Impact of natural organic matter properties on the kinetics of suspended ion exchange process

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ABSTRACT

Removal kinetics of four standard organic matter isolates under the application of strongly basic ion exchange resins (IEX) in suspended mode was studied under commercial application conditions. Suwannee River natural organic matter (SRNOM), SR fulvic acid (SRFA), and Pony Lake fulvic acid (PLFA) were greatly removed (>90%) and highly preferred by IEX resins ($\alpha > 5$, over Cl^-, and HCO_3^-) while SR humic acid (SRHA) was the least preferred organic structure among the four isolates studied ($\alpha \approx 1$). Moreover, the efficacy of removal for fulvic acids (i.e., SRFA, PLFA) was consistent over consecutive reuse of IEX resins (i.e., loading cycles) whereas it decreased for SRNOM and SRHA over the course of operation. The stoichiometric correlation between the chloride released from the resins as a result of organic molecules uptake indicated that ion exchange was the dominant mechanism. Results obtained indicated that molecular weight and charge density of isolates played a major role in the performance of ion exchange process for organic matter removal. Furthermore, various empirical and physical models were evaluated using the experimental data and pore diffusion was found to be the rate-liming step during the uptake of organic matters; hence, it was used as the appropriate model to predict the kinetics of removal. Consequently, free liquid diffusivities and effective pore diffusion coefficients of organic molecules were estimated and findings were in agreement with the literature data that were obtained from spectrophotometric methods.

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1. Introduction

Use of strongly basic ion exchange resins (IEX) is an effective tool for simultaneous removal of natural organic matter (NOM) and inorganic anions (e.g., nitrate, sulphate) that are widely present in surface waters (Fearing et al., 2004; Martijn et al., 2010). The dominant NOM removal mechanism for this process has been reported to be ion exchange with possible minor contribution from surface adsorption (Boyer and Singer, 2008a; Fu and Symons, 1990; Tan and Kilduff, 2007). Some kinetic studies on the sorption of organic molecules have concluded pore diffusion to be the rate-limiting step (Boyer et al., 2008a; Chen et al., 2002; Li and SenGupta, 2000; Weaver and Carta, 1996; Wu and Gschwend, 1986); however, film diffusion can become significant at low solute concentration i.e., high resin doses (Boyd et al., 1947; Reichenberg, 1953; Weaver and Carta, 1996; Weber Jr and DiGiano, 1996). Aside from resin properties that could impact the

efficacy of the removal process (Bazri and Mohseni, 2014; Bolto et al., 2002; Boyer and Singer, 2008a; Cornelissen et al., 2008), organic matter properties such as molecular weight (MW), polarity (i.e., hydrophobicity), and charge density could significantly influence the IEX-treated water quality. Studies focusing on the effect of NOM properties are however inconclusive and sometimes contradictory. For instance, Croué et al. (1999) observed an inverse correlation between hydrophobicity of NOM and removal performance while Mergen et al. (2008) and Boyer and Singer (2008b) reported the hydrophobic-transphilic fractions of NOM as the main targets by IEX. Furthermore, Fu and Symons (1990), Mergen et al. (2008), and Tan and Kilduff (2007) have pointed out the importance of MW while Boyer et al. (2008b) reported the charge density of the organic molecules to be the key factor in determining the removal efficiency.

Furthermore, IEX process has conventionally been operated in packed-bed columns which faces operational challenges such as clogging under high turbidity water and or biofilm formation potential inside the column (Flemming, 1987; Galjaard, 2010; Slunjski et al., 2000). These concerns have been addressed in the newly-

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developed stirred (a.k.a. suspended) IEX processes (e.g., MIEX®, SIX®) that also offer lower resin and salt consumption (Galjaard, 2010; Slunjski et al., 2000). Thus, there has been a growing investment on commercial application of suspended IEX process (Boyer and Singer, 2006; Cornelissen et al., 2009; Drikas et al., 2002; Galjaard, 2010; Gan et al., 2013; Martijn et al., 2010; Slunjski et al., 2000).

In this respect, the motive for this research was to answer key questions regarding the impact of natural organic matter properties, in particular molecular weight and charge density, on the kinetics and performance of the suspended IEX process for drinking water treatment applications. Suspended IEX process was chosen for conducting the experiments as a novel approach that has been gaining a growing attention and investment at commercial scale. Extensive kinetic experiments were carried out on four standard organic matter isolates with different MWs and charge densities (Table 1) and various mathematical/empirical and physical models were employed to investigate the underlying mechanism and rate-limiting step for NOM removal. By utilizing these models, effective pore diffusion coefficient ($D_{p,e}$), film diffusion coefficient (D_f), apparent diffusivity (D_a), and free liquid diffusivity (D_l), for each NOM isolate, were estimated and the rate-limiting step was investigated using the Biot number. The significance of this research is in understanding the major influencing NOM properties as well as underlying kinetics for the removal of different aquatic organic matters using suspended IEX process under commercial scale conditions. This can provide the basis for future studies concerning the application of suspended IEX for organic matter removal (as well as other anions e.g., nitrate, perchlorate) in drinking water applications.

2. Materials and methods

2.1. Source water and sample preparation

Each synthetic water was prepared by dissolving 20 mg of a standard IHSS isolate (International Humic Substances Society) in 1L of Milli-Q water (Table 1). The final pH was adjusted to neutral range (~7.5) by buffering with NaHCO₃ (40 mg/L), NaCl (1 mg/L), and adding NaOH (0.1 N).

2.2. Resins preparation

A strongly basic macroporous acrylic anion exchange resin (Purolite A860, manufacturer reported exchange capacity: 0.8 eq/L) was used because of the previous researches supporting its superior performance and regeneration efficiency (Bazri and Mohseni, 2014; Monosov et al., 2012). Resins received were initially regenerated using brine (10% wt.) and triple rinsed with Milli-Q water. Resins intended to use for isotherm experiments were stored in desiccator and dried for at least 24 h (hrs).

2.3. Kinetic data and isotherms

Using a Jar tester (Phipps & Bird 9900), a practical resin dose of 10 mL (Boyer and Singer, 2006; Galjaard, 2010; Mergen et al., 2008) was mixed with 1 L of water for various contact times from 5 min (min) to 24 h to establish the concentration profiles. For adsorption isotherms, 10–1000 mg of dried resins were carefully weighed and mixed with 1L of water to equilibrium (i.e., 24 h). Resins were filtered from the treated water using a pre-rinsed fast coarse filter (Whatman 113- 30 μm) and samples underwent subsequent water quality analyses.

2.4. Multiple loadings test

To simulate the performance of resins under commercial suspended operating conditions, consecutive batch treatments of raw water were carried out using 10 mL/L (corresponding to water/resin: 1000 mL/10 mL = 100 bed volumes, BV) of resins and 30 min contact time. These treatment condition were selected based on the previous evaluations by the authors as well as other researchers where a residence time of 10–30 min and resin dose of 5–20 mL/L have been reported for use in commercial scales (Bazri et al., 2016a, 2016b; Boyer and Singer, 2006; Drikas et al., 2011; Galjaard, 2010; Gan et al., 2013; Kitis et al., 2007; Mergen et al., 2008; Monosov et al., 2012; Walker and Boyer, 2011). At the end of each batch, resins were removed by a 30 μm pre-rinsed filter and then reloaded to another liter of raw water. Multiple loadings were continued for 6 cycles corresponding to 600 BV.

2.5. Analytical methods

Total and dissolved organic carbon (i.e., TOC and DOC), and dissolved inorganic carbon (DIC) measurements were performed in all stages (Shimadzu VCPH TOC analyzer). All spectrophotometric measurements (e.g., UV_{254}) were carried out using a UV–Vis spectrophotometer (Shimadzu UV mini 1240). Specific UV absorbance (SUVA, defined as UV_{254}/DOC) was also monitored in all the experiments. Chloride (Cl^-) was measured using Dionex 1100 ion chromatography unit equipped with electrical suppressor and Dionex AS22 Fast column, according to the methods of Environmental Protection Agency (EPA) 300.0 and Standard Method (SM) 4110B (Pfaff, 1993; Rice et al., 2012).

3. Results and discussion

3.1. Stoichiometry of NOM removal

Using the charge densities estimated for organic isolates at pH ~7.5 as elaborated in supplementary information (SI) (Driver and Perdue, 2014; Ritchie and Perdue, 2003), the net chloride released (meq/L) was plotted against the net TOC + DIC uptake

Table 1
Characteristics of synthetic waters.

[a]Water source	[b]Charge density (meq/g-C)	TOC (mg/L)	TOC (meq/L)	SUVA	Mw (Da)
Suwannee River NOM (SRNOM)	10.157	8.33	0.0846	4.41	[c]1030,[e]2190
Suwannee River Fulvic Acid (SRFA)	10.974	8.85	0.0971	5.23	[c]1070,[d]1910,[e]2310
Suwanee River Humic Acid (SRHA)	8.890	7.40	0.0658	7.92	[c]1520,[d]4390
Pony Lake Fulvic Acid (PLFA)	6.840	8.17	0.0559	3.20	[c]760

[a] All waters contained 40 mg/L NaHCO₃ and 1 mg/L NaCl.
[b] Estimated at pH = 7.5 using the equation provided by Ritchie and Perdue (2003), Driver and Perdue (2014), and IHSS website.
[c] Estimated Mw of humic substance using LC-OCD technique available from previous study (Bazri et al., 2016a). Data obtained are estimates only and were used for comparison only.
[d] Beckett et al., 1987.
[e] Chin et al., 1994.