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Control of natural organic matter fouling of ultrafiltration membrane by adsorption pretreatment: Comparison of mesoporous adsorbent resin and powdered activated carbon

Kai Li, Heng Liang*, Fangshu Qu, Senlin Shao, Huarong Yu, Zheng-shuang Han, Xing Du, Guibai Li

State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), Harbin Institute of Technology, 73 Huanghe Road, Nangang District, Harbin 150090, PR China

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ABSTRACT

This paper focused on the effects of mesoporous adsorbent resin (MAR) and powdered activated carbon (PAC) pretreatments on ultrafiltration (UF) membrane fouling caused by natural organic matter (NOM). Three model foulants, humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA), were adopted to represent different NOM fractions in natural waters. Moreover, the impact of the presence of adsorbent particles in UF feed water on membrane fouling was also evaluated. The results indicated that MAR adsorption exhibited remarkable performance in alleviating HA and BSA fouling, no matter whether MAR particles were removed before UF or not. In contrast, PAC pretreatment slightly ameliorated HA fouling when PAC particles were removed before UF, whereas HA fouling was exacerbated by PAC pretreatment with PAC particles present in UF feed water. BSA fouling was moderately controlled by PAC adsorption irrespective of the presence or absence of PAC particles in UF feed water. However, neither of these two pretreatments visibly influenced SA fouling. Overall, the results obtained in the current research would provide relevant information on adsorbent selection and process design of the hybrid adsorption/UF process according to the composition and properties of NOM.

1. Introduction

Membrane fouling is one of the major impediments for the widespread application of ultrafiltration (UF) membrane in water and wastewater treatment [1–3]. Extensive studies have been undertaken for more insights into UF membrane fouling, and the natural organic matter (NOM), including allochthonous humic substances and autochthonous biopolymers (mainly consisting of proteins and polysaccharides), has been generally considered as the major culprit responsible for membrane fouling [4–7]. Adsorption is an efficient technology for NOM removal, therefore it has been widely adopted as pretreatment for UF to enhance the performance of UF process [1,8–15]. However, although adsorption pretreatment always improved the quality of product water, its impact on membrane fouling is still under debate [1,13,14].

Powdered activated carbon (PAC) is the most common type of commercially available adsorbent in water treatment, and thus it has been widely applied in hybrid adsorption/UF process [14]. It was manifested in several studies that PAC adsorbed a significant proportion of NOM and efficiently controlled the membrane fouling [9,10,12,16]. However, in some other studies, PAC adsorption was reported to exert minor influence on membrane fouling although it indeed removed some NOM [8,17]. Moreover, when PAC particles were present in UF feed water, the membrane fouling in the hybrid PAC/UF process was even found to be exacerbated in comparison with that in the individual UF process [8,15,17]. The contradictory influence of PAC on membrane fouling was generally ascribed to the diversity of NOM characteristics in feed water and/or the membrane properties (e.g., surface hydrophobicity), but systematical studies on this subject were very limited [11,14].

Unlike PAC, mesoporous adsorbent resin (MAR) is an adsorbent specially developed for membrane fouling control [18]. It was reported that MAR significantly reduced both the reversible and irreversible fouling of 20 kDa polyethersulfone (PES) membrane while filtering lake water, although only a small amount of NOM was adsorbed by MAR [19]. Size fractionation results suggested

Abbreviations: BSA, bovine serum albumin; CA, cellulose acetate; EOM, extracellular organic matter; HA, humic acid; MAR, mesoporous adsorbent resin; MW, molecular weight; MWCO, molecular weight cut-off; NOM, natural organic matter; PAC, powdered activated carbon; PES, polyethersulfone; SA, sodium alginate; TMP, trans-membrane pressure; UF, ultrafiltration

* Corresponding author. Tel./fax: +86 451 86283001.
E-mail addresses: likai02007@126.com (K. Li), hitliangheng@163.com (H. Liang), qufangshu@163.com (F. Qu), shaosenlin@gmail.com (S. Shao), huarongyu@gmail.com (H. Yu), hit08hzs@163.com (Z.-s. Han), xingduxing@sina.com (X. Du), hitsteven@gmail.com (G. Li).

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that MAR preferentially adsorbed a fraction of NOM that had an apparent MW of 20–200 kDa. Li et al. [20] found that MAR mitigated the fouling of 100 kDa PES membrane caused by algal extracellular organic matter (EOM) much more efficiently than PAC did because MAR selectively removed high-MW fraction of EOM. Besides, both of the studies demonstrated that the presence of MAR particles in UF feed water at concentrations as high as 100 mg/L would not bring negative effects on membrane fouling [19,20]. The aforementioned studies indicated that MAR might be a more promising adsorbent in membrane fouling control in comparison with PAC. But the studies with respect to MAR were restricted to the fouling of PES membrane caused by NOM in lake water and algal EOM, and the comparative studies of two types of adsorbents were limited. The performances of MAR and PAC in mitigating membrane fouling caused by diverse NOM components and the underlying mechanisms are still unclear.

The main objective of this study was to obtain a comprehensive understanding of the effects of MAR and PAC pretreatments on NOM fouling of UF membrane. Because the complexity of natural water matrices made it difficult to elaborate the influence of adsorption pretreatment on membrane fouling by different NOM fractions, model foulants were employed in this study and caution should be taken when extrapolating the results obtained here to natural waters. Two types of commonly used UF membranes with different surface hydrophobicities were used in the tests. The adsorption capacities of MAR and PAC towards three foulants were investigated and UF experiments were carried out with NOM solutions before and after adsorption pretreatment. Moreover, the contribution of adsorbent particles in UF feed water to membrane fouling was also examined.

2. Materials and methods

2.1. NOM solutions

Humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA) purchased from Sigma-Aldrich (USA) were used as representatives of humic substances, proteins and polysaccharides, respectively. To prepare HA stock solution, 2 g of HA was added to 800 mL of 0.01 M NaOH solution, followed by stirring for 24 h and adjusting pH of the solution to 7.0 using 1 mol/L HCl. The solution was then diluted to 1000 mL to get the HA stock solution with a concentration of 2 g/L. The stock solutions of BSA and SA were prepared by dissolving 1 g of BSA and SA in 1000 mL Milli-Q water, respectively, followed by stirring for 24 h. The stock solutions were all stored in dark at 4 °C.

The stock solutions were diluted with Milli-Q water to obtain the NOM solutions used for adsorption tests and UF experiments. In order to simulate the solution chemistry of natural waters, 1 mmol/L $NaHCO_3$, 6 mmol/L NaCl and 1 mmol/L $CaCl_2$ were added and the pH was adjusted to 7.5 ± 0.1 with 0.1 mol/L HCl and NaOH. The concentrations of HA, BSA and SA employed in UF experiments were 10, 2 and 2 mg/L, respectively. The corresponding dissolved organic carbon concentrations were 4.38 ± 0.11, 0.81 ± 0.07 and 0.76 ± 0.12 mg C/L, respectively. Unless otherwise specified, the concentrations of model foulants reported in this paper were on the basis of the mass of model foulants rather than the content of carbon. The concentrations of BSA and SA used in UF experiments were much lower than that of HA because the concentration levels of proteins and polysaccharides were usually very low in natural surface water [21,22].

2.2. Adsorbents and adsorption tests

MAR is a type of mesoporous adsorbent synthesized following the method proposed by Clark et al. [18] and detailed steps of preparation could be found in reference [20]. Wood-based PAC was purchased from Bench Chemicals (Tianjin, China) and was used without further purification. Stock solutions of MAR and PAC with mass concentrations of 10 g/L were prepared and stored in refrigerator for use. The main properties of MAR and PAC are listed in Table 1. It can be seen that they had similar particle size and surface charge, but they displayed substantial difference in the pore structure characteristics. The BET surface area of MAR was less than 10% of that of PAC, while the pore size of MAR was much larger than that of PAC.

Table 1
Main properties of MAR and PAC.

Adsorbent	Average particle size (d_{50}, μm)	Zeta potential (mV)	BET surface area (m^2/g)	Average pore size (nm)
MAR	25.2 ± 0.8	-22.4 ± 1.0	108 ± 9	16.4 ± 0.5
PAC	32.1 ± 0.7	-23.9 ± 0.9	1219 ± 13	2.2 ± 0.1

Note: values represent average ± standard deviation, $n=3$.

Adsorption tests were conducted to characterize the adsorption of the NOM fractions onto two types of adsorbents. The concentrations of HA, BSA and SA employed in adsorption tests were 1–30 mg/L and the concentration of the adsorbent was 50 mg/L. The adsorbent was added to NOM solutions and the flasks were shaken in a rotary shaker at 120 rpm and 20 °C for 12 h. Finally, the samples were filtered with 0.45 μm mixed cellulose filters (Taoyuan, China) to remove adsorbent particles and the concentrations of HA, BSA and SA in the filtrate were measured. The retention of these NOM fractions by this filter has been proved to be negligible in preliminary tests. The adsorbed amounts of HA, BSA and SA onto the adsorbents were calculated by mass balance.

2.3. UF membranes and experimental setup

Two types of flat-sheet UF membranes with the same molecular weight cut-off (MWCO) of 100 kDa, i.e., a PES membrane (OM100076, Pall, USA) and a cellulose acetate (CA) membrane (PLHK07610, Millipore, USA), were used in this study. They have similar surface charge and roughness, but are apparently different in surface hydrophobicity [23]. The contact angles of the PES and the CA membrane were 58.2° and 19.3°, respectively, indicating that the PES membrane was much more hydrophobic than the CA membrane.

UF experiments were performed in a filtration cell (Amicon 8400, Millipore, USA) in dead-end mode at room temperature (20 ± 1 °C). UF membrane was placed on the bottom of the cell with its glossy side towards the bulk solution during filtration. A peristaltic pump was used as the suction pump to maintain a constant permeate flux of 150 L/(m^2 h). The trans-membrane pressure (TMP) was monitored by a pressure transducer (PTP708, Tuopo Electric, Foshan, China) mounted between the filtration cell and the suction pump. The pressure transducer was connected to a computer and the data was automatically logged every five seconds. Average fouling rate was calculated by dividing the increment of TMP by filtration time.

2.4. UF experiments and fouling resistance analysis

Fouling reversibility (i.e. the response of membrane fouling to physical cleaning strategies) is of great significance from the perspective of application, while the analysis of fouling resistance distribution (external vs. internal fouling) would favor the identification of fouling mechanisms [3,24,25]. In this study, external fouling was operationally classified into loosely- and strongly-attached external fouling by its response to shear stress, and