Sorption of microconstituents onto primary sludge

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ABSTRACT

The presence of microconstituents (MCs) in the environment has become an emerging concern to scientists and engineers. Sorption is one of the important removal mechanisms for MCs in wastewater treatment plants (WWTPs) since there is significant sludge production. The purpose of this study is to explore sorption kinetics and isotherms of MCs onto primary sludge. Three MCs, bisphenol-A (BPA), 17-α-ethinylestradiol (EE2) and tricosan (TCS), were chosen for this study. They are hydrophobic and have low vapor pressure, which makes sorption a potential removal mechanism. Both sorption kinetics and isotherm experiments were conducted using primary sludge collected from a local municipal WWTP. The time to equilibrium was around 7 h for all chosen MCs. A pseudo second-order rate model was better at describing the sorption rate than a pseudo first-order rate model. Linear sorption isotherm models were found to fit the experimental data, and the solid-liquid partitioning coefficients for BPA, EE2 and TCS were 81, 728 and 6,407 L/kg.

Key words | hydrophobic, partitioning, sorption isotherms, sorption kinetics

INTRODUCTION

The presence of microconstituents (MCs) in the environment has been a concern since the early 1990s (Lishman et al. 2006; Miège et al. 2009; Huerta-Fontela et al. 2011; Yu et al. 2013; Kosma et al. 2014). MCs include pharmaceuticals and personal care products, endocrine disrupting compounds (Huang et al. 2011), herbicides, pesticides and alkylphenols (Salveson et al. 2008). Wastewater treatment plants (WWTPs) are a significant point source of MCs. Conventional WWTPs provide good performance in terms of removing particulates, carbonaceous matter, pathogens and nutrients such as nitrogen and phosphorus; however, WWTPs fail to remove many MCs to an acceptable level. The concentrations of MCs in the influents to WWTPs range from hundreds of ng/L to μg/L (Huerta-Fontela et al. 2011; Jelic et al. 2011; Sun et al. 2014). Removal efficiencies for MCs based on aqueous phase concentrations, i.e., the removal efficiencies based on influent and effluent concentrations, reported by different studies vary from no removal to 100% removal (Jelic et al. 2011; Yu et al. 2015; Kosma et al. 2014; Sun et al. 2014). Some studies have even shown negative removal efficiencies for certain compounds (Jelic et al. 2011).

When solid-phase concentrations, i.e., the concentrations of MCs in sludge, are taken into consideration, many researchers found the removal efficiencies for MCs by WWTPs are actually insufficient (Jelic et al. 2011; Yu et al. 2015). Sorption is a universal phenomenon that begins in the sewer system, where MCs discharged from households come into contact with solids contained in the sewage. Long travel times in the sewer system will be beneficial to equilibrium being attained between the soluble and solid-phase concentrations. When wastewater reaches the WWTP, most of the settleable solids (that contain sorbed MCs) would be removed by the grit chamber and/or primary clarifier and then further treated by digestion. Sorption could also occur in bioreactors where a large amount of biosolids exists. This study focuses on the sorption of MCs onto primary sludge. Typical quantities of primary sludge range from 1.5 to 2.4 kg/m³ (0.9–1.4 lb dry solids/10³ gal) of wastewater, depending on the nature of the collection system and whether industrial wastewater is discharged to the system (Metcalf & Eddy Inc. et al. 2006).

Studies focusing on MCs sorbing onto primary sludge are rare. The partitioning coefficient is defined as $K_d$. The log $K_d$ of 17-α-ethinylestradiol (EE2), reported in the literature, ranges from 2.1 to 2.9 (Ternes et al. 2004; Carballa et al. 2008). No evidence shows that subsequent sludge treatment can remove all MCs to an acceptable level. Carballa et al. (2007) studied the fate of MCs during anaerobic digestion of sewage sludge. High removal efficiencies (>85%)
were observed for antibiotics, natural estrogens, musks and naproxen; medium removal efficiencies (20–60%) were observed for other studied compounds; carbamazepine showed no removal at all. As a result, some researchers claim that one of the pathways for MCs entering the environment is through the disposal of wasted sludge (Ternes et al. 2004; Yu et al. 2013).

Three MCs were selected for the study: bisphenol-A (BPA), EE2 and triclosan (TCS). All three compounds were reported to be hydrophobic with low volatility and water solubility, which makes sorption a possible removal mechanism for the chosen MCs. Except for TCS, there is no photodegradation reported for these compounds. The octanol–water partition coefficient ($K_{ow}$) is related to water solubility (Silva & Esteves 2012). Chemicals with high $K_{ow}$ are considered to be hydrophobic and have a strong tendency to sorb to sludge. According to the literature, chemicals with log $K_{ow}$ less than 2 have negligible sorption, while if log $K_{ow}$ is more than 4, sorption could be a very significant removal mechanism (van Beelen 2007). Judging from log $K_{ow}$ values in Table 1, EE2 has medium sorption potential (2.5 < log $K_{ow}$ < 4.0) while TCS has high sorption potential (log $K_{ow}$ ≥ 4.0).

Sorption is the term used here because it is not clear whether MCs will adsorb to the surface of the solids or travel further into the interior of the solids. Sorption kinetics and isotherms of MCs are influenced by the characteristics of MCs, the physicochemical characteristics, the organic carbon content of the sludge and some other environmental conditions such as water temperature or pH.

While sorption isotherms provide information about equilibrium concentrations of a system, sorption kinetics are concerned with rates of change. It is necessary to know the rate of the sorption process to deal with a dynamic system (Azizian 2004). Numerous kinetics models have been used to describe the process of sorption. In this study, only pseudo first-order and pseudo second-order rate models are discussed and used to fit experimental data. According to Azizian (2004), the rate for pseudo first-order sorption is ‘a combination of adsorption and desorption rates’. The pseudo first-order rate model is

$$\frac{dq}{dt} = k_1 (Q_e - Q_t)$$

where $Q_t$ is solid-phase concentration at equilibrium (g/g); $Q_t$ is solid-phase concentration at different times (g/g); $k_1$ is rate constant of pseudo first-order sorption (h$^{-1}$). The pseudo second-order rate model is expressed by the following equation:

$$\frac{1}{(Q_e - Q_t)} = \frac{1}{Q_e} - k_2 t$$

where $k_2$ is rate constant (h$^{-1}$). According to Azizian (2004), the pseudo second-order sorption model works when initial liquid concentrations for solutes are not too high.

Solid-phase saturation concentration is often estimated by a solids–liquid partitioning coefficient, $K_d$ (Goldberg et al. 2005; Droste et al. 2010):

$$Q_e = K_d \cdot C_e$$

where $K_d$ is solids–liquid partitioning coefficient (L/kg) and $C_e$ is the liquid-phase concentration under equilibrium condition (μg/L).

The solids–liquid partitioning coefficient $K_d$ is either determined by experiment or estimated from $K_{ow}$ (Dobbs et al. 1989; Nakada et al. 2006; Droste et al. 2010; Stevens-Garmon et al. 2011). The following relations are used:

$$K_d = f_{oc} \cdot K_{oc}$$

$$\log K_{oc} = a \cdot \log K_{ow} + b$$

where $f_{oc}$ is fraction of organic carbon present on the solid (g/g); $K_{oc}$ is organic-carbon distribution coefficient (L/kg).

### METHODS

Sorption kinetics and isotherms with primary sludge were studied for the chosen MCs. Primary sludge was collected from the local municipal WWTP in Ottawa, ON, Canada. This WWTP provides secondary treatment to about 720,000 people; there is no heavy industry in the region.
Concentrated primary sludge was collected from the bottom of the primary clarifier and stored in four 1 L glass bottles. Sludge was filtered with a P8 filter (coarse porosity, particle retention: 20–25 μm, Fisher Scientific Co., USA). The solids retained were dried in a fume hood (face velocity of 80 fpm measured at 18 inches sash height) for at least 4 h before storage at room temperature. The dewatered primary sludge was stored at 4 °C in screw-capped glass bottles with head space filled with nitrogen gas. The water content of the dewatered sludge was 78% (w:w).

BPA, EE2 and TCS were purchased from Sigma-Aldrich Co., Canada. Their purities reported by the manufacturer were >98%. Acetonitrile (ACN)/water solution (45:55; v:v) was used as the solvent for the MC stock solutions. Stock solutions were made up to contain 1, 10 and 100 mg/L of MC and were stored in glass flasks and kept in a refrigerator.

**Kinetic experiment methodology**

The sorption kinetics experiment was conducted with a mixture containing 2.5 g dewatered primary sludge and 500 mL of Milli-Q® water in a 500 mL glass flask. According to Banihashemi & Droste (2014), the total loss of MCs due to sorption to walls of the glassware is less than 5%. To inhibit bioactivation, sodium azide at a dosage of 0.2% (w:v) was added to the mixture 24 h before the sorption kinetics tests were begun. The mixture was kept at room temperature (20–25 °C) on a rotary shaker at the speed of 200 rpm to prevent sludge from settling. Aluminum foil was wrapped around the flasks to prevent photodegradation.

Since the primary sludge was generated from a local WWTP, it was possibly contaminated with MCs. Background liquid-phase concentrations were measured by taking 50 mL samples after mixing the Milli-Q® water-sludge mixture for 24 h. MCs were spiked into the mixture at the concentration of 200 μg/L. Samples of 50 mL volume were taken from the mixture at 0.25, 1, 2, 3.5, 5, 7, 20 and 24 h after the MCs were spiked. During this process, the mixture was also kept in the shaker to prevent sludge from settling and to provide good mixing. The 50 mL samples were filtered using membrane filters (0.22 μm, Durapore, EMD Millipore Co., CA, USA) immediately after collection. The filtrates were collected and cleaned up by a solid-phase extraction (SPE) procedure. Triplicate samples were analyzed.

**Isotherm experiment methodology**

Four 100 mL sludge water mixtures, containing 1.25, 0.75, 0.5 and 0.1 g dewatered primary sludge, respectively, were used for the sorption isotherm experiments. Volatile suspended solids and total suspended solids concentrations were also measured for each mixture according to standard methods. Sodium azide at a dosage of 0.2% (w:v) was again used to inhibit biodegradation.

Since solid-phase concentration is necessary for determination of a sorption isotherm, the background solid-phase concentrations of MCs in dewatered primary sludge were tested by the microwave-assisted solid extraction procedure. Details for the microwave-assisted solids extraction procedure are presented in Banihashemi (2012).

MCs were spiked into the primary sludge mixture at the initial concentration of 200 μg/L. Constant mixing was provided by putting samples on a shaker (200 rpm). The solution was mixed for 24 h to allow sorption to reach equilibrium based on the results of sorption kinetics study. Only liquid-phase concentrations were measured. Solid-phase concentrations were then determined according to the following equation:

$$Q_e = Q_o + \frac{(C_o - C_e) \cdot V}{m} \tag{6}$$

where $Q_e$ is solid-phase concentration under equilibrium condition (μg/kg); $Q_o$ is initial solid-phase concentration (μg/kg); $C_e$ is liquid-phase concentration under equilibrium condition (μg/L); $C_o$ is initial liquid-phase concentration (μg/L); $V$ is volume of solution (L); $m$ is mass of solids (kg).

All liquid-phase concentrations were analyzed by using a high-performance liquid chromatograph coupled with an ultraviolet (HPLC-UV) detection system to measure the MC concentrations. The HPLC (Hewlett-Packard, HP 1100) was equipped with a ZORBAX Eclipse Plus C18 (4.6 × 150 mm, 5 μm) analytical column. ACN/water (45:55, v/v) as mobile phase was used as a binary gradient with a flow rate of 1 mL/min at room temperature and a pressure of about 65 bars (Banihashemi & Droste 2014). Since the liquid-phase concentrations of target compounds were at the μg/L level, it was necessary to concentrate the samples by using an SPE procedure before the samples went to the HPLC-UV system.

A detailed description of the SPE and HPLC-UV detection method for BPA, EE2 and TCS is presented in the study of Banihashemi (2012). The only difference in the method used for this study is that the samples were not adjusted to pH 2; instead, they were used at their pH, which was around 7 since a slightly higher recovery rate was found for TCS at pH of 7. A recovery efficiency test was run to verify the reliability of this method. One milliliter of
standard solution, which contained the selected MCs at 1 mg/L was injected into 100 mL of Milli-Q® water and mixed well. The samples \((n = 3)\) were then treated by the SPE procedure to concentrate them by 100 times. The concentrated samples were then analyzed with the HPLC-UV system. Results are shown in Table 2. The recovery efficiencies for the whole system for BPA, EE2 and TCS were 91.8%, 96.3% and 77.3%, respectively.

**RESULTS AND DISCUSSION**

Figure 1 shows the liquid-phase MC concentrations at different times after MCs were added. From Figure 1, it can be seen that the liquid-phase concentrations of the three chosen compounds dropped rapidly in the first 0.25 h; then the concentrations slowly dropped to 150, 120 and 20 \(\mu g/L\) for BPA, EE2 and TCS, respectively, and then fluctuated. The equilibrium time for each of the three MCs was around 7 h.

<table>
<thead>
<tr>
<th>Recoveries for the selected MCs</th>
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<tr>
<td>Peak area</td>
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<td>BPA</td>
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<tr>
<td>Standard solution</td>
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<td>Recovered sample 1</td>
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<td>Recovered sample 2</td>
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<td>Recovered sample 3</td>
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The equilibrium time found in this study is close to that found in other studies. A similar experiment was conducted by Banihashemi & Droste (2014). The same MCs were added to deactivated activated sludge (AS) generated at solids retention times of 5, 10 and 15 days. The sorption equilibrium times were found to be 2, 4 and 6 h for BPA, TCS and EE2, respectively. Another study conducted by Clara et al. (2004) performed sorption kinetics experiments between BPA, EE2 and deactivated AS. The equilibrium times for BPA and EE2 were found to be 2 h and 8–10 h, respectively.

The experimental data were further analyzed for sorption kinetics models. \(Q_t\), the solid-phase concentration at different times, was calculated according to Equation (6). \(Q_e\), the solid-phase concentration under equilibrium time, was the average solid-phase concentration after 7 h reaction (after 7 h, the liquid-phase concentrations of the three MCs exhibited little change, so the system was considered to have reached steady state).

For the pseudo first-order rate model, the term \(\ln\left(\frac{Q_e - Q_t}{Q_e}\right)\) was calculated and then plotted against time. Linear regression was applied to obtain the constant rate, \(k_1\). Figure 2 shows the linear regression results for the pseudo first-order rate model. Some points at certain times series were eliminated since \(\ln\left(\frac{Q_e - Q_t}{Q_e}\right)\) was mathematically impossible to calculate. This happens when \(Q_t\) is equals to or is larger than \(Q_e\).

For the pseudo second-order rate model, the term \(t/Q_t\) is plotted against time, which is shown in Figure 3.

As seen by comparing Figures 2 and 3, the pseudo second-order rate model describes experimental data much better than the pseudo first-order rate model. The rate constants, \(k_1\) and \(k_2\), are summarized in Table 3.
Results for the initial solid-phase concentrations in primary sludge show that among the three MCs, EE2 had the highest concentration of 113 ng/g, followed by BPA, 20 ng/g, and TCS, 5 ng/g. The initial solid-phase concentrations were taken into consideration when calculating the equilibrium solid-phase concentrations.

For sorption isotherms as shown in Figure 4, good fits were found between the linear model and experimental data for EE2 and TCS. The \( R^2 \) values for EE2 and TCS were 0.99 and 1, respectively. The linear solid–liquid partitioning coefficient \( (K_d) \) found for EE2 was 728 L/kg \( (\log K_d = 2.9) \), while for TCS it was almost 10 times higher, 6,407 L/kg \( (\log K_d = 5.8) \). The experimental data for BPA have a poorer fit, but still very good, for the linear sorption model, as indicated by \( R^2 \) value of 0.91. The \( K_d \) value for BPA was 81 L/kg \( (\log K_d = 1.9) \).

Studies focusing on MCs adsorbing onto primary sludge are rare. The \( \log K_d \) of EE2, reported in the literature, ranges from 2.1 to 2.9 (Ternes et al. 2004; Carballa et al. 2008). The \( \log K_d \) of EE2 found in this study is at the higher end of the range of reported data. No similar studies were found for BPA and TCS.

### CONCLUSIONS

Sorption kinetics and isotherm experiments were conducted for primary sludge using BPA, EE2 and TCS. The three chosen MCs are hydrophobic and have low vapor pressure, which makes sorption a potentially significant removal mechanism. The equilibrium time for chosen MCs sorbed onto primary sludge was 7 h. Most of the sorption happened within the first 0.25 h of reaction. The sorption equilibrium time found in the current study is close to the equilibrium time of other MCs sorbed to primary sludge and AS found by other studies.

Pseudo second-order kinetic models were suitable to describe sorption processes for all selected MCs. Judging from \( K_d \), TCS has the strongest tendency to sorb to primary sludge followed by EE2 and BPA. \( K_d \) found for BPA, EE2 and TCS sorbed onto primary sludge was 81 L/kg \( (\log K_d = 1.9) \), 728 L/kg \( (\log K_d = 2.9) \) and 6,407 L/kg \( (\log K_d = 3.8) \), respectively.

### REFERENCES


Banihashemi, B. 2012 General Fate Model for Microconstituents under Typical Sewage Treatment Conditions, PhD Research Proposal. Ottawa-Carleton Institute for Environmental Engineering, Ottawa, Canada.


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