Separation and Purification Technology 107 (2013) 179–186

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Hybrid ozonation-ceramic membrane filtration of surface waters: The effect of water characteristics on permeate flux and the removal of DBP precursors, dicloxacillin and ceftazidime

Alla L. Alpatova [1], Simon H. Davies, Susan J. Masten *

Department of Civil and Environmental Engineering, Michigan State University, East Lansing, MI 48824, USA

ARTICLE INFO

Article history:
Received 8 August 2012
Received in revised form 10 January 2013
Accepted 10 January 2013
Available online 31 January 2013

Keywords:
Membrane filtration
Ceramic membrane
Pharmaceutical
Antibiotic
Ozone

ABSTRACT

The removal of the disinfection byproducts (DBPs) precursors, antibiotics dicloxacilline and ceftazidime by hybrid ozonation membrane filtration (HOMF) has been studied in three surface waters (Lake Huron, Lake Lansing and Huron River). This study demonstrates that, compared to membrane filtration, HOMF significantly improves the removal of dicloxacilline, ceftazidime, and disinfection byproduct precursors. At a sufficiently high ozone dosage, the concentrations of the two antibiotics in the permeate were reduced to below the detection limits in the three waters studied. Significant reductions in total organic carbon (TOC), specific UV absorbance (SUVA), and chlorinated disinfection byproducts (DBPs) were also achieved, suggesting that the system could also be effective at controlling the formation of DBPs during chlorination. The fouling behavior of the system was also studied. The degree of fouling was greater in waters with a high TOC and/or alkalinity. Alkalinity adversely affected the removal of the antibiotics and the ability of ozone to control fouling. The effect of alkalinity can be attributed to the scavenging of hydroxyl (·OH) radicals by carbonate species.

1. Introduction

In previous work our group and others have demonstrated that ozone can reduce fouling on ceramic membranes [1–5]. It has also been shown that hybrid ozonation membrane filtration (HOMF) effectively removes the high molecular weight compounds found in natural waters. These compounds are the precursors of disinfection byproducts (DBPs) that are formed during chlorination [6]. Studies have shown that HOMF removes low molecular weight species, such as salicylic acid, even though these species are too small to be retained on the membrane surface [7]. The ability of the hybrid system to remove low molecular weight species, such as salicylic acid, raises the question as to whether it is possible to also remove dissolved contaminants, such as pharmaceuticals.

In recent years there has been considerable interest in the development of water treatment technologies to remove pharmaceuticals, since they are often difficult to remove by conventional water and wastewater treatment processes [8,9]. Pharmaceutically active compounds are complex molecules with a wide range of physicochemical properties and biological activity. As they are designed to exert a certain physiological effect on humans, animals, or plants; pharmaceuticals are chemically stable, persistent to biological degradation and can accumulate in aquatic and terrestrial ecosystems [10,11]. Pharmaceutical residuals have been found in natural waters in the United States [10,12,13], United Kingdom [14,15], Switzerland [16], Germany [8,17], Denmark [18], Australia [19], Brazil [20], and South Korea [21].

Catalytic ozonation is a promising technology [22–24] for the treatment of water and wastewater secondary effluent. Catalysts, such as metal oxides, can degrade ozone to generate ·OH radicals [23,25,26], which are very strong oxidants that can degrade many contaminants [25]. For example, Parisheva and Litcheva [24] achieved 87% removal of salicylic acid using catalytic ozonation with a MnO_2 catalyst, whereas ozonation alone resulted in only 48% degradation of the salicylic acid. Similarly, Ernst et al. [23] found a higher degree of mineralization when salicylic acid was subjected to catalytic ozonation (83.5%) on Al_2O_3, than was achieved with ozonation alone (44.9%).

Ceramic membranes are well suited for use in HOMF systems because of their catalytic properties and because they are resistant to ozone [27]. Ceramic membranes have longer lifetimes, are not as easily ruptured, and exhibit greater thermal and chemical stability than polymeric membranes [28]. Metal oxides, such as titania, silica, and zirconia, are commonly used to form the separation layer on the surface of ceramic membranes [28]. The use of ozone in a

* Corresponding author. Tel.: +1 517 355 2254; fax: +1 517 355 0250.
E-mail address: masten@egr.msu.edu (S.J. Masten).
[1] Present address: Department of Civil and Environmental Engineering, 3-096 Markin/CNRL Natural Resource Engineering Facility, University of Alberta, Edmonton, AB, Canada T6G 2W2

1383-5866/$ - see front matter
http://dx.doi.org/10.1016/j.seppur.2013.01.013

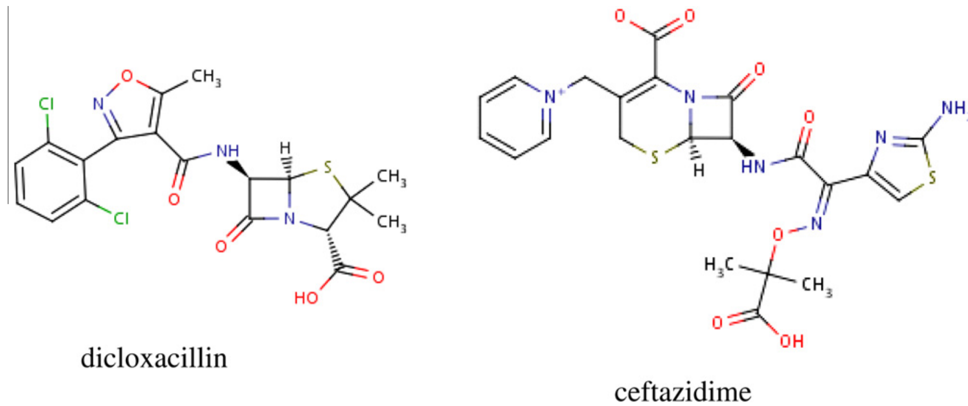

Fig. 1. Chemical structures of dicloxacilline and ceftazidime.

Table 1
Selected characteristics of the antibiotics.

Common name	Dicloxacillin	Ceftazedime
Type	β-lactam penicillin[a]	β-lactam cephalosporin[b]
Action	Treatment of skin and upper respiratory tract infections[a]	Treatment of meningitis, lower respiratory tract, urinary tract and skin infections[b]
Chemical formula	$C_{19}H_{17}Cl_2N_3O_5S$	$C_{22}H_{22}N_6O_7S_2$
MW (g mole^{-1})	470	547
Molecular volume (cm^3)[c]	7.8×10^{-22}	9.6×10^{-22}
$\log K_{ow}$[d]	3.9	−1.6
Water solubility at 25 °C (mg L^{-1})[d]	3.6	400
pK_{a1}[e]	2.7–2.8	1.8
Estimated removal in sewage treatment (%)[d]	4.99	1.85

a [29].
b [30].
c Estimated based on [45]. See Table S2 (SI) for detailed calculations.
d Estimated according to EPI Suite software (USA EPA, V.4.1).
e [29,30].

membrane filtration system offers the promise of being able to control membrane fouling and remove dissolved contaminants. The goals of this study were to investigate the effect of ozone dose on fouling and the removal of DBP precursors, along with dicloxacillin, and ceftazidime, in a HOMF system. Three surface waters (from the Huron River, Lake Huron and Lake Lansing) with different characteristics were used in our study. Dicloxacillin and ceftazidime were chosen because they are typical of the antibiotics found in surface waters [10] and have diverse modes of action against gram-positive and gram-negative bacteria [29,30]. The structures of these the antibiotics are shown in Fig. 1 and their physicochemical characteristics are shown in Table 1. Dicloxacillin and ceftazidime each contain at least one carboxylic acid group, and as they have pK_{a1} values <2.8, they both exist predominantly in the anionic form at pH values greater than 3.

2. Materials and methods

2.1. Materials

Dicloxacillin, ceftazidime, acetonitrile, sodium bicarbonate and sulfuric acid were used as received from Sigma–Aldrich (Milwaukee, WI). Sodium hydroxide and phosphoric acid were purchased from J.T. Baker (Phillipsburg, NJ). All chemicals were of analytical grade. Ultrapure water was used for preparing solutions, membrane cleaning and system flushing. The ultrapure water was supplied by a Lab Five system (USFilter Corp., Hazel Park, MI) equipped with a 0.2 μm capsule microfilter (PolyCap, Whatman, Sanford, ME).

2.2. Hybrid ozonation-membrane filtration system

The HOMF system consisted of an ozone injection system, membrane module, recirculation pump, reservoir, ozone injection system, and data acquisition system. A detailed description of this system can be found elsewhere [31]. The operating conditions for the HOMF system are summarized in Table 2. For the Lake Lansing and Lake Huron samples, ozonation-membrane filtration and membrane filtration experiments were conducted in duplicate using the samples as received and spiked with antibiotics. The Huron River samples were analyzed in duplicate but the experiment in which Huron River water was spiked with antibiotics was not replicated.

2.3. Ceramic membrane

A tubular ceramic UF membrane (Inside CéRAM, TAMI North America, Saint-Laurent, Québec, Canada) with a nominal molecular weight cut-off (MWCO) of 1 kDa, inner diameter of 0.1 cm and active length of 25 cm was used in all filtration tests. The support and

Table 2
Operating conditions for the hybrid ozonation-membrane filtration system.

Ozone gas-phase concentration (mg L^{-1})	5 ± 0.5–30 ± 0.5
Volumetric ozone-gas flow rate (mL min^{-1}):	40 ± 0.5
Ozone inlet pressure (bar):	2.5 ± 0.1
Transmembrane pressure (TMP) (bar):	2.1 ± 0.1
Volumetric cross-flow rate (L·min^{-1}):	0.55 ± 0.05
Temp. (°C):	24 ± 1