The fouling potential of colloidal silica and humic acid and their mixtures

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ABSTRACT

The fouling propensity of an inorganic colloid (silica) and an organic (humic acid) and their mixture was studied in this paper. Fouling propensity was characterized as the modified fouling index (MFI$_{UF}$) and specific cake resistance in dead-end UF at constant pressure. Experimental results for individual foulants demonstrated that MFI$_{UF}$ increased linearly with increasing particle concentration for both humic acid and colloidal silica over most of the concentration range, with deviations at the lowest concentrations. In terms of specific cake resistance, the individual foulants tended to have higher values at low concentrations that gradually declined to steady values at higher concentrations. These trends could be due to differences in cake formation and packing density with foulant flux. For the mixed foulants the presence of modest amounts of humic acid (< 15 mg/L) tended to reduce both MFI$_{UF}$ and specific resistance below that of the colloidal silica alone (50–150 mg/L). This is attributed to the effect of the humic acid on silica packing density. At higher concentrations of humic acid (> 20 mg/L) or lower concentrations of silica the mixture MFI$_{UF}$ started to exceed that of the colloid alone, possibly due to interstitial humic acid effects on cake resistance. Very low adsorption of humic acid on colloidal silica was also observed using Quartz crystal microbalance with dissipation (QCM-D) and zeta potential measurements. The results confirm that knowledge of the individual MFI$_{UF}$s could not be used reliably to predict the fouling potential of the mixture.

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1. Introduction

Ultrafiltration processes (UF) are popular for water and wastewater treatment with a relatively lower cost compared with other methods like nanofiltration (NF) or reverse osmosis (RO) [1,2]. It is also used increasingly as a pretreatment step for RO units in seawater desalination and water reclamation [3]. However, one of the most challenging problems in membrane processes is fouling which decreases the performance and increases the operational costs [4]. Membrane fouling can be affected by many parameters like feed water characteristics and solution chemistry (pH, salinity, etc.), membrane properties and operational conditions [5].

There are several methods to determine the particulate fouling potential of feed water. The most frequent and widely used method is the silt density index (SDI) which is based on 0.45 μm microfiltration (MF) membranes [6]. This method is an empirical method without a good theoretical basis [7]. The modified fouling index (MFI$_{0.45}$) has advantages over the SDI as

it is based on filtration theory and is typically linear with the foulant load [7–9]. However the MF based MFI$_{0.45}$ may not capture all potential foulants, and the modified fouling index ultrafiltration (MFI$_{UF}$) has been proposed as an alternative to capture smaller colloidal particles than that by the MFI$_{0.45}$ [10–12]. To capture even smaller particles and macromolecules the MFI-NF was proposed, but found to take longer and produce similar results to MFI$_{UF}$ [13]. Ultrafiltration membranes appear to be a good compromise for measurement of fouling potential by MFI$_{UF}$. The MFI$_{UF}$ responds to fine particles, colloids and macromolecular organics provides and an indication of the fouling propensity for UF membranes and RO membranes (other fouling types, such as scale and biofouling require other fouling monitors) [14–16]. During colloidal fouling of porous membranes, particles accumulate on the surface or within pores [17–20]. Humic substances, which are considered as a main component of dissolved natural organic matter (NOM) in surface waters, have a significant role in organic fouling of membranes. Organic fouling causes both reversible and irreversible flux decline, thus removing NOM is an important step in many pre-treatment processes [21]. Investigations of the influence of NOM on membrane fouling have been carried out by several researchers [22–25]. For example, the ultrafiltration of natural water with various organic

macromolecules and inorganic colloids indicated that organic matter had a much greater effect on the flux decline than inorganic colloids which can be attributed to the different fouling mechanisms, including pore plugging or cake formation [26].

Some studies on membrane filtration of combined foulants have been reported recently and suggested that NOM plays an important role for particle aggregation or stabilization during filtration of combined foulants [27–29].

Most fouling index studies have concentrated on individual organic or inorganic foulants and the effects of combined foulants on membrane filtration remain relatively poorly understood. Therefore the objective of this paper is to study the influence of concentration for both colloidal (silica) and organic (humic) foulants, alone and in mixtures, on membrane fouling potential under constant pressure filtration. The trends in MFI$_{UF}$ and specific cake resistances are also compared.

2. Theory

MFI$_{UF}$ has been developed based on cake filtration theory [7]. Schippers et al. [7] proposed that dead-end filtration at constant pressure takes place in three steps in sequence: pore blocking, cake filtration without compression and formation of a compressible cake layer.

According to the membrane blocking laws, there is a linear relationship between t/V and V during the cake filtration period where V refers to the filtrate volume and t is the filtration time. At the beginning of filtration, membrane resistance (R_m) controls the flux, however after cake formation; the cake resistance (R_C) becomes increasingly important. For filtration under constant pressure the following equation shows the relationship between t/V and V:

$$\frac{t}{V} = \frac{\mu R_m}{\Delta PA} + \frac{\mu I}{2\Delta PA^2} \times V \tag{1}$$

where A is membrane area, ΔP is the transmembrane pressure (TMP) and μ is filtrate solution viscosity.

The slope of the linear region of t/V vs. V is defined as the MFI$_{UF}$:

$$MFI_{UF} = \frac{\mu I}{2\Delta PA^2} \tag{2}$$

where 'I' is the fouling index or resistivity, which is a measure of the fouling potential of the feedwater for the membrane, and combines the specific cake resistance (α) and the foulant concentration (C_b), so [30]:

$$I(t) = \alpha(t)C_b \tag{3}$$

The specific cake resistance under constant pressure is constant for incompressible cakes and can be estimated using the Carman–Kozeny relationship [31]:

$$\alpha = \frac{180(1-\varepsilon)}{\rho_p d_p^2 \varepsilon^3} \tag{4}$$

Here ε is the porosity of the cake layer and d_p and ρ_p are the diameter and density of the particles, respectively. Eq. (4) is qualitatively useful as it illustrates the sensitivity of α (and hence MFI$_{UF}$) to foulant size and porosity (ε) of the formed cake. It also highlights the challenge to determine specific cake resistance for mixed foulants as it is difficult to assume a characteristic "d_p" value or porosity for a mixture.

By substituting Eq. (3) in Eq. (2), the relationship between specific cake resistance and MFI$_{UF}$ can be measured by following equation:

$$\alpha = \frac{2MFI_{UF}\Delta PA^2}{\mu C_b} \tag{5}$$

3. Materials and methods

3.1. Filtration apparatus

Fig. 1 is a schematic diagram of the dead-end filtration setup used to measure the MFI$_{UF}$. A stainless steel feed reservoir (2 l capacity) was connected to a dead-end filtration cell (maximum capacity of 120 ml) with an active membrane area of 0.0012 m^2. The required trans-membrane pressure (TMP) in constant pressure filtration was supplied via a nitrogen gas cylinder. The permeate volume and TMP were measured and recorded with an electronic weighing balance (Mettler Toledo, model PB3002-L) and pressure transducer, respectively, which were connected to the data acquisition system (National Instrument, model PCI 6014 and LabView 7). All filtration tests were conducted at standard conditions; 20 °C and 210 kPa.
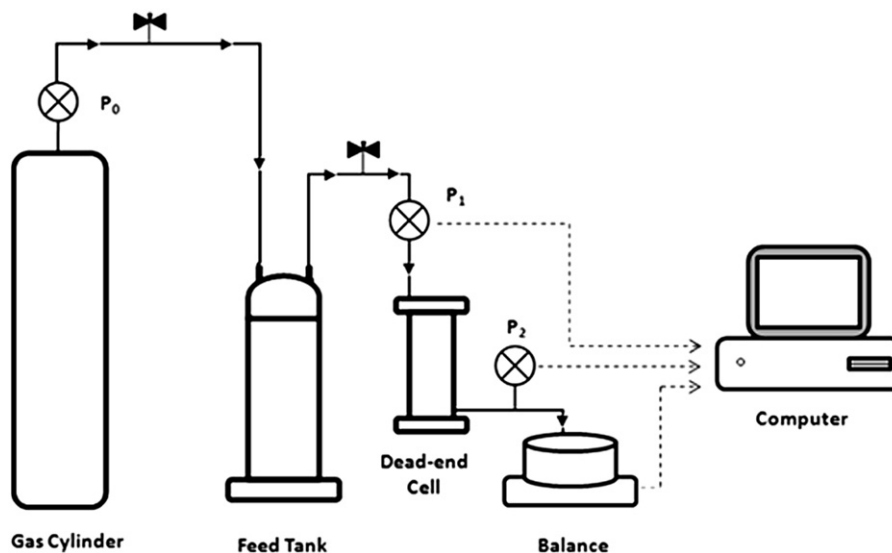

Fig. 1. Schematic diagram of dead-end constant pressure filtration device.