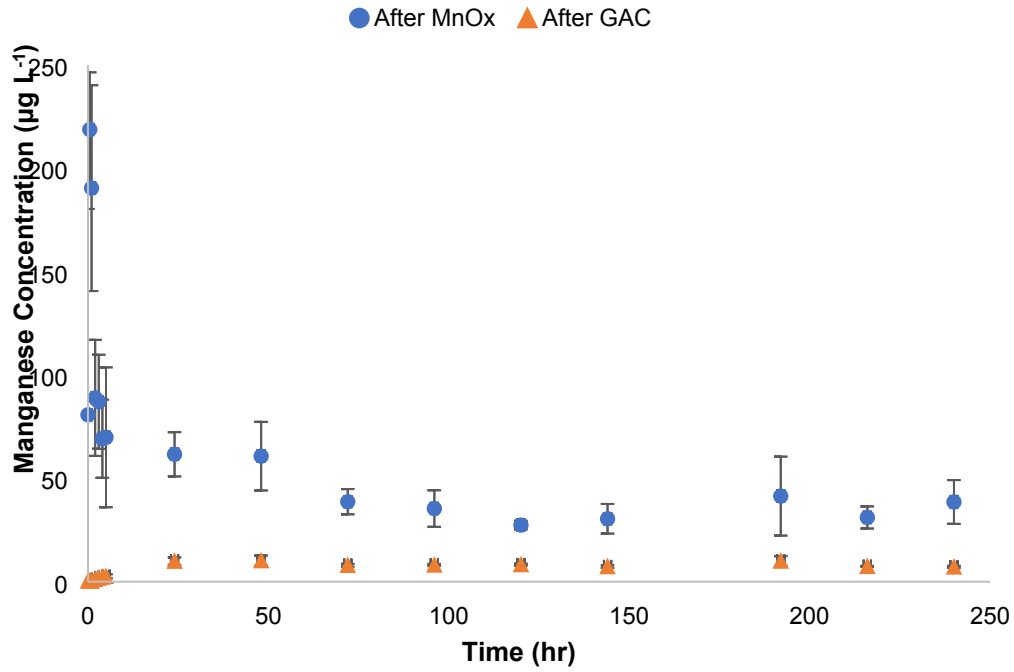
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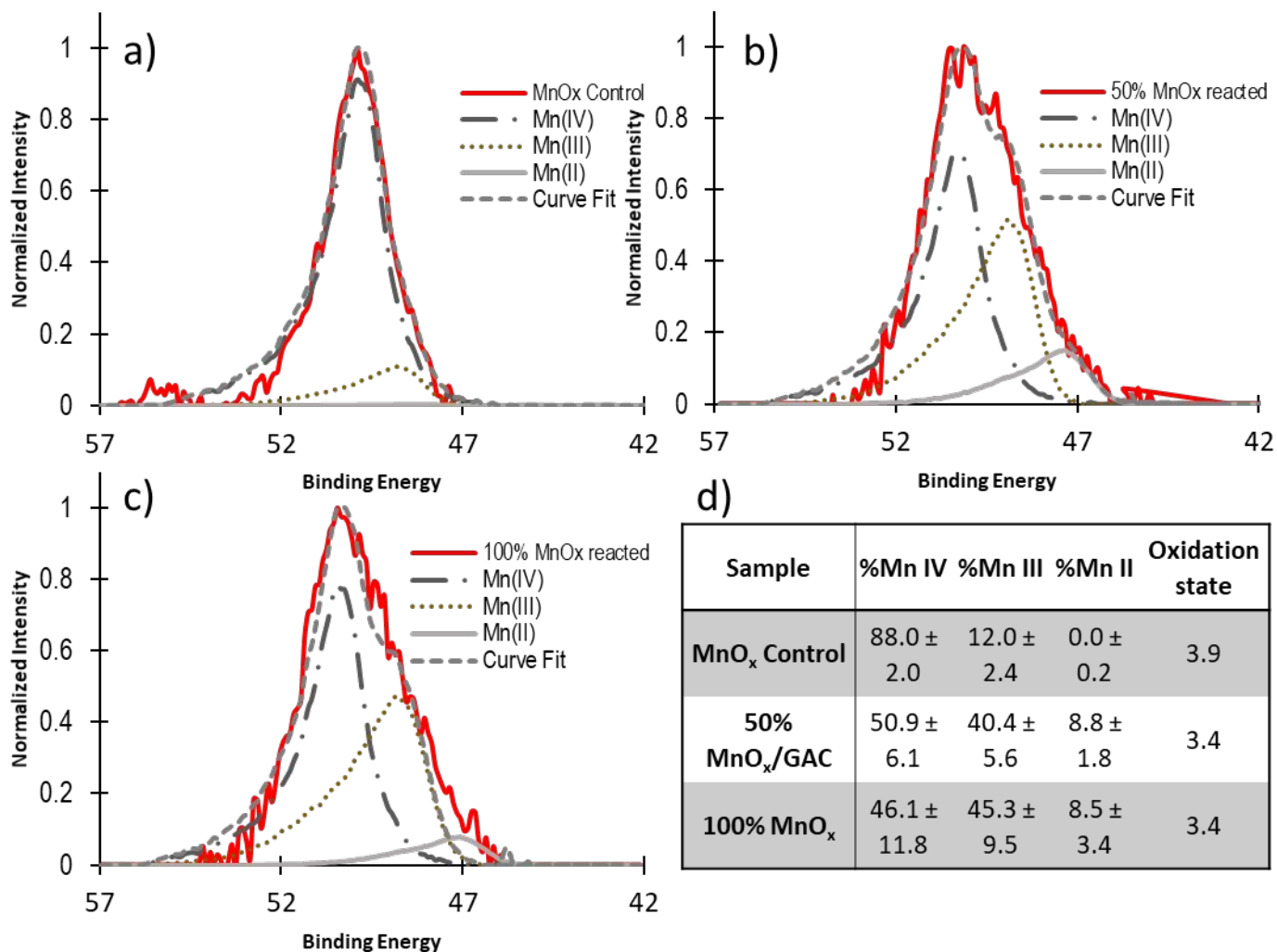
398 **Figure 2.** Normalized effluent concentrations of acetaminophen(a) and caffeine(b) of bench-
 399 scale packed columns completed columns in series, first MnO_{x(s)} followed by GAC, and fed with
 400 the spiked tap water solution. Each point was obtained by dividing the measured effluent
 401 concentration at each point in time by the initial concentration (C₀) of acetaminophen and
 402 caffeine which was 50 mg L⁻¹. Error bars represent standard deviation of triplicate data. Control
 403 1 represents an empty column with no media operated in parallel with the MnO_{x(s)} media
 404 column, and Control 2 represents another empty column with no media operated in parallel with
 405 the GAC media.



407

408 **Figure 3.** Manganese concentration from effluents of MnOx and GAC media columns
409 operated in series with spiked tap water.

410



411

412 **Figure 4.** Fitting of high resolution XPS Mn 3p spectra for the single column experiments: (a)
 413 Unreacted commercial MnO_x media before experiments were conducted. (b) Reacted MnO_x
 414 sample from 50% MnO_{x(s)}/50% GAC media combination column after experiment completion.
 415 (c) Reacted MnO_x media sample from 100% MnO_x media column after experiment completion.
 416 (d) Percent composition of the fits for each media. (uncertainty shown is standard deviation for
 417 triplicate data).

418

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