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Performance of biological magnetic powdered activated carbon for drinking water purification

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ABSTRACT

Combining the high adsorption capacity of powdered activated carbon (PAC) with magnetic properties of iron oxide nanoparticles (NPs) leads to a promising composite material, magnetic PAC or MPAC, which can be separated from water using magnetic separators. We propose MPAC as an alternative adsorbent in the biological hybrid membrane process and demonstrate that PAC covered with magnetic NPs is suitable as growth support for heterotrophic and nitrifying bacteria. MPAC with mass fractions of 0; 23; 38 and 54% maghemite was colonized in small bioreactors for over 90 days. Although the bacterial community composition (16s rRNA analysis) was different on MPAC compared to PAC, NPs neither inhibited dissolved organic carbon and ammonia biological removals nor contributed to significant adsorption of these compounds. The same amount of active heterotrophic biomass (48 μg C/cm^3) developed on MPAC with a mass fraction of 54% NPs as on the non-magnetic PAC control. While X-ray diffraction confirmed that size and type of iron oxides did not change over the study period, a loss in magnetization between 10% and 34% was recorded.

1. Introduction

Magnetic powdered activated carbons (MPAC) are composite materials made of a non-magnetic structure such as powdered activated carbon (PAC) and magnetic labels such as nano-scale iron oxides (mainly maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4)) which are responsible for the magnetic behaviour of the composite (Oliveira et al., 2002). These novel adsorbents have gained attention in the drinking water community due to their good magnetic separability on the one hand as well as their promising adsorption properties for drinking water contaminants on the other hand. So far, these composite materials have been applied in pure adsorption studies at lab-scale, e.g. as adsorbent for natural organic matter (Kondo et al., 2010; Park et al., 2015) or against contaminants of emerging interest such as herbicides (Castro et al., 2009), insecticides (Zahoor and Mahramonlioglu, 2011) and pharmaceuticals (Shi et al., 2013).

Recently, Zahoor (2014) proposed MPAC as an alternative to the use of PAC in the hybrid membrane process (HMP) which combines a high concentration PAC contactor (1–40 g/L) with low pressure membranes. In these processes PAC removes adsorbable dissolved contaminants such as taste and odour compounds or organic micropollutants, whereas the membrane removes particulate contaminants such as *Cryptosporidium* or other protozoan pathogens (Lebeau et al., 1998; Stoquart et al., 2012). When HMPs operate with PAC age > 20–30 days, heterotrophic and nitrifying bacteria colonize the PAC particles, allowing for removal of not only adsorbable, but also biodegradable dissolved contaminants such as biodegradable dissolved organic carbon (BDOC) and ammonia (Leveillé et al., 2013; Markarian et al., 2010; Stoquart et al., 2014a,b). Although HMPs with PAC age < 7 days exist in full scale processes, such as the CRYSTAL® and Opaline™ S, abrasion and severe membrane fouling resulting from the direct contact of the immersed membranes with highly concentrated and colonized PAC have limited so far the industrial application of biologically working HMPs (Leveillé et al., 2013; Stoquart et al., 2012). Alternatively, Zahoor (2014) tested an adsorption/ultrafiltration hybrid process at

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Abbreviations: PAC, Powdered activated carbon; NPs, Nanoparticles; MPAC, Magnetic powdered activated carbon; HMP, Hybrid membrane process; XRD, X-ray diffraction; HRT, Hydraulic retention time; CUR, Carbon usage rate; PGR, Potential glucose respiration rate; OTU, Operational taxonomic unit; DOC, Dissolved organic carbon; BDOC, Biodegradable dissolved organic carbon.

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lab-scale where problems related to cake formation and membrane fouling where avoided using magnetic separation to provide a low particle membrane feed. Other advantages of MPAC over PAC arise from their ease of separation. For one, it is possible to recirculate the adsorbent back into the contactor in order to maintain a high adsorbent age which translates into more efficient carbon usage (i.e. higher exhaustion) before disposal. Finally, high MPAC age offers the opportunity to operate HMPs in biological mode.

However, applying MPAC in the HMP in mixed adsorption/biodegradation raises the question if nano-size iron oxides on the surface of PAC are deleterious to biological activity. To the best of our knowledge, such evaluation has not yet been carried on and little is known about the effects of iron oxide nanoparticles (NPs) on heterotrophic and nitrifying microorganisms. In contrast to larger particles, iron oxide NPs below a critical size of 30 nm (Auffan et al., 2009) are highly reactive at their surface and have been shown to interact with the membrane of bacterial cells (Auffan et al., 2008; Luyts et al., 2013). When *Escherichia coli* bacteria were incubated with 100 mg/L of magnetite and maghemite NPs, the latter were observed to attach to the cell membranes (Auffan et al., 2008) and cell damage resulting from oxidative stress was identified as a possible mechanism of toxicity (Auffan et al., 2009). Oxidative stress can result from the disturbance of the cell's electron or ionic transport chains by reactive oxygen species (ROS) that form via redox transformations and dissolution of the atoms at the surface of the NPs (Auffan et al., 2008, 2010). Low to moderate cytotoxicity was observed towards pure culture of planktonic bacteria such as *E. coli* (Auffan et al., 2008; Hu et al., 2009) and *Pseudomonas aeruginosa* (Kafayati et al., 2013) at concentrations exceeding 500–700 mg/L Fe_3O_4 or Fe_2O_3 NPs. Arakha et al. (2015) observed antimicrobial effects of magnetite NPs towards *E. coli* and *Bacillus subtilis* even at 50 μM (11.6 mg/L). Microcosm tests on soil bacterial communities carried out by He et al. (2011) and Vittori Antisari et al. (2013) with 0.14–1260 mg/kg Fe_3O_4 NPs (10–50 nm) showed no or low inhibitory effects, a result which may be explained by the formation of extracellular polymeric substance (EPS) and other protection strategies of sessile bacteria. Although the literature indicates lower cytotoxicity of magnetic NPs compared to other metal NPs such as elemental Ag, Zn and Cu or metal oxide such as TiO_2, ZnO, CuO or NiO (Dinesh et al., 2012; Wang et al., 2010), additional studies are necessary to determine the applicability of MPAC in biological reactors for drinking water treatment.

Another aspect to consider is the long term stability of magnetic adsorbents which is crucial for industrial applications where changes in magnetization or dissolution of iron oxide NPs are not desired. Auffan et al. (2008) found that magnetite NPs were subjected to structural modifications especially in the presence of bacteria. The surface of magnetite NPs was entirely oxidized to a more stable iron species resembling maghemite. According to Mohan et al. (2011) magnetite NPs are generally not very stable at ambient conditions and can easily be oxidized to maghemite. This phenomenon is related to the high mobility of electrons within the Fe(II)/Fe(III) structure of magnetite and the release of Fe(II) ions into solution (Auffan et al., 2008). As maghemite is a ferrimagnet with similar magnetic properties as magnetite (Cornell and Schwertmann, 2003), oxidation should not lead to a loss of magnetization and is therefore no constraint for MPAC applications. While Lee et al. (2005) reported a decrease of nearly 50% in saturation magnetization of their magnetic adsorbent after 5 months, Safarik et al. (2013) observed a stable magnetic response of different magnetic adsorbents containing magnetite after several months. Yang et al. (2008) also confirmed magnetic stability of a rice husk based magnetic carbon that was stirred in water for 2 months. Dissolution of iron oxide NPs is pH dependent and was studied by Zahoor and Mahramonlioglu (2011) in a range of pH 1 to 8. Dissolution occurred below pH 4.8 leading to a loss of iron content in MPAC. With typical pH values between 6 and 8 in drinking water treatment processes, dissolution of magnetic NPs is therefore not expected.

While previous studies on MPACs focussed solely on the adsorption properties of MPACs, this study was designed to evaluate its performances both as an adsorbent and as a support for biological growth for its application within the HMP. The research question of this study can be stated as follows: Do iron oxide NPs on the PAC surface prevent biological growth or inhibit activity of heterotrophic and nitrifying bacteria?

Five small bioreactors containing MPACs with increasing iron oxide mass fractions (0%, 23%, 38% and 54%) were fed for 90 days with nutrient enriched, de-chlorinated tap water. Dissolved organic carbon (DOC) and ammonia removals were monitored weekly whereas active heterotrophic biomass and the composition of the bacterial population were only measured at the end of the study. The originality of this project lies in (i) the application of a magnetic adsorbent in a mixed adsorption/biological drinking water treatment process, (ii) the systematic evaluation of the impact of iron oxide NPs content on biomass development and (iii) the evaluation of the potential degradation of the magnetic adsorbent in a biological process.

2. Materials and methods

2.1. Magnetic powdered activated carbon

Commercially available Aquasorb® MP23 (Jacobi, formerly Picahydro MP23 from PICA™) was used in the colonization assay and as a base material for MPAC preparation. This mineral based PAC with an iodine number of 900 mg/g and a median volume diameter of 15–35 μm was washed and dried before usage to reduce its basicity below pH 8.0. This carbon has been chosen among others in adsorption pre-tests for its good DOC removal from the water matrix used during this study (data not shown).

MPAC was prepared by an alkaline co-precipitation process as proposed by Oliveira et al. (2002) and then characterized for its physico-chemical properties (Table 1). Three different MPACs with mass fractions of 23%, 38% and 54% iron oxide NPs were prepared (hereafter referred to as MPAC-23%, MPAC-38% and MPAC-54%). The NPs on the PAC surface mainly consisted of maghemite and had an average particle size of 17 nm, as determined by x-ray diffraction (XRD) analysis, using the Scherrer formula for the average crystallite diameter. According to the NP mass fraction, the apparent density of the magnetic adsorbents varied between 0.40 g/cm^3 and 0.79 g/cm^3.

2.2. Colonization study

Five PAC/MPAC bioreactors with a volume of 1 L each were equipped with blade stirrers (120 rpm) to prevent settling of the adsorbents. For the current study, magnetic separation of the MPAC was not performed. Instead, the adsorbents were kept in the reactor using a 10 μm nylon mesh strainer located on the effluent (at the top of the reactors, see Fig. 1). Increasing pressure of the reactors due to blockage of the strainer required regular opening of the reactors and manual cleaning every 2 days. The reactors were fed continuously at a flow rate of 1 L/h (HRT = 1 h) for 43 days which was subsequently decreased to 0.25 L/h (HRT = 5 h) for a period of 35 days once the pilot operated in biological mode in order to reduce maintenance time. Two weeks before the end of the study, the flow rate was again increased to 0.5 L/h (HRT = 2 h).