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Research article

Reuse of spent granular activated carbon for organic micro-pollutant removal from treated wastewater

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ABSTRACT

Spent granular activated carbons (sGACs) for drinking water treatments were reused via pulverizing as low-cost adsorbents for micro-pollutant adsorption from a secondary treated wastewater effluent. The changes of physicochemical characteristics of the spent carbons in relation to the fresh carbons were determined and were correlated to the molecular properties of the respective GAC influents (i.e. a surface water and a groundwater). Pore size distribution analysis showed that the carbon pore volume decreased over a wider size range due to preloading by surface water, which contains a broader molecular weight distribution of organic matter in contrast to the groundwater. However, there was still considerable capacity available on the pulverized sGACs for atrazine adsorption in demineralized water and secondary effluent, and this was particularly the case for the groundwater spent GAC. However, as compared to the fresh counterparts, the decreased surface area and the induced surface acidic groups on the pulverized sGACs contributed both to the lower uptake and the more impeded adsorption kinetic of atrazine in the demineralized water. Nonetheless, the pulverized sGACs, especially the one preloaded by surface water, was less susceptible to adsorption competition in the secondary effluent, due to its negatively charged surface which can repulse the accessibility of the co-present organic matter. This suggests the reusability of the drinking water spent GACs for micro-pollutant adsorption in the treated wastewater.

1. Introduction

The occurrence of emerging organic micro-pollutants in the aquatic environment has received widespread concerns and has undergone much research over the last few decades (Daughton and Ternes, 1999; Fatta-Kassinos et al., 2011; Heberer, 2002). Traditional wastewater treatment plants are typically not designed to remove micro-pollutants and, consequently, most of these contaminants are present in the treated wastewater and subsequently enter the receiving aquatic ecosystem (Fent et al., 2006). In practice, wastewater tertiary treatment includes a sand filter that aims at removing suspended solids, phosphate and ammonia; its efficiency for micro-pollutant removal may not be significant. To this end, the addition of powdered activated carbon (PAC) before the sand filter has been proposed as an approach to enhance micro-pollutant elimination (Boehler et al., 2012; Joss et al., 2008; Margot et al., 2013). However, PAC particles retained on top of the sand filter are being frequently flushed out by backwashing and discharged into the sewage system, much of which might not have reached the maximum adsorption capacity. This would be an economic issue since a large quantity of the commercially fresh PAC is required.

In this study, cheaper PACs were obtained by pulverizing the spent granular activated carbons (sGACs) from drinking water companies. These PACs could potentially be recycled as replacements of the fresh PACs for the aforementioned purpose. The hypotheses lie in:

(1) The decreased ability of sGACs to remove organic pollutants (e.g. the dissolved organic carbon, DOC), is not indicative of their capacity to remove the micro-pollutants with comparatively lower concentrations and smaller molecules (Drikas et al., 2009). Therefore, sGACs can continue to be used rather than regenerated;
(2) The reduction of the carbon particle size might help to open up pores to create adsorption sites, for instance, the sGAC pores previously occupied by the influent natural organic matter (NOM) might be recovered as a consequence of mechanical pulverizing;

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(3) Wastewater effluent typically contains higher concentrations of micro-pollutants than drinking water does (i.e. the influent of the GAC filter). According to the classical Freundlich adsorption equation, a higher background adsorbate concentration would induce a higher adsorbate loading on the same PAC. This "double-stage" PAC usage strategy was demonstrated as capable of effectively exploiting PAC sorption capacity (Boehler et al., 2012).

In drinking water facilities, a GAC filter is continuously loaded by the influent NOM, causing "site competition" or "pore blockage" for the successive uptake of the target micro-pollutants. These two mechanisms cannot be distinguished easily. Normally, at the lower NOM loading in a GAC filter's initial operation, site competition is more obvious and contributes mainly to the adsorption reduction of the micro-pollutants. After a long run, pore blocking predominates and leads to both reduced adsorption capacity and kinetics (Yu et al., 2009). Concerning the pore blocking phenomena, the extent can be attributed to the physicochemical properties of the GAC applied (Newcombe et al., 1997, 2002), and the molecular composition (e.g. the molecular weight distribution, MWD) of the influent NOM (Karanfil et al., 2006; Li et al., 2003b; Yuasa et al., 1997). By virtue of the size exclusion chromatography technique, NOM can be fractionated into biopolymers, humic substances (HS), building blocks (BB) and the low molecular weight (LMW) based on their molecular weight (Huber et al., 2011a, 2011b). With respect to their adsorbability on activated carbon, biopolymers tend to be refractory due to their relatively large size; for the other NOM fractions, the adsorbability generally increases with a decrease in molecular size (Velten et al., 2011).

In view of the adsorption competition, the low molecular weight NOM with strong adsorption potential is able to migrate into the inner micropores, thus reducing the uptake of target micro-pollutants considerably (Wigton and Kilduff, 2004). By contrast, the larger molecular weight NOM which is unlikely to access the same pore region as the target micro-pollutants is capable of constricting the pore entrance, thereby reducing their adsorption kinetics (Li et al., 2003a, 2003b). However, most of these observations were derived from the batch-scale experiments under conditions not representative of the full-scale GAC filters. By monitoring the variation of GAC porosity over one year's operation, it was concluded that the intermediate HS and the GAC super-microporosity (0.7–2 nm) appear to be the best removed fraction and the most occupied pore range (Gibert et al., 2013), respectively.

In addition to the pore occupation effect, NOM adsorbed on the activated carbon serves to alter the carbon surface chemical characteristics as well. Due to the presence of acidic (e.g. carboxyl, phenolic) functional groups in the NOM moieties, the adsorbed NOM inevitably imparted a net negative charge to the carbon surface at ambient pH conditions (Morris and Newcombe, 1993). An increase in the carbon surface acidity was reported to reduce adsorption of both NOM and the hydrophobic organic contaminant (Karanfil and Kilduff, 1999; Karanfil et al., 1999). Additionally, preloading with the more hydrophobic NOM was found to result in a stronger adsorption reduction of the investigated pharmaceuticals, due to a higher competition on the altered carbon surface (De Ridder et al., 2012).

The above shows that both pore occupation and surface chemistry changed by NOM preloading can affect the adsorption of micro-pollutants. The goal of this study is to understand these physicochemical changes on sGACs saturated with different influent NOM (i.e. surface water and groundwater), and to determine the remaining adsorption capacity of the spent GACs via mechanical pulverizing. Meanwhile, atrazine has been selected as a micro-pollutant to study how the altered carbon characteristics influence its adsorption, and if the drinking water spent GACs can be reused for micro-pollutant removal from the treated wastewater.

2. Materials and methods

2.1. Activated carbons

Two field-spent GACs were obtained from the drinking water companies Waternet and Oasen in the Netherlands. Waternet treats surface water by coagulation, rapid sand filtration and ozonation before the GAC filter; while Oasen extracts groundwater to feed the GAC filter having a different carbon origin. The sGACs were sampled after a full period of filtration (around 1 year) and just before their thermal regenerations. To ensure that the sGACs were completely saturated, they were collected from the top layer of the filters. In addition, the regenerated GACs were also collected to serve as the fresh references. Upon arrival in the lab, the GACs samples were thoroughly washed with demineralized water to remove the impurities. Afterwards, the GACs were pulverized in wet form with a disk mill (HSM100, Herzog, Germany) to obtain PAC slurry. Freeze-drying was performed to dry the wet GACs and PAC slurry in order to minimize destruction of the preloaded organic substances. The final carbon samples were stored in the desiccator until use. sGACs loaded by surface water and groundwater were denoted as sGAC-SW and sGAC-GW, respectively, and their pulverized forms were denoted as sPAC-SW and sPAC-GW respectively. In the same manner, the regenerated fresh carbons were named as fGAC-SW, fGAC-GW or fPAC-SW, fPAC-GW. Nominal particle size of the GACs ranged from 0.4 mm to 0.5 mm in width according to the wet sieving results. The obtained PAC particles were shown to be below 10 μm by particle counter analysis (Model 3000, Pacific Scientific Instruments, the Netherlands).

2.2. Water types

Influents of the two GAC filters were sampled during carbon collection. After being treated by 0.45 μm glass fiber syringe filters (Whatman, UK), the two influents were analyzed by liquid chromatography coupled with organic carbon detection (LC-OCD) in the WDRC lab (KAUST, Thuwal, Saudi Arabia) to determine the NOM molecular weight distribution. The secondary-treated wastewater effluent was obtained from the Leiden Noord municipal wastewater treatment plant (Leiden, the Netherlands); 1 μm wound polypropylene filter medium (Syntech Fibres Ltd, US) was used to remove the visible suspended solids and bacteria in the wastewater effluent before being stored in the refrigerator at 4 °C.

2.3. Target micro-pollutant

Atrazine was purchased as analytical standard from the Sigma–Aldrich Company (the Netherlands). A stock solution (2 mg/L) was prepared by mixing atrazine powder in demineralized water for at least three days to ensure complete dissolving. An enzyme-linked immunoassay kit (Abraxis LLC, Warminster PA, the USA) was used to quantify the concentration of atrazine. A calibration curve was established for each measurement using the standards provided by the manufacturer, and samples were measured carefully in triplicate under constant temperature without sunlight. A microplate reader (TECAN Infinite M200, Switzerland) was employed to record the final absorbance data under a 450 nm UV wavelength. Sample concentrations were determined by interpolating the detected absorbance data against the calibration curve