Journal of Environmental Management 211 (2018) 278–286

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Elimination of micropollutants by activated carbon produced from fibers taken from wastewater screenings using hydrothermal carbonization

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ARTICLE INFO

Article history:
Received 12 October 2017
Received in revised form
18 January 2018
Accepted 23 January 2018

Keywords:
HTC
Activated carbon
Waste water treatment
Sieving
Emerging substance
Chemical activation

ABSTRACT

Activated Carbon (AC) can be used to reduce organic micropollutants (OMPs) in wastewater treatment plants (WWTPs). While producing ACs conventionally still damages the environment, this can be reduced by using renewable raw material from waste streams und producing AC locally. In this study, fibers (toilet paper) were separated out of wastewater by screening WWTP influents in full scale and then used as a no-cost, carbon-rich and heavy metal-poor raw material to produce ACs. Pretreatment was hydrothermal carbonization (HTC). Thereafter, they were activated using KOH to generate activated carbons (HTC-ACs). Their functional groups were characterized using FT-IR, and the alteration of their chemical composition was traced by elementary analysis. Adsorption tests were performed with nitrogen (BET surface) and methylene blue as standard tests. The adsorption capacity was tested with WWTP effluent and the removal of UVA_{254} as a surrogate for OMP removal was measured. After HTC and activation 13–16% of the fibers dry mass was obtained as HTC-ACs. Higher dehydration and formation of aromatic structures on the HTC-ACs were detected with FT-IR as HTC and activation temperature increased. BET surface and methylene blue adsorption of some HTC-ACs was higher than the Reference AC. Nevertheless, their ability to reduce OMPs is still lower than the Reference AC due to the different nature of their functional groups and their microporous structure that is not fully accessible for OMPs in real wastewater. Further research has to be carried out to adjust the production process so as to obtain mesoporous HTC-ACs tailored to reduce OMP concentrations and to close the carbon loop within WWTPs.

1. Introduction

Organic micropollutants (OMPs), such as pharmaceuticals and substances from personal care products, can be found nearly everywhere in the water cycle, and some of them harm aquatic life (Petrie et al., 2015). One major source of OMPs are effluents from municipal wastewater treatment plants (WWTP) since many OMPs are poorly biodegradable (World Health Organization, 2012). In order to eliminate them from this effluent, WWTPs can be upgraded using adsorption on activated carbon (AC) as an additional treatment step.

AC is commonly found in two different forms: powdered activated carbon (PAC) and granular activated carbon (GAC). PAC is dosed in the water to be treated and has to be separated together with the activated sludge in a separation step, whereas GAC is used as stationary filter bed (Sontheimer, 1988; Benstoem et al., 2017). PAC can be fed directly in the conventional activated sludge system (CAS) to allow good encapsulation in the activated sludge; it can be dosed upstream of a deep-bed filter in the effluent of a WWTP, or an additional adsorption step is employed (BAFU, 2012; Hu et al., 2016).

Measuring the elimination of OMPs in WWTP effluents is labor-intensive, needs costly equipment such as high resolution LC-MSs and is, therefore, expensive. As a spectroscopic method, UVA_{254} has proven to be an easy-to-apply surrogate to trace the elimination of OMPs by adsorption on activated carbon (Zietzschmann

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https://doi.org/10.1016/j.jenvman.2018.01.065

et al., 2014; Anumol et al., 2015). The dissolved organic carbon content (DOC), in contrast, does not show such high correlations for the elimination of OMPs (Anumol et al., 2015).

PAC is usually derived from natural raw materials, such as coconut shells, wood, peat and bituminous coal, which are initially carbonized, then activated. The carbonization step takes place in a dry, oxygen-free atmosphere at 800–1.000 °C and enriches the carbon content by casting out volatile substances (Kienle and Bäder, 1981). This step is usually done in pits, which release these volatile, energy-rich greenhouse gases, such as carbon monoxide or methane, in the environment without using them. When the coke is heated in rotary kilns at 800–1.000 °C and water vapor used as an oxidizing agent, the process activates the coke because pores form. The exothermic carbonization releases high amounts of greenhouse gases to the atmosphere, whereas the activation is energy intensive (Mousel et al., 2017). Carbonization and activation have recently been employed in low-income Asian countries, where environmental standards for the production of commercial AC are low. Furthermore, raw materials – often exhaustible peat and coal – are also used in other industrial processes, thus leading to greater demand and, thus, higher prices.

There is, however, a new approach for obtaining this raw material: from screenings taken from WWTPs. By sieving wastewater, operators can retain a carbon rich material that mainly consists of fibers, which are very common in municipal wastewater from countries whose inhabitants use toilet paper. They are available with a high reliability, and their amount is high because these countries consume 12–25 kg toilet paper per capita and year (Berardi 2006). Nowadays, fibers are transferred into the sludge and have to be disposed of, thus leading to higher costs. Using these fibers as a free raw material for the production of PAC will not only reduce CO_2 emissions, i.e. when compared to raw material based on fossil resources (peat and coal), but will also lower waste reduction and transportation costs compared to AC from Asia. Moreover, WWTP screenings exceed the content of organics in comparison to primary WWTP sludge, which predestinates them for the production of AC. Another advantageous characteristic is its low heavy metal content in comparison to WWTP sludge (Ruiken et al., 2013).

A common pyrolysis technique to produce activated carbon needs a dry precursor and leads to porous materials with low amounts of surface functional groups. Hydrothermal carbonization (HTC) starts with wet material, utilizing its water content, and leads to coal-like material (hydrochar) with a high amount of surface-bound functional groups. In particular, the oxygen-containing groups, such as carboxylic, hydroxylic, phenolic and carbonylic groups, lead to hydrophilic properties of hydrochar and promote the often reported high adsorption capacity for heavy metals along with a certain hydrophilicity (Hu et al., 2010; Regmi et al., 2012). Surface functionalities also influence adsorption capacity of certain organic pollutants (Fernandez et al., 2015). Hydrochars possess these functionalities due to their formation mechanisms and are, therefore, ideally suited for the subsequent production of activated carbon.

HTC is a chemical process that can convert wet biomass to lignite-like or subbituminous char, termed hydrochar. The conversion takes places under an oxygen-free atmosphere with temperatures between 180 and 270 °C and elevated pressures (10–55 bar) in environmentally friendly reaction-medium water. Imitating natural coal formation, HTC reduces the reaction cascade of biomass degradation from millennia to several hours (Funke and Ziegler, 2010). Hot compressed water changes its properties, such as its ionic product, leading to the promotion of acid- and base-catalysed reactions at the same time. These changes generate to higher reaction rates, making water into reaction medium, reaction partner and catalyst in one (Kruse and Dinjus, 2007).

In case of carbohydrates, HTC starts with hydrolysis and fragmentation (decarboxylation, dehydration) of the compounds followed by polymerization and condensation reactions to form colloidal coal particles (Kruse et al., 2013). HTC is known to promote improved compressibility in the final product and, therefore, dewaterability of sewage sludge, the latter being a crucial factor for energy efficiency. For these reasons, HTC is a promising and emerging technology in sewage treatment. Recently, adsorbents derived from sewage sludge, especially from hydrochar, were found to have certain advantages in the production of activated carbon, thus providing water treatment plants with the opportunity to produce their own adsorbents from self-generated waste (Hadi et al., 2015; Jain et al., 2016).

The conversion of hydrochar into activated carbon can be done by physical activation with air, CO_2 or water steam (Román et al., 2013), which leads to adsorbents with low BET surface area (approx. 500 m^2g^{-1}) and high amounts of functional surface groups (either acidic or basic groups as air or CO_2 is used). Furthermore chemical activation by means of alkali salts like KOH (Regmi et al., 2012; Falco et al., 2013; Islam et al., 2015) leads to highly microporous materials with very high BET surface areas ($\gg$ 1000 m^2g^{-1}). Regarding the removal of OMPs from water by modified hydrochars, Liu et al. (2016) had promising results using the physical activation of corncob hydrochar in an N_2-atmosphere. They tested the resulting performance of the adsorbents by measuring the removal of phenol and p-nitrophenol. A direct correlation between low degrees of carbonization in the precursor hydrochar and a better performance of the corresponding AC could be seen. Since high nitrogen content in ACs – present as basic functional groups – are favorable for OMP adsorption, efforts for enhancing nitrogen content in HTC-ACs have been made (Laginhas et al., 2016), especially in combination with supermicro- and mesopores present in the produced adsorbent (Dastgheib et al., 2004). As a precursor for activation, sewage sludge-based hydrochars are beneficial in this term because they have a high nitrogen content (Kirschhöfer et al., 2016; Liu et al., 2016). However the high anorganic content (e. g. sand/silt/clay) that cannot be activated and high concentrations of heavy metals present in sewage sludge limit its application as a precursor for activated carbons.

In this study hydrochars were produced from fibers taken from WTTP screenings. These hydrochars were chemically activated using KOH to produce activated carbons (HTC-ACs). These HTC-ACs were characterized using FT-IR to determine the functional groups present on their surface and elementary analysis was used to trace the alteration of its chemical composition from the raw material to the ready-to-use HTC-AC. Adsorption tests were performed with the HTC-ACs using nitrogen (BET surface) and methylene blue as standard tests; their performance was compared to a commercially available AC used in wastewater treatment. Finally, the adsorption capacity of the HTC-ACs was tested with WWTP effluent, and the removal of UVA_{254} as a proven surrogate for OMP removal was measured.

2. Material and methods

2.1. Recovery and analysis of WWTP screenings

A full scale sieve of Huber SE, Berching (Germany) with a mesh size of 0.3 mm was tested at a German municipal WWTP (50,000 population equivalents). Before entering the sieve drum, municipal wastewater passed a 6 mm rack and a sand trap. Wastewater was pumped from the effluent of the sand trap into the inlet chamber of the sieve at a flow rate of 30 L s^{-1}. It passed the sieve drum that was covered with a waved metal fabric in an inside-out mode, whereby most particles were retained. Afterwards the sieved water entered