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Sorption of antibiotics to biofilm

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ABSTRACT

Using a continuous-flow rotating annular bioreactor, sorption of three selected antibiotics (sulfamethoxazole (SMX), ciprofloxacin (CIP), and erythromycin (ERY)) to bacterial biofilm was investigated. CIP had the greatest biofilm partition coefficient (K_{oc} = 92,000 ± 10,000 L/kg) followed by ERY (K_{oc} = 6000 ± 1000 L/kg) and then SMX (K_{oc} = 4000 ± 1000 L/kg). Antibiotic sorption to biofilm did not correlate with experimentally-determined K_{ow} values (CIP: −0.4; ERY: 0.98; SMX: <-0.59 at pH 7), suggesting that hydrophobic interactions do not drive the sorption of these relatively hydrophilic compounds to the biofilm. It appears that speciation (i.e. charge) and molecular size of the antibiotics are important in explaining their sorption to typically negatively charged biofilm. SMX is neutral to negatively charged at circumneutral pH while CIP and ERY are both positively charged. The decreased extent of sorption of ERY relative to CIP is likely due to the larger molecular size of ERY that results in a decreased rate of mass transfer (i.e. diffusion) to and through the biofilm. In conclusion, the results of this research suggest that hydrophobic interactions (predicted by K_{ow}) do not control sorption of relatively hydrophilic antibiotics to biofilm and that antibiotic speciation and molecular size are important factors affecting the interactions between antibiotics and biofilm.

1. Introduction

Antibiotics have been detected in surface waters around the world at concentrations up to 1.9 μg/L (Kolpin et al., 2002; Pena et al., 2007). The presence of antibiotics in surface waters is of concern for several reasons. First, antibiotic resistance can develop in bacteria with exposure to sub-inhibitory concentrations (Ash et al., 2002). Also, aquatic organisms (algae, nitrifying bacteria, zooplankton) can be adversely affected by mixtures of antibiotics at low concentrations (i.e. 0.1–50 μg/L) (Flaherty and Dodson, 2005; Yang et al., 2008; Ghosh et al., 2009).

Finally, although the human health effects of sustained exposure to antibiotics at sub-therapeutic doses are currently unknown, there is heightened public awareness over the presence of antibiotics and other pharmaceutical compounds in drinking water supplies (Benotti et al., 2009). Thus there is interest in approaches to remove antibiotics and other pharmaceutical compounds from water supplies.

Antibiotics are not effectively removed via conventional water treatment (i.e. coagulation/flocculation/sedimentation/filtration) or lime softening (≤33%, Adams et al., 2002; Westerhoff et al., 2005). Free chlorine (1 mg/L for 40 min) effectively removes (≥90%) some antibiotics (sulfonamides, carbodox, and trimethoprim) from surface water, although sulfamethoxazole (SMX) may reform during dechlorination (Adams et al., 2002; Dodd and Huang, 2004). Unfortunately, little is known about the products of antibiotic chlorination and their activity and toxicity. Chlorine dioxide and ozone also effectively remove antibiotics (e.g., sulfonamides and macrolides) at reasonable doses and contact times (Huber et al., 2005; Westerhoff et al., 2005), but this is not the case

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for chloramines (Chamberlain and Adams, 2006). Fresh granular activated carbon (GAC) effectively removes erythromycin (ERY) and SMX (7.6-min empty-bed contact times), with spent GAC still exhibiting some removal (<40% for SMX and <55% for ERY) (Westerhoff et al., 2005; Snyder et al., 2007). Regarding membrane filtration, only reverse osmosis and nanofiltration are effective at rejecting antibiotics (Ngheim et al., 2005; Snyder et al., 2007). Finally, photodegradation of tetracyclines, quinolones and ionized sulfonamides occurs in low turbidity waters (Torniainen et al., 1997; Moore and Zhou, 1994) and may contribute to observed removals in treatment facilities using UV disinfection systems.

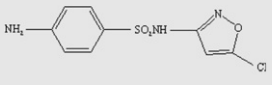
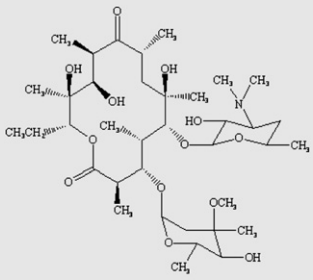
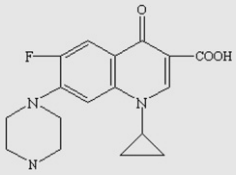
Biofiltration systems, including slow rate filtration (i.e. slow sand filtration, bank filtration) and biologically-active rapid filtration, have been used in the water industry for many decades, especially in Europe (Bouwer and Crowe, 1988; Hiscock and Grischek, 2002). Interest in biofiltration in the U.S. has increased in recent years because of the many potential water quality benefits these systems provide. For example, biofilters effectively remove a variety of organic pollutants including: disinfection byproduct precursors, pesticides, and pharmaceuticals (Eighmy et al., 1993; Collins et al., 1989; Hiscock and Grischek, 2002; Weiss et al., 2003). Removal mechanisms include biodegradation and sorption, with potential sorbents including the filter media (e.g., GAC), natural organic matter (NOM) sorbed onto the filter media, and biofilm. Although there are reports of antibiotic sorption to GAC (Westerhoff et al., 2005; Snyder et al., 2007), sand (Thiele-Bruhn, 2003), manure, and digested sludge (Loke et al., 2002; Carballa et al., 2008), we are unaware of any studies concerning antibiotic sorption to biofilm. Understanding antibiotic sorption to biofilm could be useful for predicting the fate of antibiotics in biofiltration systems used for treatment of water or wastewater. Herein, we report on the results of laboratory experiments performed to quantify the sorption of three selected antibiotics to biofilm as a first step in characterizing the fate of antibiotics in biofilters.

2. Materials and methods

2.1. Antibiotics, chemicals, and reagents

The sorption of three selected antibiotics (Table 1) to biofilm was investigated using a continuous-flow rotating annular bioreactor (CFRAB). SMX, ERY, and Ciprofloxacin (CIP) were selected for the following reasons: (1) they represent three prominent classes of antibiotics with differing chemical characteristics and (2) they have been detected in surface water. SMX (a sulfonamide) and ERY (a macrolide) occur in surface waters at concentrations up to 1.9 and 1.7 μg/L, respectively (Kolpin et al., 2002). CIP is a fluoroquinolone with reported surface water concentration of up to 119 ng/L (Pena et al., 2007). The *octanol–water partition coefficient* (K_{ow}), defined as the concentration of a chemical in octanol to that in water at equilibrium, is a commonly used parameter for predicting the fate of a chemical in the environment or of a pharmaceutical compound in the human body. Compounds with relatively high K_{ow} are more likely to partition to natural organic matter, bioaccumulate in aquatic organisms, or partition into hydrophobic compartments in the human body such as lipid bilayers. Reported logK_{ow} (pH 7.4 and 25 °C) values for SMX, ERY, and CIP are −0.9, 1.58, and −1.1, respectively (Hansch et al., 1995; Drakapoulos and Ioannou, 1997). The logK_{ow} determined at pH 7.4 (i.e. the physiological pH of blood serum) is often termed the *octanol–water distribution coefficient* (log$D_{7.4}$). For ionizable compounds, the logK_{ow} value determined at a pH where the neutral chemical species predominates is also called the *octanol–water partition coefficient* but often expressed as log*P*. Reported log*P* values for SMX, ERY, and CIP are 0.89, 3.06, and 0.4, respectively (Drakapoulos and Ioannou, 1997; McFarland et al., 1997; Congliang et al., 2007). The pH values where these compounds are predominantly non-ionic (i.e. >95% of species; 4.3 for SMX, 10.2 for ERY, and ~10.0 for CIP), however, are obviously quite different

Table 1 – Antibiotics Selected for Study.

Antibiotic	Sulfamethoxazole	Erythromycin	Ciprofloxacin
pK_a(s)[a]	1.85, 5.60	8.90	3.0, 6.1, 8.7, 10.6
Molecular weight	253.3	733.9	331.3
Molecular structure	 $C_{10}H_{11}N_3O_3S$	 $C_{37}H_{67}NO_{13}$	 $C_{17}H_{18}FN_3O_3$

a Qiang and Adams (2004).