Anoxic conditions are beneficial for abiotic diclofenac removal from water with manganese oxide (MnO$_2$)

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Abstract
This is the first study examining pharmaceutical removal under anoxic conditions with MnO$_2$. This study compares the abiotic removal of seven pharmaceuticals with reactive MnO$_2$ particles in the presence of oxygen (oxic conditions) and in the absence of oxygen (anoxic conditions). Due to the novelty of pharmaceutical removal under anoxic conditions, the influence of phosphate buffer, pH, and MnO$_2$ morphologies is also examined. Results show that over 90% of diclofenac is removed under anoxic conditions. Additionally, we found that (1) anoxic conditions are beneficial for diclofenac removal with MnO$_2$, (2) phosphate buffer affects the pharmaceutical removal efficiencies, (3) higher pharmaceutical removal is obtained at acidic pH compared to that at neutral or alkaline conditions, and (4) amorphous MnO$_2$ removes pharmaceuticals better than crystalline MnO$_2$. The pharmaceutical molecular structure and properties, MnO$_2$ properties especially reactive sites of the MnO$_2$ surface, are important for degradation kinetics. This study provides a fundamental basis towards understanding pharmaceutical degradation with MnO$_2$ under anoxic conditions, and development of a cost-effective, sustainable technology for removal of pharmaceuticals from water.

Keywords Manganese oxide · Abiotic pharmaceutical removal · Anoxic conditions · pH effects · MnO$_2$ morphologies · MnO$_2$ reactivity mechanism

Introduction
Pharmaceuticals in the water cycle threaten the aquatic environment and drinking water resources. Already at low concentrations (ng/L–μg/L) (Simazaki et al. 2015; Ternes et al. 2015), pharmaceuticals can be toxic to aquatic organisms (Farré et al. 2008; Gilroy et al. 2014). As a result, pharmaceuticals discharged to water systems are seen as a priority concern of environmental regulators, and the European Union has added one of them, diclofenac, to the “Watchlist” (European Union 2013).

Removal of many pharmaceuticals such as carbamazepine, diclofenac, or metoprolol is poor in conventional wastewater treatment processes, such as activated sludge processes, due to the low biodegradability and limited sorption properties of many pharmaceuticals (Vieno and Sillanpaa 2014). Advanced technologies such as ozonation or photodegradation successfully remove selected pharmaceuticals from water and wastewater (He et al. 2016; Javier Benitez et al. 2009). However, these technologies require more energy inputs and operational costs, in addition to often high construction and maintenance costs, and produce intermediate compounds with unknown environmental effects.

A promising alternative method may be based on using manganese oxide (MnO$_2$) to remove pharmaceuticals from water. MnO$_2$, mainly referring to the oxide of manganese(IV) in previous studies, is also known as manganese dioxide (Chen et al. 2011; Hée et al. 2012; Huguet et al. 2013; Huguet et al. 2014). Using MnO$_2$ can efficiently remove persistent pharmaceuticals like carbamazepine, and produce intermediates which are less toxic to the environment (He et al. 2012; Huguet et al. 2013). MnO$_2$ is a common oxidant in soil, sediment, and marine environments, and these environments contain oxic (oxygen present) and/or anoxic
example, various MnO₂ morphologies have been tested to
amorphous MnO₂ (birnessite) as most effective and most used
remove pharmaceuticals and other organic compounds, with
effects of oxygen, phosphate, pH, and MnO₂ morphologies
ceuticals were selected and tested in the experiments. The
wastewater treatment facilities. Seven widely used pharma-
simulating the conditions encountered in nature as well as in
anoxic conditions.
Overall, these studies indicate that little is known about the
abiotic removal of pharmaceuticals under anoxic conditions
with MnO₂. Further investigation under anoxic conditions
might contribute to understanding how to improve the phar-
maceutical removal with MnO₂. From an application perspec-
tive, water treatment technologies commonly include oxic and
anoxic steps. Investigating pharmaceutical removal under an-
oxic conditions with MnO₂ may extend the application of this
pharmaceutical removal technology. Additionally, applying
anoxic conditions can reduce the construction and operation
cost of maintaining oxic conditions in water treatment sys-
tems, which is an extra benefit using anoxic conditions.
Furthermore, the effect of oxygen on pharmaceutical removal
is inconsistent in different studies. Therefore, more studies are
required to address pharmaceutical removal with MnO₂ under
both oxic and anoxic conditions, and to improve the under-
standing of the removal mechanisms.
Phosphate, pH, and MnO₂ morphologies are known to af-
flect the removal of organic compounds with MnO₂ (Gao et al.
2012; Shin and Cheney 2004; Yao and Millero 1996). For
example, various MnO₂ morphologies have been tested to
remove pharmaceuticals and other organic compounds, with
amorphous MnO₂ (birnessite) as most effective and most used
(Remucal and Ginder-Vogel 2014). However, little is known
about how these parameters affect the removal process under
anoxic conditions.
In this study, a series of batch experiments with pharma-
ceuticals were conducted under oxic and anoxic conditions
simulating the conditions encountered in nature as well as in
wastewater treatment facilities. Seven widely used pharma-
ceuticals were selected and tested in the experiments. The
effects of oxygen, phosphate, pH, and MnO₂ morphologies
were studied to better understand the removal processes in-
volved and to optimize these towards the application of tech-
nology using reactive MnO₂ for pharmaceutical removal.

Materials and methods

Chemicals
Caffeine, carbamazepine, diclofenac, metoprolol, naproxen,
and propranolol were purchased from Sigma-Aldrich while
ibuprofen was purchased from MP Biomedicals (detailed
information in Table S1). Other chemicals were purchased
from Sigma-Aldrich at 98% purity (for solids), or at HPLC
or UPLC quality (for solvents). Pharmaceutical stocks were
prepared with ultrapure water (18.2 MΩ cm, TOC = 18 ppb,
Millipore, USA) and stored in amber glass bottles at −20 °C.
Other solutions were prepared with demineralized water
demiwater). Details are described in Text S1.

MnO₂ preparation
Amorphous MnO₂ was obtained by freshly synthesizing prior
to experiments as described (Langenhoff et al. 1997). Briefly,
equal amounts of MnCl₂ and KMnO₄ were mixed, pH level
was adjusted to ~ 10 with NaOH, and MnO₂ was washed by
centrifugation (Text S2). Amorphous MnO₂ was used in all
experiments unless specification. Crystalline MnO₂ was pur-
chased from Sigma-Aldrich (Fig. S1, S2).

Batch experiments
One hundred twenty-five-milliliter glass bottles were filled
with 50 mL MnO₂ suspension (7 mM) in demiwater. Oxic
experiments were prepared at atmospheric oxygen level.
Experiments under anoxic conditions were prepared in the
anaerobic glovebox with anoxic water and closed with a rub-
er stopper and aluminum cap before taking them out of the
anaerobic glovebox. Outside the glovebox, the headspace was
exchanged with 100% N₂. All the experimental bottles were
closed with rubber stoppers, crimped with aluminum caps,
wrapped in aluminum foil to prevent photodegradation, and
incubated without shaking at 30 °C.
Experiments were started by spiking bottles to achieve the
final pharmaceutical concentration of 1 mg L⁻¹. Aliquots were
collected, and reactions were quenched immediately for anal-
ysis by centrifugation (10,000 rpm for 10 min). Blank exper-
iments without MnO₂ were prepared and conducted simulta-
aneously with each batch of experiments. Sample collection
and preparation before analysis are described in Text S3.
Experiments in 50 mM phosphate buffer with only
diclofenac were conducted to compare the process under oxic
and anoxic conditions. In addition, effects of pH and MnO₂
morphologies under anoxic conditions were investigated with
phosphate buffer solutions at pH 4–5 (4.5), pH 7.0, and
pH 8–9 (8.5) (Text S1).

Analysis
The pharmaceutical analysis was conducted as described pre-
viously using an ultra-performance liquid chromatography
(UPLC, ultimate 3000, Thermo, USA) with a diode array
detector (He et al. 2016). The pH level was determined by a
pH meter (PHM210, MeterLab, Radiometer analytical). The
Mn²⁺ analysis was conducted by an inductively coupled
plasma spectrometer with optical emission spectroscopy (ICP-OES). MnO_2_ morphologies were characterized by X-ray diffraction. The MnO_2_ before and after the reaction with diclofenac and metoprolol was characterized via a Fourier-transform infra-red (FTIR, Bruker TENSOR 27) spectrometer. The figures of this study are analyzed and generated by Origin Pro 2015 and Microsoft PowerPoint 2007. Details are described in Text S3.

**Results and discussion**

**Pharmaceutical removal under oxic versus anoxic conditions**

In the absence of MnO_2_, no removal is observed for all seven pharmaceuticals within 24 h under both oxic and anoxic conditions in all experiments (Table S3). In the presence of MnO_2_, metoprolol, propranolol, and diclofenac are removed within 24 h in both demiwater (Fig. 1a, b) and phosphate buffer (Fig. 1c), while no removal is observed for the other four pharmaceuticals (Fig. S3). Furthermore, the results show that removal efficiency of diclofenac is higher under anoxic conditions, while higher removal is observed under oxic conditions for metoprolol and propranolol. Diclofenac removal efficiencies of 78% under anoxic conditions and 59% under oxic conditions were observed after 24 h, incubating a solution of mixed pharmaceuticals in demineralized water (Fig. 1a). However, only 33% metoprolol was removed under anoxic conditions compared to 69% under oxic conditions. Similarly, 51% propranolol was removed under anoxic conditions compared to 84% under oxic conditions (Fig. 1a). Diclofenac removal efficiency in a mixture together with other six pharmaceuticals (Fig. 1a) was found to be lower than that in a demiwatery system which only diclofenac was present (Fig. 1b). Under anoxic conditions, 92% diclofenac is removed with MnO_2_, while under oxic conditions, 69% diclofenac removal is observed (Fig. 1b).

In order to eliminate the effects of pH and ionic strength on pharmaceutical removal with MnO_2_ (Gao et al. 2012; Huguet et al. 2013), we control pH (~7) with 50 mM phosphate buffer and maintain the ionic strength (0.1 M) with NaCl. In further experiments with phosphate buffer, 90% of diclofenac is removed under anoxic conditions while nearly complete removal of diclofenac is observed under oxic conditions (Fig. 1c). The removal efficiency of diclofenac is similar under anoxic and oxic conditions. In previous studies, removal efficiency of organic matters including pharmaceuticals under anoxic conditions is either similar or lower than that under oxic conditions (Barrett and McBride 2005; Gao et al. 2012; Zhang and Huang 2005a). However, we notably observe that the removal efficiency of diclofenac under anoxic conditions can be higher than that under oxic conditions. This unique result directs our further studies on the mechanism of pharmaceutical removal under anoxic conditions with MnO_2_.

A pseudo-first-order model with an initial incubation period was applied to analyze the removal kinetics (Table 1), as performed in previous studies under oxic conditions (Jiang et al. 2010a; Zhang et al. 2008; Zhang and Huang 2005a). Comparison of the initial removal rate (v_0) and the initial removal rate constant (k_0) of different pharmaceuticals shows that oxygen affects pharmaceutical removal with MnO_2_. In demiwater with the pharmaceutical mixture and with only diclofenac, diclofenac removal is accelerated under anoxic conditions; metoprolol and propranolol removal rates are lower under anoxic conditions. Furthermore, diclofenac was removed at the highest rate when dissolved as a sole compound in oxic phosphate buffer containing MnO_2_.

**Influence of pH and MnO_2_ morphologies on diclofenac removal**

pH is an important parameter affecting pharmaceutical removal with MnO_2_. Previous studies show that MnO_2_ morphologies also influence pharmaceutical removal (Shin and Cheney 2004). However, our novel observation of diclofenac removal under anoxic conditions with MnO_2_ indicates that the removal mechanisms of pharmaceuticals with MnO_2_ under anoxic conditions might be different from removal mechanisms under oxic conditions. Therefore, it is important to investigate the effect of pH and MnO_2_ morphologies on diclofenac removal to understand the removal mechanism. We investigate the effect of pH and MnO_2_ morphologies using both amorphous MnO_2_ and crystalline MnO_2_ under anoxic conditions at pH ~4.5, pH ~7.0, and pH ~8.5 established with a 50 mM phosphate buffer.

Diclofenac removal efficiencies with MnO_2_ under anoxic conditions are inversely related to pH (Table 2). Within 48 h, diclofenac removal under anoxic conditions varies from 100% at around pH ~4.5 and pH ~7.0, to 70% at pH ~8.5 with amorphous MnO_2_. In contrast, diclofenac removal is notably lower with crystalline MnO_2_. Only 21% of diclofenac is removed with crystalline MnO_2_ at pH ~4.5. In the experiments carried out at pH ~7.0 and pH ~8.5, no diclofenac removal is observed with crystalline MnO_2_.

**Discussion**

Generally, removal of organic matters with MnO_2_ is a two-step process including adsorption and oxidation (Remucal and Ginder-Vogel 2014). The contribution of the two steps is various from different compounds (He et al. 2012; Xu et al. 2008; Zhang and Huang 2005b). Under oxic conditions, pharmaceutical removal can be accelerated by oxygen (Gao et al. 2012). However, this fails to explain why anoxic conditions are suitable for diclofenac removal in demiwater when oxygen is not
present to participate in the removal process (Fig. S4). There are different intermediates formed under oxic and anoxic conditions during diclofenac removal with MnO$_2$ (Fig. S4, S5). These intermediates have different adsorption affinities for the reactive sites on the MnO$_2$ surface, which is possibly the key to explaining the differences between oxic and anoxic conditions. Based on the results, two factors appear to influence the efficiency of pharmaceutical removal and are elaborated below: (1) the pharmaceutical molecular structure and chemical properties, and (2) the MnO$_2$ properties.

**Pharmaceutical molecular structure and chemical properties**

The molecular structure and chemical properties of pharmaceuticals are important in organic compound removal with MnO$_2$. Previous studies show that oxidation with MnO$_2$ in the presence of oxygen involves cleavage of the C – N bond of the organic compound. Metoprolol and propranolol have C – N bonds, in which the N atom is bound to an alkyl group. These compounds are similar to those tested in previous studies (Table S1, S2) in which oxic conditions promote the removal of pharmaceuticals. However, under anoxic conditions, these compounds are less susceptible to removal due to their chemical properties.

**Table 1** Initial removal rate ($r_{\text{obs, init}}$, mg L$^{-1}$ h$^{-1}$, $R^2 = 0.80$–0.97) and initial removal rate constant ($k_{\text{obs, init}}$, h$^{-1}$, $R^2 = 0.85$–0.99) of pharmaceutical removal with MnO$_2$ based on pseudo-first-order in first 5 h

| Experimental solution | Matrix          | pH   | Compound(s)       | $r_{\text{obs, init}}$ ($10^{-2}$ mg L$^{-1}$ h$^{-1}$) | $k_{\text{obs, init}}$ ($10^{-2}$ h$^{-1}$) |
|-----------------------|-----------------|------|-------------------|------------------------------------------------------|---------------------------------------------|
| Mixture of seven pharmaceutical | Demiwater       | ~ 8.5 | Metoprolol        | 7.39                                                 | 9.21                                        |
|                       |                 |      | Propranolol        | 10.10                                                | 14.18                                       |
|                       |                 |      | Diclofenac         | 5.33                                                 | 5.96                                        |
|                       |                 |      |                   |                                                      |                                            |
| Only diclofenac present in solution | Demiwater       | ~ 8.5 | Diclofenac$^b$    | 4.70                                                 | 5.56                                        |
|                       |                 |      |                   |                                                      |                                            |
| Only diclofenac present in solution | 50 mM phosphate buffer | ~ 7.0 | Diclofenac$^b$    | 10.48                                               | 57.32                                       |

$^a$Both $r_{\text{obs, init}}$ and $k_{\text{obs, init}}$ were calculated based on the periods 0–4 h

$^b$Both $r_{\text{obs, init}}$ and $k_{\text{obs, init}}$ were calculated based on the periods 0–9 h
removal. This C–N bond cleavage can result in the formation of radicals in the presence of oxygen (Barrett and McBride 2005; Gao et al. 2012). Oxidation of diclofenac involves hydroxylolation and decarboxylation instead of C–N cleavage (Huguet et al. 2013), which is a different mechanism than that of metoprolol and propranolol. This shows that the removal mechanism is closely related to the pharmaceutical molecular structure and chemical properties.

The pharmaceutical’s properties are also affected by pH. Due to the low pKa of diclofenac (pKa = 4.15), lower pH level results in a less negatively charged compound. This leads to less electrostatic repulsion between diclofenac and MnO2, which is also negatively charged (Murray 1974). It is speculated that lower pH level will lead to a higher affinity of diclofenac to adsorb onto the MnO2 surface and therefore has a more favorable first step in removal with MnO2.

**Table 2** Diclofenac removal efficiency under anoxic conditions at different pH conditions with two MnO2 morphologies after 48 h. Experimental conditions: [MnO2]0 = 7 mM, [diclofenac]0 = 1 mg L−1, [ionic strength] = 0.1 M

| MnO2 morphologies    | ~pH 4.5 (%) | ~pH 7.0 (%) | ~pH 8.5 (%) |
|---------------------|-------------|-------------|-------------|
| Amorphous MnO2      | 100         | 100         | 71          |
| Crystalline MnO2    | 21          | 0           | 0           |

**MnO2 properties**

The properties of MnO2 are also affected by pH. At acidic pH, MnO2 is also less negatively charged due to its isoelectric point, resulting in less electrostatic repulsion and better adsorption of organic compounds. In addition, the MnO2 redox potential increases from 0.76 V at pH 8.0 to 0.99 V at pH 4.0 (Lin et al. 2009). Thus, the degradation reaction is energetically more favorable at lower pH. Both factors may lead to faster degradation, as shown in our study (Table 2). This experiment uses neutral pH, which was found unfavorable for oxidation of pharmaceuticals in previous studies (Chen et al. 2011; He et al. 2012; Xu et al. 2008). In addition, there are less protons at the low redox potential of MnO2 at higher pH, which is crucial for the electron transfer from Mn(IV) to Mn(II). As a result, no removal of caffeine, carbamazepine, ibuprofen, and naproxen was observed in this study (Fig. S3), while the removal efficiency of metoprolol and propranolol is low under bothoxic and anoxic conditions.

Different MnO2 morphologies have different properties affecting diclofenac removal. In our research, diclofenac removal is better with amorphous MnO2 than that with crystalline MnO2, which is in line with previously reported findings (Remucal and Ginder-Vogel 2014; Shin and Cheney 2004; Ukrainczyk and Mcbride 1992). Amorphous MnO2 particles are usually smaller than crystalline particles. Thus, the amorphous MnO2 particles have a larger surface area, which increases pharmaceutical removal. Unfortunately, due to the analytical limits, size analysis of amorphous MnO2 appeared technically not feasible (Fig. S6). In addition, amorphous MnO2 contains small amounts of Mn(III) which can increase MnO2 reactivity and oxidizing ability (Remucal and Ginder-Vogel 2014), thus promoting pharmaceutical removal even further.

In the presence of phosphate, diclofenac removal with MnO2 is slightly enhanced under oxic conditions than that under anoxic conditions. Using O2 to oxidize Mn(II) to Mn(III) is a thermodynamically favorable reaction. In the presence of phosphate buffer, phosphate can form Mn3(PO4)2 with Mn(II) from diclofenac oxidation (Eq. 1) (Jin et al. 2014).

\[
3\text{Mn}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Mn}_3(\text{PO}_4)_2
\] (1)

Computations show that the chemical structure of Mn3(PO4)2 can stabilize Mn(III) and thereby facilitate Mn(II) oxidation to Mn(III) under oxic conditions (Jin et al. 2014). The Mn2+ analysis shows the presence of higher Mn(III) concentrations in phosphate buffer than in demiwater, which we explain as a result of larger amounts of Mn(III) formed under oxic conditions. Higher Mn(III) concentration is likely the reason that more diclofenac is removed than under anoxic conditions, as we observed (Fig. 1) and mechanically present in Fig. 2.

**Reactive sites on the MnO2 surface**

The adsorption of organic molecules onto a reactive metal oxide surface is found to be the key parameter dictating removal of many organic compounds, and specifically to reactive sites on the MnO2 surface (He et al. 2012; Xu et al. 2008; Zhang and Huang 2005b). Our results with the mixed pharmaceutical solution in the demiwater suggest competition for reactive sites between diclofenac and the other different pharmaceuticals. This is evidenced by the lower diclofenac removal in the presence of other pharmaceuticals (Fig. 1a, b).

Based on our FTIR results, there was no obvious disappearance of reactive sites during diclofenac removal with MnO2 under both oxic and anoxic conditions (Fig. S5), possibly due to a relatively high concentration of MnO2 in the experiment. However, it is clear that the FTIR spectrums are different between the MnO2 before and after reacting with diclofenac, especially under anoxic conditions. This indicates that the intermediates from diclofenac change the MnO2 structure. This change may contribute to the better diclofenac removal with MnO2 under anoxic conditions.

In phosphate buffer, phosphate can reduce the diclofenac removal by being adsorbed onto the MnO2 surface and competing with DFC for the reactive sites of MnO2 (Yao and Millero 1996). Consequently, although the lower pH level in phosphate buffer should promote diclofenac removal (pH 7 in
buffer versus pH 8–9 in demiwater), diclofenac removal is better in demiwater because MnO$_2$ reactive sites are not blocked by phosphate (Table 1). However, similar removal efficiencies and kinetics in demiwater and phosphate buffer under anoxic conditions are observed (Fig. 1). This indicates there is a mechanism promoting diclofenac removal in phosphate buffer, which competes with the inhibition by phosphate adsorbing and occupying the reactive sites on the MnO$_2$ surface. From previous studies, it is known that Mn(II) can occupy reactive sites on the MnO$_2$ surface and then inhibit pharmaceutical removal (He et al. 2012; Xu et al. 2008). Our removal results in phosphate buffer show that 1.54 μM Mn$^{2+}$ was generated under oxic conditions while 2.16 μM was generated under anoxic conditions. Less Mn(II) under oxic conditions resulted in possibly less formation of Mn$_3$(PO$_4$)$_2$ via Eq. 1, which presumably led to more available reactive sites for diclofenac removal. Under anoxic conditions, the balance of these promoting and inhibiting effects by adsorbing phosphate leads to similar diclofenac removal in demiwater and phosphate buffer.

**Conclusions**

In conclusion, this study addresses the knowledge gap surrounding pharmaceutical removal under anoxic conditions (absence of oxygen) with MnO$_2$. Results show that anoxic conditions are beneficial for diclofenac removal with MnO$_2$. In demiwater, anoxic conditions show higher diclofenac removal compared to oxic conditions. In phosphate buffer, anoxic conditions resulted in similar diclofenac removal (10% difference) compared to oxic conditions. Both pH and MnO$_2$ morphologies influence the removal process and its efficiency. Since both demiwater and phosphate buffer suggest that anoxic conditions are as good as, or even better than, oxic conditions in diclofenac removal from water with MnO$_2$, the less potential cost in processes under anoxic conditions is more attractive and promising in treating water and wastewater containing pharmaceuticals. The results show that amorphous MnO$_2$ is the most suitable material for further research and application, and the most optimal and applicable conditions are at neutral pH in anoxic systems. By using a more favorable pH (acidic pH), the removal of all the pharmaceuticals can be expected under anoxic conditions. To our knowledge, this is the first study discussing pharmaceutical removal with MnO$_2$ under anoxic conditions. Using anoxic conditions is less energy-consuming compared to using oxic conditions (aeration), and Mn can be regenerated and recycled via a biological or chemical process (Jiang et al. 2010b; Liu et al., Biological regeneration of manganese (IV) and iron (III) for anaerobic metal oxide-mediated removal of pharmaceuticals from water, submitted; Tebo et al. 2004). Overall, this study contributes to (1) understanding pharmaceutical removal in the absence of oxygen, (2) improving the knowledge of pharmaceutical removal mechanisms with MnO$_2$, and (3) providing fundamental insight into a MnO$_2$-based process which may lead to a more sustainable technology for pharmaceutical removal.

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**Compliance with ethical standards**

**Conflict of interest**

The authors declare that they have no conflict of interest.

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