



Removal of diclofenac by conventional drinking water treatment processes and granular activated carbon filtration



Eliane Sloboda Rigobello^{a,*}, Angela Di Bernardo Dantas^b, Luiz Di Bernardo^c, Eny Maria Vieira^a

^a Department of Chemistry and Molecular Physics, Institute of Chemistry of São Carlos, University of São Paulo, 13566-570 São Carlos, Brazil

^b University of the Association of Schools of Ribeirão Preto (UNAERP), 14906-900 Ribeirão Preto, Brazil

^c Department of Hydraulics and Sanitation, São Carlos School of Engineering, University of São Paulo, 13566-570 São Carlos, Brazil

HIGHLIGHTS

- We evaluate the removal of diclofenac in conventional water treatment processes.
- Aquatic humic substances were used in the water of this study.
- The use of chlorine and chlorine dioxide as pre-oxidant were investigated.
- Conventional treatment followed by activated carbon filtration was also studied.
- Byproducts formed in the oxidation of diclofenac were identified by LC–MS/MS.

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ABSTRACT

This study was carried out to evaluate the efficiency of conventional drinking water treatment processes with and without pre-oxidation with chlorine and chlorine dioxide and the use of granular activated carbon (GAC) filtration for the removal of diclofenac (DCF). Water treatment was performed using the Jar test with filters on a lab scale, employing nonchlorinated artesian well water prepared with aquatic humic substances to yield 20 HU true color, kaolin turbidity of 70 NTU and 1 mg L⁻¹ DCF. For the quantification of DCF in water samples, solid phase extraction and HPLC–DAD methods were developed and validated. There was no removal of DCF in coagulation with aluminum sulfate (3.47 mg Al L⁻¹ and pH = 6.5), flocculation, sedimentation and sand filtration. In the treatment with pre-oxidation and disinfection, DCF was partially removed, but the concentration of dissolved organic carbon (DOC) was unchanged and byproducts of DCF were observed. Chlorine dioxide was more effective than chlorine in oxidizing DCF. In conclusion, the identification of DCF and DOC in finished water indicated the incomplete elimination of DCF through conventional treatments. Nevertheless, conventional drinking water treatment followed by GAC filtration was effective in removing DCF (≥99.7%). In the oxidation with chlorine, three byproducts were tentatively identified, corresponding to a hydroxylation, aromatic substitution of one hydrogen by chlorine and a decarboxylation/hydroxylation. Oxidation with chlorine dioxide resulted in only one byproduct (hydroxylation).

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1. Introduction

The occurrence and fate of pharmaceutical compounds and their metabolites in the aquatic environment have been recognized as an emerging issue. There is concern because little is known regarding the potential effects of these compounds on non-target organisms, mainly chronic toxicity and possible additive effects of a vast range of pharmaceuticals present in the aquatic environment, even at trace levels (ng L⁻¹ or µg L⁻¹) (Huang et al., 2011; Rodil et al., 2012).

The presence of pharmaceutical residues in effluents from wastewater treatment plants (WWTPs) shows that not all pharmaceuticals are completely removed during treatment (Zhang et al., 2008; Morasch et al., 2010; Rodil et al., 2012). Consequently, they have been widely found at concentrations in the ng L⁻¹–µg L⁻¹ range in surface waters, which is the main source of raw water in drinking water treatment plants (DWTPs) (Vieno et al., 2007; Vulliet et al., 2011; Montagner and Jardim, 2011; Valcárcel et al., 2011a,b) and groundwater (Lapworth et al., 2012). Due to their inefficient treatment in DWTPs and their hydrophilic properties, a number of pharmaceuticals have also been found in drinking water at concentrations in the order of ng L⁻¹ (Ziyilan and Ince, 2011; Vulliet et al., 2011; Valcárcel et al., 2011a,b; Rodil et al., 2012).

* Corresponding author. Tel.: +55 44 35253175.

E-mail address: elisloboda@hotmail.com (E.S. Rigobello).

Among the most consumed non-steroidal anti-inflammatory drugs frequently found in aquatic environments are aspirin, acetaminophen, ibuprofen, naproxen and diclofenac (DCF) (Fent et al., 2006). The DCF has been found in drinking water at concentrations $<10 \text{ ng L}^{-1}$ (Rabiet et al., 2006; Vulliet et al., 2011).

Although the pharmaceuticals are still not regulated in drinking water, it is of great importance to know if the treatments applied to DWTPs can eliminate pharmaceutical compounds. Moreover, little is known about the occurrence and fate of byproducts (metabolites and transformation products) formed during drinking water treatments and their (eco)toxicological effects (Touraud et al., 2011). Research on the possible byproducts formed through the biodegradation and chlorination of some pharmaceuticals during treatments at WWTPs and DWTPs has been reported (Quintana et al., 2005, 2010; Soufan et al., 2012). However, no study has reported on the byproducts of DCF formed by oxidation with chlorine dioxide.

Conventional treatments have been reported ineffective in the removal of most pharmaceuticals, with an efficiency of $<5\text{--}40\%$ (Vieno et al., 2007; Pojana et al., 2011). However, processes and unit operations, such as ozonation (Ikehata et al., 2006), adsorption on activated carbon (Kim et al., 2007) and membrane filtration, such as nanofiltration and reverse osmosis (Radjenovic et al., 2008; Boleda et al., 2011), have shown effective in the removal of a relatively large number of pharmaceuticals ($>99\%$). In general, the percentage removed depends on several factors, such as molecular structure of pharmaceuticals, type and dosage of coagulant, presence and characteristics of dissolved organic matter (DOM), mechanism of coagulation and experimental conditions (Vieno et al., 2007; Pojana et al., 2011). Nevertheless, the use of advanced processes in DWTPs is still limited due to their high cost, especially in developing countries, as Brazil.

Most studies on the removal of pharmaceuticals have focused on a small set of processes or operations of water treatment. Moreover, they have used humic substances extracted from peat instead of water, which have different characteristics, including a lower content of humic acids than fulvic acids, molecules of lower molecular weight and less condensed structures, which may hinder the removal of pharmaceuticals (Rigobello et al., 2011).

This study was carried out to evaluate the efficiency of conventional drinking water treatment processes (coagulation, flocculation, sedimentation, sand filtration and chlorine disinfection) combined with pre-oxidation using chlorine and chlorine dioxide and adsorption on granular activated carbon (GAC) in the removal of DCF in water containing aquatic humic substances (AHSs). Additionally, the byproducts formed during the oxidation of DCF with chlorine and chlorine dioxide were tentatively identified by LC-MS/MS. The selection of the analyte DCF was based on its high consumption, high frequency of detection in the aquatic environment and low biodegradability and polarity, which favor its spread in natural waters (Vieno et al., 2007; Zhang et al., 2008).

2. Materials and methods

2.1. Chemicals and reagents

Acetonitrile and methanol were of HPLC grade (Baker) and high-purity water was obtained from a Milli-Q water system (Millipore) equipped with a UV radiation source. The coagulant used was a commercial liquid of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O}$, 50%, w/w) containing 7.3% Al_2O_3 (w/w) with specific density of 1.3 g cm^{-3} and 3.85% aluminum (w/w). The chlorine dioxide solution ($300 \text{ mg ClO}_2 \cdot \text{L}^{-1}$) generated from the sodium chlorate was supplied by Eka Chemicals SA of Brazil – Akzo Nobel Company. The chlorine solution was prepared from a solution of sodium hypochlorite with 12.9% active

chlorine and 1.22 g cm^{-3} density provided by the DWTP of São Carlos – SP, Brazil. The solutions of chlorine and chlorine dioxide were prepared at the desired concentrations by dilution with water (Milli-Q system, $18.2 \text{ M}\Omega \text{ cm}$ at 25°C). The analytical standard of DCF (sodium salt, CAS number 15307-79-6) had $>99\%$ purity and was supplied by Sigma–Aldrich. DCF has a K_{ow} of 4.51 and a pK_a of 4.15 (Vieno et al., 2007). A stock solution of DCF was prepared in methanol at a concentration of 200 mg L^{-1} and stored in a refrigerator at 4°C .

2.2. Water sample collection and extraction of AHS

The AHS used to adjust the color of the synthetic water samples were extracted from the water collected in a tributary of the Itapanhaú River (Latitude $23^\circ47'19.35'' \text{ S}$ and Longitude $46^\circ3'29.32'' \text{ W}$) in Bertioga, São Paulo, Brazil (tropical forest). The AHS were isolated by adsorption chromatography on XAD-8 non-ionic macroporous resin (Supelco) according to the method of Thurman and Malcolm (1981). The water samples collected exhibited a true color of 184 HU, turbidity of 4.38 NTU, $\text{pH} = 4.9$, dissolved organic carbon (DOC) of 17.4 mg C L^{-1} , alkalinity of $6 \text{ mg CaCO}_3 \text{ L}^{-1}$ and UV absorbance at a wavelength of 254 nm (UV_{254}) of 4.79. Overall, characterization results indicated that the AHS fraction contained a greater aliphatic than aromatic carbon content and a relatively high percentage of oxygen atoms (higher content of fulvic acids than humic acids). The AHS were characterized as described by Rigobello et al. (2011).

2.3. Analytical methods

The turbidity of the samples was measured using a HACH 2100P turbidity meter. A Shimadzu 5000A total organic carbon (TOC) analyzer spectrophotometer was used to determine the DOC content in the water samples. UV_{254} and color were measured by a HACH DR4000 spectrophotometer at 254 and 455 nm, respectively. All samples were filtered through a $0.45 \mu\text{m}$ membrane (Millipore, cellulose ester, 90 mm diameter) prior to both UV_{254} and UV_{278} , DCF and DOC analyses to remove particles. The pH of the water samples was measured using an Orion 420A potentiometer. The chlorite ion present in the water samples after the pre-oxidation with chlorine dioxide was determined by a colorimetric method with a Prominent DT4 instrument. The UV/Vis analysis was performed using a UV/Vis JASCO – 630 V spectrophotometer. The concentrations of Cl_2 and ClO_2 were quantified by reaction with N,N-diethyl-p-phenylene diamine (DPD) using a HACH DR4000 spectrophotometer at 530 nm. The analysis of ClO_2 with DPD was performed according to the manufacturer's instructions.

2.3.1. HPLC-DAD analysis

The DCF was extracted from the water samples using solid phase extraction (SPE) with Phenomex C_{18} sorbent (6 mL; 500 mg of resin weight). Each C_{18} sorbent was pre-conditioned with 5 mL of methanol and 5 mL of purified water (Milli-Q) at a flow rate of 2 mL min^{-1} . Next, 100 mL of water (pH between 6.0 and 8.0) was passed through the C_{18} sorbent at a flow rate of 5 mL min^{-1} . The DCF was eluted with 5 mL of methanol in a volumetric flask. The samples were then analyzed on an HPLC coupled to a DAD detector operating at $\lambda = 278 \pm 4 \text{ nm}$ (Agilent Technologies) with an autosampler using a Zorbax C_{18} ($250 \text{ mm} \times 4.6 \text{ mm}$ id $\times 5 \mu\text{m}$ particles) column. The flow rate was 0.8 mL min^{-1} , the injection volume was $20 \mu\text{L}$, the column oven was set to 25°C and the retention time was 10 min. An isocratic mobile phase of acetonitrile:water (65:35, v/v) was used and both components were acidified with 0.05% trifluoroacetic acid (99.9% purity).

The method employed was validated according to resolution number 899 of the National Agency of Sanitary Vigilance (ANVISA, 2003). The limit of quantification (LOQ) was $3 \mu\text{g L}^{-1}$ and the limit

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