



Study on PVDF-TiO₂ mixed-matrix membrane behaviour towards humic acid adsorption



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ABSTRACT

Despite the expansion and successful application of membrane systems in water industry, membrane fouling which predominantly caused by the irreversible adsorption is still a critical problem. The objective of this work is to study the adsorptive behaviour of membrane for the removal of humic acid (HA). Apart of neat membrane that has very often been used in adsorption study, PVDF-TiO₂ mixed-matrix membranes (MMMs) with varied titanium dioxide (TiO₂) concentration (0.001 g/L, 0.01 g/L, and 0.1 g/L) were explored in the present work. A dynamic stirring cell with continuous stirring for 24 h at 250 rpm was applied in this study. Different operating parameters such as initial HA solution concentration, calcium chloride (CaCl₂) concentration, and HA solution pH were performed in this study. HA adsorption ratio in each single batch of experiment was determined by measuring the HA adsorbance as a function of time. The results, interpreted in terms of adsorption ratio (A/A_0) yield severe HA adsorption at low pH and high initial HA solution concentration. In addition, it was found that, increased CaCl₂ concentration reduces the electrostatic repulsion between HA aggregates and membrane surface, consequently appears to be more adapted to HA adsorption.

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1. Introduction

Humic acid (HA) acts as a major constituent in soil organic matter humus, contributes to soil chemical and physical quality, is the precursor of some fossil fuels [1]. It can also be found in peat, coal, many upland streams, dystrophic lakes, and ocean water. However, despite the importance of HA in soil fertility, its presence in environment has become a great problem due to the formation of complex HA-metal ions which leads to metal transportation when release in soil [2]. Another major concern is due to its high tendency in forming a host of disinfection by products (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs), and other halogenated organics during conventional water treatment process which have been shown to be detrimental to human beings [3,4]. Consequently, the importance of removing HA from water is a well-known issue, as a result of their relation to various health problems.

According to World Health Organization (WHO), the concentration of HA in potable water should be limited to less than 100 ppb [5]. Several treatment methods have been developed for the removal of HA including coagulation, electrocoagulation, flotation, and oxidation process. However, the application of the proposed methods is associated with a number of disadvantages, such as fouling of the electrodes, high operating cost, maintaining cost, and energy requirements, application dependent (depend on types of compound to be removed, treatment objectives, concentration, etc). Thus, the advance, simple, and cost-effective membrane separation process is being emerged as an innovative HA treatment technology.

Despite the expansion and successful application of membrane system in water industry, a decline in membrane performance over a period of time toward high susceptibility fouling effect is still a critical problem. Consequently, current research and development in membrane technology had focused on fouling problem and directed towards the drastic improvement in developing membranes that are less prone to fouling to reduce the economics burden of process.

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Attribute to its unique large surface-to-volume ratio and strong reactivity properties, nano-sized colloidal particles have extended their advance application into membrane technology by improving their synergetic effects on water and wastewater treatment [6]. Among different metal oxide nanoparticles (NPs), titanium dioxide (TiO₂) with photocatalytic and hydrophilic properties emerging as highly promising candidate to be incorporated into polymeric matrix in improving the membrane permeability, fouling-resistance, and self-cleaning properties [6,7].

Many investigators have examined the fouling characteristics of HA and it was demonstrated that the bulk flux decline was predominantly caused by the irreversible HA adsorption. Since membrane fouling was strongly dictated by the adsorption characteristics and most of the studies made by other researcher in indentifying the fouling mechanism only reported on neat membrane, there is a strong motivation to understand the limiting conditions of HA adsorption before assessing the dynamic properties (self-cleaning/photodegradation) of polyvinylidene fluoride-titanium dioxide (PVDF-TiO₂) mixed-matrix membrane (MMM).

The objective of this work is to study the potential of HA adsorption in membrane process for HA removal. Influences of solution physiochemical properties such as pH, initial HA concentration, and ionic strength as well as membrane surface property on membrane adsorptive behaviour have been investigated by performing static adsorption experiment under various conditions.

2. Materials and methods

2.1. Materials

Ultrafiltration (UF) flat sheet membranes were fabricated by dissolving PVDF (TA6010/1001, Solvay Solexis, Shanghai) in *N,N*-dimethylacetamide (DMAc) (Merck, Germany) (assay (GC, area%) ≥ 99%) solution and were cast at 200 μm thickness. Commercial TiO₂ purchased from TitanPE Technologies, Inc., China (trade name: PC-20; primary particle size of 20 nm) was used as hydrophilic filler in MMMs. As reported by the manufacturer, PC-20 contains about 85% anatase and 15% rutile. It was used as received.

Synthetic HA with molecular weight mainly ranging from 20,000 to 50,000 g/mol was obtained from Sigma-Aldrich and used as the organic adsorbate during the experiment without further purification. Sodium hydroxide (NaOH) (Sigma-Aldrich, USA) solution was used to improve the dissolution of HA in water. Feed solutions were prepared by dissolving a pre-weighed quantity of HA powder in distilled water. The solution pH was adjusted to the desired values by adding small quantities of 0.1 M NaOH under vigorous stirring. To study the effect of ionic strength, the analytical grade inorganic salt, anhydrous calcium chloride (CaCl₂) (R&M Chemicals, UK) was added to adjust the total ionic strength of the HA feed solution. Distilled water was used throughout the experiment.

2.2. Membrane formation and in-situ particle embedment

The neat UF flat sheet membrane was fabricated using phase inversion method. In order to produce PVDF-TiO₂ MMMs, PVDF solution layers were immersed into the coagulation bath with TiO₂ colloidal suspension as described in our previous report [8–12]. The preparation conditions of the membranes were summarized in Table 1.

2.3. Membrane characterization

2.3.1. Atomic force microscope (AFM)

AFM, model XE-100 (Park Systems, USA) was employed to analyze the surface morphology and roughness of the membranes.

Table 1
Membrane dope and coagulation bath formulation.

Membrane Number	PVDF Wt%	Solvent Wt%	TiO ₂ Type	TiO ₂ Concentration (g/L)
M	18	82	–	0.000
M1	18	82	PC 20	0.001
M2	18	82	PC 20	0.010
M3	18	82	PC 20	0.100

The measurement was carried out at atmospheric pressure and the membranes were dried at room temperature prior to surface analysis. Approximately 1 cm² of the prepared membrane was cut and secured on the top of a microscope's slide glass. The membrane was taped with double-sided tape to ensure that sample was totally flattened. The membrane surface was then scanned with a laser beam reflected by the cantilever within a scanning area of 10 μm × 10 μm. Generally, three parameters are used to define roughness: the mean roughness (R_a), the root mean square roughness (R_q) and the average difference in the height between the highest and the lowest points (R_z). In this study, R_q was used as the evaluation parameter to compare the roughness of the membrane produced, and was then studied using the AFM XE Data Acquisition program in non-contact mode. The term was defined as the average value of the surface relative to the centre plane for which the volumes enclosed by the images above and below the plane were equal. This parameter was calculated using the following equation:

$$R_q = \left[\frac{1}{S} \int_0^a \int_0^b \{f(x, y) - z_m\}^2 dx dy \right]^{\frac{1}{2}} \quad (1)$$

where $f(x, y)$ is the height in the specified area, S is the specified area, a and b are the length of the sample, and Z_m is the mean height value.

2.3.2. Streaming potential

The surface properties of the membranes were examined using streaming potential device (ZetaCAD) (CAD Instruments, USA). The streaming potential was evaluated using a device constructed from two Plexiglas chambers with Ag/Ag/Cl electrodes inserted at each end. Data were obtained using 10 mM NaCl at pH 7.0, with the fluid flow across the membrane surface. When an electrolyte flows tangentially across a flat membrane, in the streaming potential method, the measurable potential difference (E_z) between the two ends of the system can give direct information on the electrostatic charge at the shear plane of the electrical double layer. Using E_z and other parameters, the apparent zeta potential (ξ) was evaluated from the slope using the Helmholtz-Smoluchowski equation [13–18], which is applicable to an electrolyte with a relatively high ionic strength [14].

$$\xi = \left(\frac{\eta \Lambda_o}{\epsilon_o \epsilon_r} \right) \frac{dE_z}{d\Delta P} \quad (2)$$

where E_z is the streaming potential (mV), ΔP the hydrodynamic pressure difference (Pa), η the liquid viscosity (0.89×10^{-3} Pa s), Λ_o is the solution conductivity (mS/m), ϵ_o is the permittivity of free-space ($\epsilon_o = 8.854 \times 10^{-12}$ s m⁻¹), and ϵ_r is the liquid permittivity ($\epsilon_r = 78.38$).

As streaming potential is linearly dependent on the applied pressure differential, it allows the apparent zeta potential to be evaluated directly from Eq. (2). Several studies have shown that Eq. (2) provides useful information on the charge characteristics of membranes even though the Helmholtz-Smoluchowski equation neglects the effects of surface conductance and overlapping double layers [15,16]. All results in this study are reported in terms of apparent zeta potential data as calculated from Eq. (2).

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