



Influence of activated carbon preloading by EfOM fractions from treated wastewater on adsorption of pharmaceutically active compounds



Jingyi Hu^{*}, Ran Shang^{**}, Bas Heijman, Luuk Rietveld

Faculty of Civil Engineering and Geoscience, Delft University of Technology, P.O. Box 5048, 2600GA Delft, The Netherlands

HIGHLIGHTS

- Wide pore-size-distributed GAC is susceptible to EfOM preloading.
- Smaller-sized organic molecules in NF permeate directly compete with PhACs.
- Site competition is more prominent than pore blocking.
- Electrostatic interaction governs for PhAC adsorption on preloaded GACs.

ARTICLE INFO

Article history:

Received 17 November 2015

Received in revised form

25 January 2016

Accepted 29 January 2016

Available online 15 February 2016

Handling Editor: Keith Maruya

Keywords:

Effluent organic matter

Preloading

Granular activated carbon

Pharmaceutically active compounds

Site competition

ABSTRACT

In this study, the preloading effects of different fractions of wastewater effluent organic matter (EfOM) on the adsorption of trace-level pharmaceutically active compounds (PhACs) onto granular activated carbon (GAC) were investigated. A nanofiltration (NF) membrane was employed to separate the EfOM by size, and two GACs with distinct pore structures were chosen for comparison. The results showed that preloading with EfOM substantially decreased PhAC uptake of the GACs; however, comparable PhAC adsorption capacities were achieved on GACs preloaded by feed EfOM and the NF-permeating EfOM. This indicates that: (1) the NF-rejected, larger EfOM molecules with an expectation to block the PhAC adsorption pores exerted little impact on the adsorbability of PhACs; (2) the smaller EfOM molecules present in the NF permeate contributed mainly to the decrease in PhAC uptake, mostly due to site competition. Of the two examined GACs, the wide pore-size-distributed GAC was found to be more susceptible to EfOM preloading than the microporous GAC. Furthermore, among the fourteen investigated PhACs, the negatively charged hydrophilic PhACs were generally subjected to a greater EfOM preloading impact.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Pharmaceutically active compounds (PhACs) can enter the urban sewage system via various pathways, e.g. human excretion, improper discharge, or leaching from the urban area during rainfall (Margot et al., 2013). Some PhACs have been shown to persist through conventional wastewater treatment processes, rendering the wastewater treatment plant (WWTP) effluents main sources of PhAC inputs into the aquatic environment (Zhang and Zhou, 2008;

Yang et al., 2011). Nowadays, environmental quality standards have been increasingly raised because of the detection of PhACs and other trace organic contaminants in the freshwaters (C. Götz et al., 2010; R. Kase et al., 2011; EC, 2013). PhACs, such as diclofenac, are becoming a future consideration for modification of the existing European or national regulations (Mailler et al., 2015).

In this context, additional treatment of the WWTP effluents is required if these new regulatory limits come into force (Jekel et al., 2015). Several treatment approaches have been attempted to update the conventional WWTPs for an effective PhAC removal in both pilot- and large-scale investigations, e.g. activated carbon adsorption (Boehler et al., 2012; Margot et al., 2013; Mailler et al., 2015), advanced oxidation (Reungoat et al., 2012; Margot et al., 2013), and 'dense' membrane filtration (Christian Abegglen et al.,

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: j.hu-1@tudelft.nl (J. Hu), r.shang@tudelft.nl (R. Shang).

2009). Granular activated carbon (GAC) filtration has been recognized as a suitable advanced treatment technology for PhAC control (Grover et al., 2011; Corwin and Summers, 2012), due to the absence of harmful by-products as compared to ozonation, and no concentrated brine that needs to be disposed of as compared to nanofiltration (NF) and reverse osmosis. Additionally, GAC might be more sustainable than powdered activated carbon (PAC), given that GAC can be regenerated once adsorption saturation occurs.

A crucial factor impacting PhAC adsorption by GAC from a complex water matrix (e.g. the WWTP effluent) is the depletion of pollutant adsorption sites, due to competition with other co-present adsorbates via either site competition or pore blocking. In a fixed-bed GAC adsorber, the mass transfer zone of organic matter (as a background of the target PhACs) usually moves ahead of the mass transfer zone of a PhAC. As a consequence, the target compound has to adsorb on GAC granules that have already been loaded with organic matter (Li et al., 2003; Karanfil et al., 2006). This preloading effect greatly impairs GAC adsorption of the target PhACs. It has been acknowledged that organic matter is a heterogeneous mixture, which comprises organic components with varying adsorbability onto GAC (Velten et al., 2011; Gibert et al., 2013), and thus exhibiting varying competitiveness to the adsorption of the target PhACs. Investigation of the GAC-associated adsorption competition induced by different fractions of the wastewater effluent organic matter (EfOM) is then necessary, so as to understand the major adsorption competitors and to exploit the maximum GAC usage efficiency towards PhACs in an EfOM background.

In addition, the properties of GAC, especially the pore structure, is important for dictating the degree to which organic matter (e.g. EfOM) influences PhAC adsorption (Karanfil et al., 2006). GAC with micropores exclusively accessible for PhACs is postulated to have a good performance because a low amount of organic matter would enter the pores to compete, though it is prone to pore blocking. On the other hand, GAC with pores of a wide size range can adsorb both EfOM and PhACs, thus, less pore blocking would occur; whereas it is susceptible to site competition. As such, the dominant adsorption competition mechanism remains to be identified, for selecting an appropriate GAC type for PhAC removal from WWTP effluent under a preloading condition.

In this study, we examined the EfOM preloading effects on PhAC adsorption using two types of GAC with different pore structures. A NF membrane with a proper molecular weight cut-off was chosen to separate the EfOM by size, and the produced permeate was then in the same size range as most of the PhACs (e.g. between 100 and 1000 g/mol (Zietzschmann et al., 2014)). A collection of PhACs (at a $\mu\text{g/L}$ level) was investigated, which made it possible to determine the responses of different PhACs to the preloading effects. The primary objectives of this study were to: (1) examine the preloading effects of different EfOM size fractions on the adsorptive performance of GAC towards PhACs; (2) identify an appropriate type of GAC which is less prone to EfOM preloading.

2. Materials and methods

2.1. Materials

Fourteen PhACs (Sigma Aldrich, The Netherlands) were selected for this study to cover a diverse range of physicochemical properties (supporting information Table S1). To prevent a co-solvent effect and a possible biological growth in the subsequent experiments, tap water (City of Delft, The Netherlands), instead of methanol, was used to prepare the cocktail PhAC stock solution (2 mg/L per PhAC) (Verliefde et al., 2008). Two commercially available coal-based GACs were used as adsorbents: HD4000

(Hydrodarco 4000, Norit Inc., The Netherlands) and UC830 (Ultra-Carb 830, Siemens Inc., USA). In order to promote the adsorption process, both GACs were gently grinded and sieved to obtain a comparatively identical grain size of 0.3 mm.

The obtained GACs were thoroughly washed with demineralized water to discard impurities and the finer particles. A commercial spiral wound NF membrane (NP010, Microdyn Nadir GmbH, Germany) was employed as a means to separate the EfOM of the WWTP effluent by size. According to the manufacturer, the NF membrane has an Na_2SO_4 retention rate between 2 and 55% and an approximate molecular weight cut-off of 800 Da.

2.2. Water samples

The secondary effluent was collected from the secondary clarifier of a domestic WWTP (Leiden Noord, The Netherlands), which adopts a conventional mechanical/activated sludge treatment process. Upon the water sample's arrival in the lab, suspended solids (and bacteria) were removed by a 1 μm wound polypropylene filtering medium (Syntech Fibres Ltd, US). The filtered water was denoted as feed water (FW). A portion of the FW was further treated by the NF membrane operated as follows: 5 bar as the feed pressure, 0.012 m/s as the crossflow velocity and 6 L/(m² h) as the permeate flux; the recovery rate was maintained around 10%. The produced permeate (PW) was stored together with the FW at 4 °C, and were used within 48 h to avoid biological degradation. Demineralized water as a non-organic reference was obtained by passing the tap water through an ion exchange-reverse osmosis combined system. The dissolved organic carbon (DOC) concentration of this demineralized water was measured to be constantly lower than 0.1 mg/L. A phosphate buffer (0.2 M K_2HPO_4 and 0.2 M NaH_2PO_4) was added to the demineralized water to maintain a constant pH value (pH = 7.4) during the subsequent adsorption isotherm tests.

2.3. Activated carbon preloading and PhAC adsorption

In the preloading experiment, a relatively high organic matter concentration to activated carbon dose ratio (500 mg DOC/g GAC) was followed in accordance with a previous study (Karanfil et al., 2006). To allow for a theoretically identical preloading of organic carbon on the GAC granules while using different doses of these GAC granules per bottle for the PhAC isotherm tests, the following method was applied: the pre-calculated amounts (23 mL, 46 mL, 92 mL, 185 mL, 460 mL and 920 mL) of FW (with ~13 mg/L DOC concentration) were brought into contact with the fresh GACs with corresponding doses of 0.6 mg, 1.2 mg, 2.4 mg, 4.8 mg, 12 mg, and 24 mg in 6 × 2 L Duran glass bottles for a period of 7 d. For the PW (with ~8 mg/L DOC concentration), the pre-calculated amounts were 37 mL, 75 mL, 150 mL, 300 mL, 750 mL and 1500 mL, respectively.

An orbital incubator (Innova 44, Eppendorf, USA) was used to shake the bottles continuously in the dark at 22 °C and 150 rpm for 7 d. Thereafter, the supernatant was drained and the buffered demineralized water was introduced into each bottle; meanwhile, a predetermined amount of the cocktail PhAC stock solution was spiked to reach an initial concentration of 5 $\mu\text{g/L}$ per PhAC in a final working volume of 250 mL. The bottles were agitated again for an additional 7 d in the same conditions as before to determine the PhAC adsorption isotherms on the preloaded GACs. Additionally, EfOM (both in FW and PW) and PhAC adsorption isotherms of the fresh GACs were determined in the same conditions as that of the preloaded GACs. In each adsorption isotherm test, a blank with the same spiked PhAC concentrations while no GAC dosing was placed simultaneously, in order to check any loss of PhACs, and to serve as

Download English Version:

<https://daneshyari.com/en/article/6306754>

Download Persian Version:

<https://daneshyari.com/article/6306754>

[Daneshyari.com](https://daneshyari.com)