Membrane fouling by extracellular polymeric substances after ozone pre-treatment: Variation of nano-particles size

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ABSTRACT

The application of ozone pre-treatment for ultrafiltration (UF) in drinking water treatment has been studied for more than 10 years, but its performance in mitigating or exacerbating membrane fouling has been inconclusive, and sometimes contradictory. To help explain this, our study considers the significance of the influent organic matter and its interaction with ozone on membrane fouling, using solutions of two representative types of extracellular polymeric substances (EPS), alginate and bovine serum albumin (BSA), and samples of surface water. The results show that at typical ozone doses there is no measurable mineralization of alginate and BSA, but substantial changes in their structure and an increase in the size of nano-particle aggregates (micro-flocculation). The impact of ozonation on membrane fouling, as indicated by the membrane flux, was markedly different for the two types of EPS and found to be related to the size of the nano-particle aggregates formed in comparison with the UF pore size. Thus, for BSA, ozonation created aggregate sizes similar to the UF pore size (100 k Dalton) which led to an increase in fouling. In contrast, ozonation of alginate created the nano-particle aggregates greater than the UF pore size, giving reduced membrane fouling/greater flux. For solutions containing a mixture of the two species of EPS the overall impact of ozonation on UF performance depends on the relative proportion of each, and the ozone dose, and the variable behaviour has been demonstrated by the surface water. These results provide new information about the role of nano-particle aggregate size in explaining the reported ambiguity over the benefits of applying ozone as pre-treatment for ultrafiltration.

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1. Introduction

Membrane technology has been used in water treatment for more than 20 years, and will be one of the most important treatment technologies in the future for drinking water, waste water and sea water applications (Shannon et al., 2008; Elimelech and Phillip, 2011; Logan and Elimelech, 2012). However, the phenomenon of membrane fouling is still a major limitation that affects the selection and operation of membrane processes, and some fouling is considered inevitable for situations such as large drinking water treatment plants (Touffet et al., 2015). In many cases, some forms of pre-treatment have been used to control membrane fouling, such as coagulation (Liu et al., 2011a), adsorption (Pramanik et al., 2015) and oxidation (de Velasquez et al., 2013), by removing soluble and

particulate contaminants. Among such contaminants, bacteria and associated extracellular polymeric substances (EPS)/biopolymers are particularly influential in causing reversible and irreversible fouling after a long period of ultrafiltration (UF) operation, and their removal or avoidance is an effective method of controlling UF fouling (Yu et al., 2014).

The source of much of the EPS/biopolymers comes from the substantial numbers of bacteria present in most surface waters, which are impacted by effluent discharges and overflows, and land runoff; for example the northwestern Mediterranean area (Gonzalez et al., 2008). Such bacteria and associated biopolymers inevitably exist on the surface of flocs or on the membrane surface in drinking water treatment systems (Nguyen et al., 2012). There is a strong adhesive force between the biopolymers and membrane/filter cake (Myat et al., 2014a). Polysaccharides were identified as dominant foulants in UF and nanofiltration (NF) treatment of surface water (Amy and Cho, 1999), even though polysaccharide concentrations in surface waters were comparatively low. The presence of EPS may affect floc deposition on the membrane surface and

subsequently affect the biofouling propensity of the membrane (Herzberg et al., 2009; Chen et al., 2014).

A range of specific oxidation methods have been widely studied and applied in drinking water treatment, some of which have been considered as a pre-treatment for membrane processes; these include ozone (Liu et al., 2011b), chlorine (Yu et al., 2014), chlorine dioxide, hydrogen peroxide, potassium permanganate (Lu et al., 2015), and electrochemical oxidation (Qi et al., 2015). However, most of these have undesirable secondary effects in their use; for example, chlorine is associated with the production of halogenated by-products, and permanganate increases sludge production and the risk of elevated, residual Mn concentrations. In contrast, ozone produces relatively less side-effects and can have beneficial effects such as the destabilization of particles, polymerization of dissolved organics and algae flocculation; the various potential mechanisms of interaction by ozone have been reviewed elsewhere (Jekel, 1994).

The application of ozone pre-treatment to membrane processes has been considered by several researchers previously (Liu et al., 2011b; Park et al., 2012) and it is evident from these studies that there is no clear consensus that ozone mitigates membrane fouling. Some researchers found that when applied solely as a pretreatment, ozone was able to reduce membrane fouling (de Velasquez et al., 2013). Among possible reasons for this was that ozonation caused a significant degradation of biopolymers that led to a lower reduction in flux for both UF and microfiltration (MF) filtration systems (Filloux et al., 2012). Also, the combination of ozone with ceramic membrane filtration was found to decrease fouling (by around 25%) (Stylianou et al., 2015). Several researchers have also explained that ozone treatment was effective at degrading colloidal natural organic matter (or biogenic colloids) which were most likely responsible for the majority of membrane fouling (Lehman and Liu, 2009; Barry et al., 2014). A further study has shown that O_3 oxidation caused a significant alleviation of membrane fouling for all investigated NF membranes in drinking water treatment (Van Geluwe et al., 2011). It was considered that this was caused by the selective removal of unsaturated bonds and hydrophobic components in the dissolved organic matter, and by the decomposition of molecular chains into smaller fragments by O_3 (Van Geluwe et al., 2011; Barry et al., 2014). However, it is possible that the degradation of organic matter can result in products (e.g. biopolymers) of a molecular size similar to the size of NF membrane pores, which can cause significant membrane fouling. Also, some researchers found that pre-ozonation may aggravate membrane fouling (Zhu et al., 2010). Recently, problems (membrane fouling, and safety) associated with applying ozonation before ultrafiltration (UF) led to the processes being out of service for an extended period of maintenance when treating surface water from Lake Ontario (Siembida-Losch et al., 2015).

The results of previous studies cannot be generalized because the effects of ozonation are likely to vary with the nature of the source water DOC and other factors (Tobiason et al., 1990). However, the application of ozone to raw water, prior to the addition of coagulants and coagulant aides, was shown to reduce coagulant and coagulant aid doses; small ozone doses significantly improved effluent quality, and an increase in the flocs' settling velocity due to a larger average size was found in wastewater treatment (de Velasquez et al., 1998; Jasim et al., 2008). Therefore, the characteristics of organic matter in water after ozonation are likely to be altered and some products may act as polymer/flocculation aids, and thus improve the coagulation efficiency, as indicated previously (Jekel, 1994).

In this paper we examine the reasons for the variation in membrane performance when ozone is applied as a pre-treatment. This involved laboratory tests designed to elucidate the fundamental interaction between two common types of EPS, polysaccharide (specifically, alginate) and protein (specifically, bovine serum albumin), and two representative UF membranes, with and without ozone pre-treatment, and with the EPS separately and mixed. The results, described subsequently, indicate that ozone has different impacts on the EPS/UF interaction arising from the relative sizes of the EPS products from ozonation and the UF pore size, which can explain the contradictory behaviour of ozonation on membrane fouling, and the results were also confirmed by the surface water.

2. Materials and methods

2.1. Test solutions

Sodium alginate (A18565, Alfa Aesar, UK) and bovine serum albumin (BSA, Sigma, USA) were obtained as reagent grade chemicals. Fresh solutions at a total concentration of 10 g/L were prepared using deionized (DI) water. Sodium alginate was easy to dissolved in the DI water, and the BSA solution was prepared by dissolving BSA in 0.1 M phosphate buffer solution (PBS) (Ma et al., 2014). The stock solution was stored in the dark at 4 °C and was brought to room temperature prior to use in tests before working solutions were made, and the stock solution was used within 3 days. The mixed alginate/BSA solution was prepared with 5 mg/L alginate and 5 mg/L BSA. Samples of surface water were obtained from a nearby recreational lake in west-central London; the lake is of moderate quality and subject to algal growth and contamination from aquatic animals. All chemicals used in the tests were analytical regent grade.

2.2. UF experiments

Short period (5–8 min), dead-end flow experiments were undertaken using flat sheet UF membranes in a stirred cell (Amicon 8400, Millipore) with a constant upstream pressure (0.1 MPa) under nitrogen gas. The fouling characteristics of the UF membrane were studied by applying dilute (10 mg/L) solutions of alginate and BSA, or samples of surface water. Before each experiment the alginate or BSA solution was diluted in DI water (300 ml), with 5 mM $NaHCO_3$, to give the test solution. Then the pH of the final solution was adjusted and maintained at 7.0 by adding either 0.1 M NaOH or 0.1 M HCl. Subsequently, the alginate solution, BSA solution or surface water were exposed to a range of ozone doses between 0 and 1 mg/L in a close glass bottle. The ozone was added in gaseous form (generated from air) and the dose was determined by the difference on ozone concentration entering and leaving the test solution; the ozone concentration was determined by passing the gaseous inlet and outlet flows through potassium iodide solution, and employing the potassium iodide/thiosulfate titration method, in accordance with APHA Standard Methods (APHA, 2005).

Two representative types of PVDF ultrafiltration membrane (from Millipore, USA, and Ande membrane separation technology & engineering (Beijing) Co., Ltd, China) were used in these tests to ensure consistency of the results, both with a nominal molecular weight cutoff of 100 kDa (~10–20 nm). The zeta potential and contact angle of the Millipore membrane and Chinese membrane were determined as −56 mV and 35.2°±4.9°, and −42 mV and 56.3°±3.8°, respectively. Prior to use each membrane was placed in DI water for at least 24 h to remove impurities and production residues. Immediately before the stirred cell test the DI water flux of the membrane was determined by passing DI water through the membrane until a stable permeate flux was reached. After filtration with water samples by 1 bar for 300 mL, UF membrane was put at the opposite side, and washed by DI water (25 mL) with 1 bar (backwash). After that, the membrane was put as previous side and