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Removal of aqueous nC_{60} fullerene from water by low pressure membrane filtration

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ABSTRACT

The potential environmental and health risks of engineered nanoparticles such as buckminsterfullerene C_{60} in water require their removal during the production of drinking water. We present a study focusing on (i) the removal mechanism and (ii) the elucidation of the role of the membrane pore size during removal of nC_{60} fullerene nanoparticle suspensions in dead-end microfiltration and ultrafiltration mimicking separation in real industrial water treatment plants. Membranes were selected with pore sizes ranging from 18 nm to 500 nm to determine the significance of the nC_{60} to membrane pore size ratio and the adsorption affinity between nC_{60} and membrane material during filtration. Experiments were carried out with a dead-end bench-scale system operated at constant flux conditions including a hydraulic backwash cleaning procedure. nC_{60} nanoparticles can be efficiently removed by low pressure membrane technology with smaller and, unexpectedly, also by mostly similar or larger pores than the particle size, although the nC_{60} filtration behaviour appeared to be different. The nC_{60} size to membrane pore size ratio and the ratio of the cake-layer deposition resistance to the clean membrane resistance, both play an important role on the nC_{60} filtration behaviour and on the efficiency of the backwash procedure recovering the initial membrane filtration conditions. These results become specifically significant in the context of drinking water production, for which they provide relevant information for an accurate selection between membrane processes and operational parameters for the removal of nC_{60} in the drinking water treatment.

1. Introduction

The increasing use of engineered nanoparticles (eNPs) in consumer products like food, paints, coatings, cosmetics, personal care products, etc. (Benn et al., 2011; Murayama et al., 2004; Osawa, 2002) will lead to direct and indirect release of eNPs to the environment and to sources for drinking water. Specifically Buckminsterfullerene (C_{60}) (Kroto et al., 1985) has received a considerable amount of attention due to its particular chemical physical properties (Guldi and Prato, 2000) i.e. high hydrophobicity, heat resistance and superconductivity, which explains its wide spread use in different applications (Baena et al., 2002; Osawa, 2002). Although non derivatized C_{60} nanoparticles have a very low solubility in water (Heymann, 1996) and are highly hydrophobic ($K_{ow} = 6.67$ (Jafvert and Kulkarni, 2008)) C_{60} nanoparticles can form nano-sized colloidal aggregates in water (usually and here as well referred to as nC_{60}) (Deguchi et al., 2001) and could therefore end up in aquatic environments when released to the environment. Several studies reported C_{60} toxicity to various organisms (Chae et al., 2009; Lyon et al., 2006; Sayes et al., 2005; Song et al., 2012). These results are still under debate because it is not completely clear if the toxicity reported is related to the C_{60} itself or that the preparation method of nC_{60} colloidal suspensions as well influences the toxicological results (Zhu et al., 2006). However, due to this possible toxicological nature, the removal of nC_{60} from water becomes mandatory to ensure the production of safe drinking water and to minimize human exposure to eNPs via ingestion. Moreover, eNPs can serve as pollutant carriers (Hofmann and von der Kammer, 2009; Navarro et al., 2008; Stone et al., 2010) potentially resulting into inadequacy of existing treatment processes. This uncertainties on nC_{60} toxicity and the nC_{60} potentiality as pathogens carrier result in a mandatory removal of nC_{60} in water treatment plants. Low pressure membranes are a viable solution in removing contaminants that are similar in size to nNPs such as viruses, protozoa cysts

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(H. Guo et al., 2010a,b) and colloids (Schafer, 2000). Thus it is expected that eNPs can be effectively removed by low pressure membrane filtration as well. However so far, detailed studies on the effectiveness of the filtration for eNPs, their filtration behaviour and their exact removal mechanism are lacking.

Some studies focused on a single specific aspect related to interactions between eNPs and low pressure membranes have been carried out in different fields of membrane research, such as eNP characterization (Baalousha et al., 2011), eNP size separation (Akamatsu et al., 2010; Xie et al., 2009) and membrane integrity tests (H. Guo et al., 2010a,b), but to the best of our knowledge only very few studies dealt with the understanding of the removal mechanism of eNPs by membrane filtration techniques. Destabilized fullerene suspensions (nC_{60} and fullerol) were filtered through 20 nm ceramic membranes under variable ionic strength, ionic composition and pressure gradients (Jassby et al., 2010). The removal efficiency was below 80% at a transmembrane pressure of 20 kPa. The separation of fullerenes from the aqueous suspension increased, or decreased, depending on the solution pH and ionic strength, while transmembrane pressure only affected the retention of fullerol. The interactions between a set of functionalized eNPs and polymeric membranes composed of different materials and pore sizes (ranging from 2 nm to 200 nm) were investigated as well (Ladner et al., 2011). The authors observed in general (i) a dependency of the particle size to membrane pore size ratio on the removal efficiency and (ii) that removal mechanisms were influenced by the surface affinity between nanoparticles and membranes, facilitating also the removal of eNPs smaller in size than the membrane pores. They also concluded that the eNP properties appeared to be more important in determining the transport behaviour than the membrane properties. Although the aforementioned studies provided valuable knowledge on the interactions between eNPs and low pressure membranes, the results are difficult to translate to real water treatment plants because none of the reported studies (i) was performed under typical full-scale conditions such as a constant flux operating mode in dead-end membrane systems and (ii) used a hollow fiber membrane configuration typically used in water treatment plants (Crozes et al., 1997; Howe et al., 2007; Tarabara et al., 2002). To bridge this gap the focus of the present study is on (i) the removal mechanism of nC_{60} fullerene nanoparticles from suspensions in dead-end hollow fiber microfiltration and ultrafiltration and (ii) the elucidation of the role of membrane pore size on the removal and removal mechanisms of nC_{60} fullerene nanoparticles. To the best of our knowledge this work is the first one reporting nanoparticle filtration experiments performed under constant flux operating mode in dead-end membrane systems using commercially available hollow fiber membranes and including a backwash cleaning procedure with multiple cycles. Removal and removal mechanisms were evaluated by analysing transmembrane pressure (TMP) changes during filtration, measuring permeability recovery and performing membrane autopsy by visual and electron microscopy observation of the deposition of nC_{60} on the inner membrane surface.

2. Theory

Based on previous studies (Jassby et al., 2010; Ladner et al., 2011), particle size distribution is expected to play an important role in determining the removal efficiency and removal mechanism by low pressure membrane filtration. A high removal of nanoparticles by tight membranes (pore size smaller than nanoparticle diameter) is expected and size exclusion is expected to be the dominant separation mechanism, whereas for the more open membranes (pore size larger than nanoparticle diameter) a lower removal is expected, where removal is predominantly due to a combination of adsorption onto the membrane material and pore entrapment in the internal membrane structure. Removal can also occur when the membrane pore size is much larger than the nanoparticle diameter (Ladner et al., 2011) if membrane and nanoparticles have an adsorption affinity (Fig. 1c).

Retention can occur (a) by deposition onto the membrane surface resulting in external deposition (cake layer formation) and pore blocking (Fig. 1a: the pore size is smaller than the nanoparticles diameter), (b) by deposition into the membrane internal structure resulting in pore entrapment and pore narrowing (Fig. 1b: the pore size is larger than/comparable to the nanoparticle diameter) and (c) by adsorption onto the internal and external membrane surface due to nanoparticle and membrane adsorption affinity (Fig. 1c). Retention cannot occur if the membrane pore size is larger than the eNPs diameter and there is no adsorption affinity between eNPs and the membrane material (Fig. 1d).

Some eNPs accumulated on the membrane surface or in the

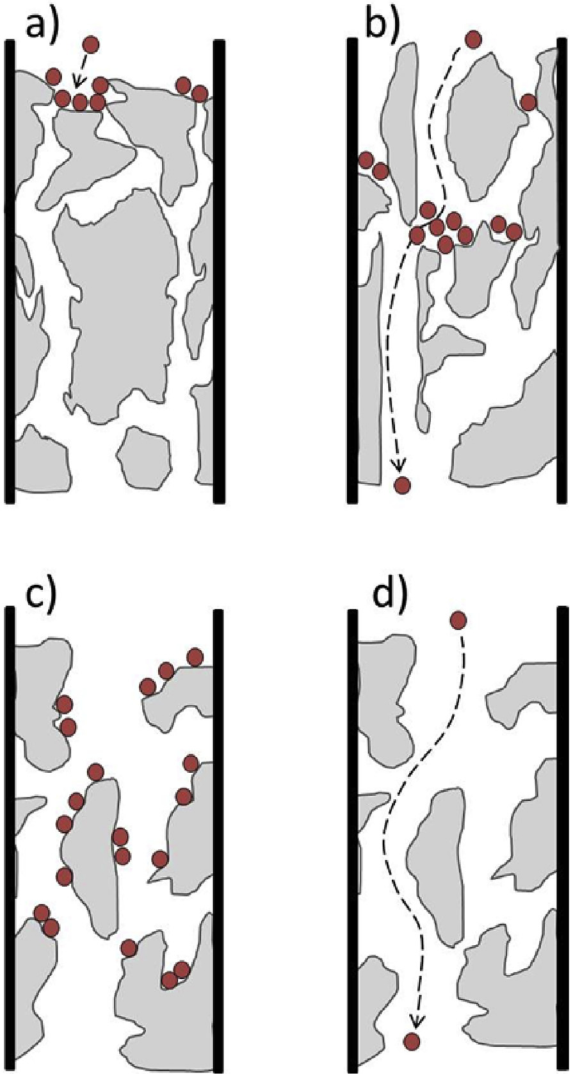

Fig. 1. Different nC_{60} removal mechanisms expected for low pressure membranes: a) Pore size smaller than nC_{60} size resulting in high removal efficiency and surface layer deposition combined with pore blocking; b) Pore size larger/comparable than nC_{60} size resulting in partial removal and internal membrane deposition (pore entrapment and pore narrowing); c) Pore size larger than nC_{60} size and adsorption affinity resulting in partial removal of eNPs; d) Pore size larger than nC_{60} size without adsorption affinity resulting in eNPs breakthrough (adapted from (Ladner et al., 2011)).