



Effect of calcium ions on fouling properties of alginate solution and its mechanisms

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ABSTRACT

In this study, effect of calcium ions on the filtration behaviors of alginate solution and its underlying mechanisms were systematically investigated. It was found that, the filtration resistance of the formed gel layer and the specific filtration resistance (SFR) of alginate solution showed a unimodal pattern with increase in Ca^{2+} concentration, and the maximal SFR was as extremely high as $3.63 \times 10^{15} \text{ m} \cdot \text{kg}^{-1}$. Series analyses showed that Ca^{2+} concentration exerted no apparent impact on pore clogging resistance, composition of functional groups and elements of the formed gel. In contrary, increase in Ca^{2+} concentration caused transitions of colloid formation and alginate polymer micromorphology in solution, well corresponding to the unimodal pattern of filtration behaviors. It was proposed that, Flory-Huggins mechanism governed the extremely high SFR of the alginate gel. Meanwhile, it was suggested that initial calcium binding by alginate occurred in intermolecular rather than intramolecular, which was the key mechanism governing the development of micromorphology and SFR of alginate gel with increase in Ca^{2+} concentration. These findings offered deep insights into alginate gel fouling associated with calcium ions, and also gave implications to membrane fouling control in membrane bioreactors.

1. Introduction

Due to many distinct advantages, such as reduced footprint, enhanced effluent quality and low surplus sludge yield, over conventional activated sludge process (CAS), membrane bioreactor (MBR) has been extensively implemented for wastewater treatment and reclamation [1,2]. However, membrane fouling, which would decrease the treatment efficiency, shorten the membrane life and then increase the operation cost, highly limited the widespread application of MBRs [3–5]. Therefore, it is of primary interest for MBR technology to investigate the mechanism and control strategies of membrane fouling [6–8].

In practice, the wastewater subjected to treatment by MBRs generally contains significant amount of calcium ions. It was reported municipal wastewater typically contained calcium concentrations of 0.5–3 mM [9]. Moreover, it is generally accepted that calcium ions are involved in several processes related with membrane fouling in MBRs, e. g. sludge bioflocculation, gel layer formation, and calcium carbonate scaling [10,11], due to abundant negatively charged functional groups within the extracellular polymeric substances (EPSs) of sludge substances [7]. Accordingly, considerable attention has been recently paid

on effects of calcium on membrane fouling [9,12–14]. In spite of that, the results obtained from the literature studies are controversial. Some studies reported that calcium significantly reduced membrane permeability [15–17], whereas, some other studies showed the opposite results [12,18–20]. Furthermore, Mo et al. [21] and Mahlangu et al. [22] reported that membrane fouling firstly increased and then decreased when Ca^{2+} concentration continuously increased (unimodal pattern of fouling). The underlying causes for the inconsistency among the different studies regarding effects of calcium ion on membrane fouling have not been comprehensively investigated. Nonetheless, these inconsistent results demonstrate the complexity of roles of calcium in membrane fouling, and deserve further investigation.

In MBRs, EPSs are known to be the key substance affecting membrane fouling [7]. In presence of EPSs, calcium is expected to act as “bridging agents”, which would preferentially bind to the carboxylic functional groups of EPSs and form bridges between the molecules. Such an effect would facilitate to the processes including sludge bioflocculation, gel layer formation, and inorganic scaling related with membrane fouling. These different processes are inter-related, and difficult to be individually studied [10]. These different processes may have different effects on membrane fouling. This is

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probably one of the reasons why conclusions regarding effects of calcium on membrane fouling in the literature were inconsistent. Sodium alginate (SA) has been frequently used to model polysaccharides in EPSs [13,15,23] because it similarly behaves to EPSs during filtration [24]. Associating with calcium ions, sodium alginate is easy to form a gel through ionotropic gelation (IG) where the sodium present in the polymer chains is replaced by calcium and the crosslinking process is initiated [25]. It is, therefore, hypothesized that, by isolating gel formation with SA, the exact roles of calcium in membrane fouling can be addressed. However, none study has tested this hypothesis to our knowledge.

Foulant interception by the membrane unit in MBRs would always result in build-up of a foulant layer on membrane surface. In lots of cases, the foulant layer was present in form of gel layer [11,26,27]. It was frequently reported that, gel layer was very porous with a very high content of water (more than 90%) but simultaneously had very low Darcy permeability [28,29]. This phenomenon cannot be explained by the conventional filtration theory represented by Carman-Kozeny equation [30]. As calcium could involve into gel layer formation, investigating roles of calcium in membrane fouling might provide important clues to this phenomenon, and thus give significant insights into membrane fouling mechanisms.

The main objective of this paper is, therefore, to investigate how variation of calcium ion concentration affects the fouling behaviors of alginate solution. Accordingly, series of SA solution with different calcium additions were prepared, and then subjected to filtration. Effects of calcium on membrane filterability of SA were investigated. Characterizations including dead-end filtration, FT-IR spectrometer, X-ray photoelectron spectroscopy (XPS) and optical microscope observation were performed. The underlying mechanisms of the filtration behaviors were proposed.

2. Materials and methods

2.1. SA solutions preparation

The SA applied in this study was purchased from Sinopharm Chemical Reagent Co., Ltd. The alginate solutions (1.0 g/L) were prepared by dissolving 1.00 g SA powder into 1000 mL deionized (DI) water, followed by continuous stirring for 2 h until the dispersions were completely blended. After that, series amount of CaCl₂ (with Ca²⁺ concentrations of 0, 0.5, 1, 1.5, 2, 2.5, 3, 4 and 6 mM) were further added in the solutions, and then, the solutions were magnetically stirred for 2 h. All the solutions were prepared at room temperature (25 °C). For all the prepared solutions, no other background electrolyte was added. The high SA concentration (1.0 g/L) was selected in this study in order to facilitate formation of apparent gel layer in dead-end filtration process during relatively short period. Similar or even higher SA concentration was typically used for lab-scale studies in the literature [31,32]. Experimental results also indicated the appropriateness of the adopted SA concentration.

2.2. Filtration resistance tests

Both filtration resistance and specific filtration resistance (SFR) were determined by the batch filtration tests (in dead-end mode) with a stirred cell (MSC300, supplied by Shanghai SINAP Co. Ltd., China) (effective filtration area was 0.00332 m²) with 300 mL effective filtration volume. A gas cylinder with pressurized nitrogen was applied to provide a constant pressure (40 kPa), and a digital balance was used to record the permeate weight. The membrane utilized in this study was made from polyvinylidene fluoride (PVDF) material (Shanghai SINAP Co. Ltd., China). The membrane was characterized as 0.1 μm pore size and 140 kDa molecular weight cut-off (MWCO). Prior to the tests, all the membranes were submerged in deionized (DI) water for 24 h and then compacted with 40 kPa pressure for 20 min until the flux of DI

water was stabilized. The filtration resistance of membrane, pore clogging and alginate gel layer were determined according to Darcy's law:

$$R_{Tot} = \frac{\Delta P}{\sigma J} = R_m + R_p + R_g \quad (1)$$

where ΔP is the trans-membrane pressure (TMP, kPa); σ represents the dynamic viscosity of permeate (Pa s); J is filtration flux; R_{Tot} , R_m , R_p and R_g stand for total filtration resistance, membrane filtration resistance, pore clogging resistance and gel layer resistance, respectively.

Value of R_m was obtained by filtration through virgin membrane with DI water. The fouled membrane was acquired by filtering SA hydrogels formed with different Ca²⁺ concentrations (0, 0.5, 1, 1.5, 2, 2.5, 3, 4 and 6 mM) through virgin membrane for 5 min, followed by rinsing with DI water. Values of R_p were reckoned by filtrating DI water through the fouled membrane according to the following equation:

$$R_p = \frac{\Delta P}{\sigma J} - R_m \quad (2)$$

In order to investigate the effect of Ca²⁺ concentration on the R_g of SA hydrogel, 20 mL SA solution with series of Ca²⁺ concentration was first filtrated in the stirred cell to form a gel layer, and then, 250 mL DI water was used to filtrate through the formed gel layer. R_g can be calculated by Eq. (3):

$$R_g = \frac{\Delta P}{\sigma J} - R_m - R_p \quad (3)$$

Specific filtration resistance (SFR) of SA solution can be calculated according to Wang et al. [33]:

$$SFR = \frac{2A_m^2 \Delta PK}{\sigma C_{SA}} \quad (4)$$

where A_m is the effective membrane area (m²); C_{SA} represents the concentration of SA (kg/m³); K is the time-to-filtration ratio, yielded from the slope of the curve plotting the ratio of filtration time to filtration volume (t/V) versus the filtration volume (V).

2.3. Evaluation of membrane fouling

The particle blocking and deposition phenomena regarding membrane fouling during filtration process can be described by blocking filtration model (Eq. (5)) and cake filtration model (Eq. (6)), respectively [34].

$$J = J_0 \exp(-K_p t) \quad (5)$$

$$J^2 = \frac{J_0^2}{1 + J_0^2 K_c t} \quad (6)$$

where J_0 is the initial filtration flux; K_p and K_c are the constants of pore blocking model and cake filtration model, respectively. Although the models were derived from a dead-end filtration mode, they can also be applied to a cross-flow filtration mode [35]. Substituting Eqs. (5) and (6) into Eq. (1) gives Eqs. (7) and (8).

$$\ln R_p = \ln R_m + K_p t \quad (7)$$

$$R_g^2 = R_m^2 + \frac{K_g \times \Delta p^2}{\mu^2} t \quad (8)$$

By plotting the filtration resistance to filtration time, the fitness of the above two models to the filtration data can be assessed, and then, the major cause of membrane fouling during filtration process can be evaluated.

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