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Transformation of paracetamol into 1,4-benzoquinone by a manganese oxide bed filter

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HIGHLIGHTS

- Manganese oxide transformed paracetamol into 1,4-benzoquinone in column reactor for residence times <5 min.
- Paracetamol oxidation and benzoquinone formation decreases when pH increases.
- Dimer formation is a minor pathway for manganese oxide bed filter and low concentration of paracetamol
- The presence of natural organic matter inhibits the formation of the toxicant benzoquinone.

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ABSTRACT

This study investigates the transformation of paracetamol (PRC) by a granular manganeseoxide in a column bed reactor. Paracetamol was quantitatively transformed into p-benzoquinone(BZQ) for empty bed residence times (EBRT) <5 min at pH 6.0. For 5 mM MOPS (3-morpholinopropane-1-sulfonic acid) and pH 7.0, the mean removal yield of PRC was 77% for initial PRC concentrations ranging from 0.1 to 50 μM. Conversion of PRC and formation of BZQ decreased when pH increased from 6 to 8. Dimer of PRC was observed at pH 7.0, which could explain the lower conversion into BZQ when pH increased. The presence of organic buffer MOPS and natural organic matter (NOM) reduced the oxidation of PRC because of competition reactions for active sites. The formation of the toxic BZQ metabolite was reduced in presence of NOM because of cross-coupling reactions between phenoxyl radicals and NOM. Results suggest that manganese oxide bed filter can be used to remove pharmaceutical compounds including phenolic moiety in their structure.

1. Introduction

Paracetamol (PRC) or acetaminophen (*N*-acetyl-para-aminophenol) is an antipyretic analgesic prescribed for fever or moderate pain. It was the most sold pharmaceutical drug in France in 2010 [1] as Doliprane®, Dafalgan® and Efferalgan®. Paracetamol was detected in aquatic system although it is easily removed from waste water treatment plant (WWTPs) [2]. In Europe, values from 59 to 220 ng L^{-1} for effluent of WWTPs and from 12 to 777 ng L^{-1} for freshwaters were determined [3]. These authors also reported values from 24.7 to 65.2 ng L^{-1} in freshwaters of North America. Paracetamol concentrations up to 71 ng L^{-1} were reported in French surface waters [4]. As a consequence of the occurrence of paracetamol in the environment, many studies explored the fate and the behavior of paracetamol during water treatment. Ozonation and advanced oxidation processes such as photocatalytic processes showed a great efficiency for the removal of paracetamol with mineralization degrees up to 30% for ozonation and 40% for H_2O_2 photolysis [5]. High removal was also reported by biodegradation in membrane bioreactor [6]. Chlorination transformed paracetamol into *N*-Acetyl-p-benzoquinone imine (NAPQI) and p-benzoquinone [7]. The half-life time of the reaction with hypochlorite (57 μM) was 7.2 min in pure water at pH 7. Both NAPQI (*N*-acetyl-para-benzoquinone imine) and 1,4-benzoquinone are also toxic metabolites produced by the human body when paracetamol is taken at very large doses. NAPQI causes damage to liver and 1,4-benzoquinone induces nephrotoxicity [8,9].

Many studies report the importance of manganese oxides in the environmental processes because of their occurrence in soils and sediments [10]. Manganese oxides such as synthetic birnessite are known to oxidize phenols and aromatic amines [11–15]. Rate

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constants of oxidation of phenolic compounds by manganese oxide depend on the effect of substituents. While electron-withdrawing groups reduced the rate constants, electron-donating groups such as hydroxyl and methyl enhanced the oxidation rate [16]. Compared to phenol, paracetamol incorporates an acetamido group in the para position. The acetamido group is a moderately activating group with Hammett constants of $\sigma_m = 0.21$ and $\sigma_p = -0.01$ [17]. A low effect of the acetamido group in para position is then expected for paracetamol compared to phenol, which is illustrated by the similar pK_a values of 9.5 and 9.9 for paracetamol and phenol, respectively. Thus, paracetamol is expected to be oxidized by manganese oxide with similar rate constants than for phenol. First electron transfer between manganese oxide and phenols results in the formation of phenoxy radical. At high phenol concentration, they can couple to form dimer species. Transfer of a second electron with manganese oxide results in the formation of stable quinone end-products [16,18] or phenoxy radicals can also react with other solutes such as natural organic matter by cross-coupling reactions [19,20]. Rapid transformation of PRC by δ-MnO_2 was recently confirmed and dimer and trimer species were proposed as by-products [21]. Increasing the pH from 4 to 6 and the presence of co-solutes such as dissolved manganese and model compounds of humic substances significantly reduced the rate of transformation of PRC [21]. The presence of co-solutes like phosphate and natural organic matter can significantly affect the oxidation rate of organic substrate by manganese oxide because of competitive sorption on the active surface sites [22,23].

Most of the studies related to the oxidation of organic contaminants by manganese oxides have been performed in batch reactor using synthetic birnessite as model manganese oxide whereas only few studies investigated the reactivity of granular manganese oxide used in water treatment. The objective of this study was to evaluate the efficiency of manganese oxide for the removal of paracetamol in conditions used during water treatment. The granular manganese oxide is used in full-scale drinking water treatment plant for iron and manganese removal and was used for the adsorption of arsenic [24]. The experiments were conducted in column at lab-scale for different initial conditions such as flow rates, paracetamol concentration, pH and the presence of co-solutes (Mn^{2+} and NOM).

2. Materials and methods

2.1. The natural manganese dioxide and chemical reagents

Paracetamol (4-acetamidophenol; 98%) was purchased from Acros Organics. MOPS (99.5%) (3-morpholinopropane-1-sulfonic acid) purchased from Sigma was used as organic buffer. Standards of 1,4-benzoquinone and hydroquinone were purchased from Sigma–Aldrich. Manganese chloride, sodium chloride and sodium hydrogen carbonate were purchased from Carlo Erba, Fisher Scientific and VWR, respectively. Suwannee River NOM (SRNOM) isolated by using reverse osmosis and purchased from IHSS (International Humic Substances Society) was used as model organic matter.

The natural manganese oxide (79% MnO_2) is approved for drinking water treatment and was used in previous studies [25,26]. The manganese oxide was rinsed with ultra pure water to eliminate the fines before experiments. The selected size fraction was in the range of 300–700 μm. The specific density was 3.88. Specific surface area determined by BET method using N_2 as adsorbate was 16 $m^2\,g^{-1}$ (see N_2 adsorption–desorption curves in Fig. SI–1 in the supporting information) in agreement with the value of 17.0 $m^2\,g^{-1}$ determined by Ouvrard et al. [27] for the same material and size fraction. XRD diffraction showed the presence of two manganese oxides: cryptomelane [$K(Mn^{4+},Mn^{2+})_8O_{16}$] and birnessite [$Na_{0,55}Mn_2O_4{,}1{,}5H_2O$], and two manganese hydroxides: lithiophorite [$(Al,Li)Mn^{4+}O_2(OH)_2$] and nsutite [$Mn^{4+}{}_{1-y}Mn^{3+}{}_yO_{2-y}(OH)_y$] (See Fig. SI–2). The natural manganese oxide has a complex porous structure with both amorphous and well crystallized manganese phases including impurities of quartz and iron oxyhydroxides. The isoelectric point (pH_{iep}) determined by electrophoretic measurement (Malvern Zetameter) on <1 μm powder was 4.46 ± 0.27 (see Fig. SI–3) which was similar to the pH_{zpc} = 4.7 obtained by Ouvrard et al. [27] from potentiometric titration.

2.2. Column experiments

Column experiments were carried out with a chromatographic glass column (2.5 cm internal diameter ID, Fig. SI–4) packed with 200 g of dry manganese oxide. The length of the porous bed was 20 cm. The bulk density was 1.94 g cm^{-3}. The pore volume (Vp = 0.52 mL mL^{-1}) was estimated by the displacement method of a water volume.

The columns were fed upward at flow rates between 3.9 and 67 mL min^{-1} corresponding to empty bed residence times between 1.5 and 25.9 min. Columns were fed with PRC solutions buffered by MOPS in presence of sodium chloride used as an inert conservative tracer. The columns were previously equilibrated with 1 mM NaCl in MOPS buffer before the columns were fed by PRC solution in MOPS buffer and 10 mM NaCl. PRC and its by-products were analyzed by HPLC, chloride by ion chromatography and dissolved manganese by spectrophotometric test. An experiment was performed with 456 μM PRC solution in absence of buffer for the identification of by-products by mass spectrometry. Manganese oxide was always changed between each experimental condition except when different flow rates were tested for a same PRC solution.

Experiments were also conducted with tap water diluted with 2 volumes of MilliQ water and spiked with PRC and manganese chloride or natural organic matter to study the influence of co-solutes. Tap water was stored for 24 h at room temperature to eliminate chlorine residual before use. After dilution with MilliQ water, the water (pH 7.8) was characterized by high carbonate (4.3 mM HCO_3^-) and calcium (4.1 mM Ca^{2+}) content and low dissolved organic carbon (DOC = 0.5 ± 0.2 mg L^{-1}).

2.3. Analytical methods

The HPLC analysis of PRC and its by-products were performed by using a Kromasil C18 stationary phase with an eluent consisting of 20% methanol, 79.9% water, and 0.1% acetic acid. The injection volume was 100 μL and the compounds were detected at 242 nm. Standards of BZQ and PRC were prepared by dissolution of pure products in MilliQ water. Standards of BZQ were prepared daily.

HPLC–UV–MS analyses were performed with a Thermo Scientific Accela Chromatographic system (Villebon sur Yvette, France) equipped with a Accela diode array detector and a Q Exactive high resolution mass spectrometer. Detection was carrying out by using atmospheric pressure chemical ionization in positive and negative mode. The separation of paracetamol and degradation products was obtained with a Kromasil C18 column (5 μm 250 mm × 3.2 mm) and using a mobile phase consisting in (A) formic acid/methanol (1:1000 v/v) and (B) formic acid/water (1:1000 v/v) pumped at a flow rate of 0.3 mL min^{-1}. The elution started at 10% of A for 20 min and increased to 100% of A over 45 min. Then, mobile phase 100% A was maintained for 10 min. Finally, in order to equilibrate the HPLC system for the next injection, the mobile phase was returned to 10% A in 5 min and maintained for 15 min. The injection volume was 100 μL. Mass