Evaluation of fouling mechanisms for humic acid molecules in an activated biochar-ultrafiltration hybrid system

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HIGHLIGHTS

- Activated biochars (ABs) were suggested to be a useful adsorbent in an ultrafiltration hybrid system.
- The O-/N-AB were compared with coal-based PAC based on HA removal and membrane flux.
- N-AB in the UF hybrid system showed significantly better performance than coal-based PAC.

GRAPHICAL ABSTRACT
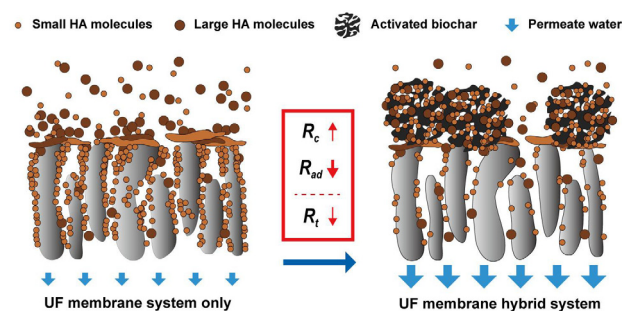
ABSTRACT

Activated biochar (AB), produced by incomplete biomass combustion of waste or byproducts, was found to be an effective adsorbent in an ultrafiltration (UF) hybrid system. Three different adsorbents, powdered activated carbon (PAC) and oxygen-/nitrogen-based AB (O-/N-AB), were characterized and quantified by elemental composition and aromatic carbon fractions. Based on the results, the economical O-/N-AB could be used as an alternative to coal-based commercially available PAC due to their enhanced inner pore site density. In particular, the adsorption capacity of N-AB (1.306 $(mg/g)(mg/L)^{1/n}$) for hydrophobic humic acid (HA) molecules was significantly higher than those of PAC (1.208 (mg/g) $(mg/L)^{1/n}$) and O-AB (1.230 $(mg/g)(mg/L)^{1/n}$). Although the UF hybrid system with all adsorbents showed a higher reversible fouling rate (11.1%) than a UF membrane system alone, due to the added adsorbents for HA filtration, the adsorbents adsorbed relatively small HA molecules, leading to a significantly lower feed-HA concentration in the membrane system, resulting in a decrease in the irreversible fouling rate (38.1%). Consequently, N-AB in the UF hybrid system showed better performance than PAC in terms of flux decline (12.9%) and HA rejection (4.1%), due to higher hydrophilicity and polar interactions with polar functional groups.

1. Introduction

Ultrafiltration (UF) membrane systems are used widely in water and wastewater treatment fields, because UF membranes can remove most particulate and colloidal molecules. However, natural organic matter (NOM), as one of the major foulants, contributes to membrane fouling in UF membrane systems [1–3]. In particular, dissolved NOMs (DOMs; tannic acid, fulvic acid, and humic acid (HA)) are generally considered extreme case of membrane fouling in such systems. The fouling mechanisms of DOMs are well-known: adsorption of the DOMs on the membrane pores,

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accumulation on the membrane surface by gel layer/cake formation, and aggregation of these DOMs on the membrane surface and pores [4–6]. Although DOM fouling has been widely reported, the fouling mechanisms of hydrophobic HA molecules remain unclear and incompletely demonstrated. Furthermore, the evidence for membrane fouling is still weak for classified reversible and irreversible fouling by HA molecules.

To reduce membrane fouling, previous studies have suggested many effective methods, such as membrane surface modification [7–11], frequent physical cleaning (e.g., backwashing) [12–14], and chemical pretreatment (e.g., coagulation and/or adsorption) [15–18]. In particular, the adsorbent application of powdered activated carbon (PAC) as an upstream or direct pretreatment in the membrane system is generally used to minimize the influence of the accumulated foulant and cake formation causing reversible membrane fouling. A previous study reported that a membrane fouling rate of one-third for the treatment of DOM (approximately 3 mg/L) in ground water could be reduced by the addition of 25 mg/L PAC [19]. Although adsorption with PAC significantly reduced DOM fouling in the membrane system, the effects of hydrophobic HA molecules on membrane fouling cannot be predicted, because adsorbent-adsorbed HA molecules may severely foul the membrane with more complex mechanisms than the HA molecules alone.

Even the use of adsorbents in a membrane system (termed a 'hybrid system' in this paper) can lead to the exacerbation of membrane fouling (i.e., a higher flux decline) due to hydrophobic interactions between the membrane and HA molecules or adsorbent and/or between the HA molecules and adsorbent. In a hybrid system with PAC for treating synthetic water, the flux decline caused by hydrophobic HA fouling was exacerbated by the addition of PAC to the system, even though PAC showed substantial rejection of the dissolved organic carbon (DOC) [16,17,19,20]. This suggests that the higher aromaticity of the adsorbent caused destructive interference in the particulate or colloidal molecules, resulting in higher adsorption capacity. Additionally, membrane fouling can be accelerated due to the higher hydrophobicity of the adsorbent and HA molecules. Thus, the physicochemical properties of adsorbents are important factors for membrane fouling in a hybrid system.

Activated biochar (AB), produced from the incomplete combustion of black carbon biomass in waste or byproducts, has recently attracted interest in soil remediation, carbon sequestration, and water and wastewater treatment [21,22]. Additionally, oxygen- and nitrogen-ABs (O- and N-ABs) can be generated under conditions of atmospheric and pure nitrogen gas, respectively, due to the loading limitations of sample amounts in a tube furnace, with different adsorption abilities [23]. These economical ABs have been suggested as alternatives to replace coal-based PAC, due to their low hydrogen and oxygen contents, via pyrolysis processing at lower thermal temperatures (<500 °C). Moreover, ABs strongly adsorb hydrophobic organic molecules of NOM due to their large specific surface area (SSA) with high negatively charged surfaces. A previous study reported that AB was superior to coal-based PAC for hydrophobic HA removal by adsorption [24].

Nevertheless, for hybrid systems with AB, there is a lack of information on membrane fouling, in comparison with the use of PAC. Particularly, no performance evaluation as to which types of ABs may possibly cause reversible and irreversible fouling has yet been reported for the rejection of hydrophobic HA molecules in a hybrid system. As a first attempt to address these issues, in this study, three adsorbents (PAC, O-AB, and N-AB) were characterized and quantified by elemental composition and aromatic carbon fractions, respectively. Then, adsorption isotherm and removal experiments for the hydrophobic HA molecules were performed to evaluate the adsorption abilities of these adsorbents. Additionally, filtration tests were conducted in the absence and presence of these adsorbents to evaluate the effects of HA fouling on the membrane. Finally, the fouling mechanisms in the hybrid system with these adsorbents were compared for reversible and irreversible fouling via various models.

2. Materials and methods

2.1. Adsorbents and characterization

Coal-based PAC was purchased from Calgon Carbon Co. (Pittsburgh, PA, USA) and used to compare adsorption abilities with those of O-/N-AB prepared in the laboratory. The oxygen-based (7% oxygen + 93% nitrogen, O-AB) and nitrogen-based biochars (pure nitrogen gas, N-AB) were prepared by thermal treatment of pieces of dried loblolly pine with bark (15 mm × 6 mm) for 15 min at 300 °C in a batch-scale OTF-1200X tube-furnace (MTI Co., Richmond, CA, USA). After these two biochars were created in several batches, the weight loss of samples from the thermal treatment was fixed with a ±3% difference for further experiments, resulting in yields of 64.2% for oxygen-based and 42.3% for nitrogen-based biochars, respectively. To obtain the O-AB and N-AB, 3 g of each pyrolyzed-biochar was activated with 40 ml of 4 M NaOH for 2 h and dried at 105 °C for 24 h. Then, these O-/N-AB were separated from the NaOH solution using a Buchner filter funnel and heated at 800 °C for 2 h then cooled (10 °C/min) with a nitrogen gas flow (2 L/min). The pH of the dried O-/N-AB was adjusted to 7 with 0.1 M HCl. Finally, these O-/N-AB were milled and passed via a 74-μm sieve, and then dried at 105 °C.

The three adsorbents, PAC, O-AB, and N-AB, were characterized by elemental analysis, solid-state ^{13}C direct polarization/magic angle spinning (DP/MAS) nuclear magnetic resonance (NMR) spectra, and N_2 Brunauer–Emmett–Teller (BET) SSA measurements. The elemental composition was analyzed with a PerkinElmer 2400 Series II Elemental Analyzer (Waltham, MA, USA). Based on the elemental analysis, the oxygen content can be calculated by subtracting the contents of carbon, hydrogen, nitrogen and ash. The solid-state ^{13}C NMR spectra were obtained with a 3.2-mm MAS probe and a Varian INOVA-500 spectrometer (Palo Alto, CA, USA). To quantify structural analyses of PAC, O-AB, and N-AB, dipolar-recoupled NMR methods were applied to the ^{13}C NMR spectra. Detailed NMR analyses with various experimental conditions were have been described previously [25]. In addition, the SSA and total (micro- and macro-) pore volumes of the adsorbents (N_2 gas at 77 K temperature in the relative pressure range ($P/P_0 = 0.95$) were measured by BET and Barrett–Joyner–Halenda (BJH) methods using a Gemini VII 2390p SSA analyzer (Micromeritics, Norcross, GA, USA) with N_2 sorptometry (SSA-N_2) [26,27].

2.2. Adsorption isotherm and removal experiments

Sigma-Aldrich HA (St. Louis, MO, USA) was used as a representative NOM to simulate the hydrophobic molecules of NOM. A 1000 mg/L as DOC of dissolved HA stock solution was prepared using deionized (DI) water, and filtered with both a 0.7-μm GF/F glass microfiber filter (Whatman Inc., Piscataway, NJ, USA) and a 0.45-μm Durapore membrane filter (Millipore Inc., Billerica, MA, USA). To obtain the desired HA concentration, this HA stock solution was then diluted with DI water for the adsorption isotherm and removal experiments. The concentration of HA was measured by Agilent 8453 ultraviolet–visible (UV–Vis) spectroscopy (Santa Clara, CA, USA). The pH was adjusted with 0.1 M HCl and 0.1 M NaOH with 1 mM phosphate buffer solution to get the desired pH of nearly 7. The conductivity was also adjusted to 300 μS/cm by the addition of 0.1 M NaCl solution.