Cleaning strategies for iron-fouled membranes from submerged membrane bioreactor treatment of wastewaters

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ABSTRACT

Cleaning strategies for iron-fouled membranes from submerged membrane bioreactors (MBRs) dosed with iron salts are investigated here. Severe membrane fouling resulting from iron dosing was observed with amorphous ferric oxyhydroxide particles and gelatinous assemblages containing Fe(III) bound to polysaccharide materials responsible particularly for irreversible membrane fouling. Sodium hypochlorite (NaOCl) and citric acid, the most commonly used chemical cleaning agents, were not particularly effective in removing iron species from the membrane surface while the Fe(III) reducing agents ascorbic acid and sodium dithionite were very effective in removing iron-containing deposits under the conditions used in this study. In the presence of oxygen, the Fe(III)-catalysed oxidation of ascorbic acid and direct oxygen-mediated oxidation of dithionite control the dissolution rate constant. Use of NaOCl followed by ascorbic acid at concentrations of 10–20 mM is recommended as a reasonable balance between cleaning effectiveness and cost though further investigation of cleaning of fouled membranes from full scale MBRs is required.

1. Introduction

Membrane bioreactor (MBR) technology is widely viewed as being state of the art for wastewater treatment due to the ability to achieve good contaminant removal whilst possessing small footprint and decreasing capital and operating cost [1]. However, the management of membrane fouling remains a key challenge for the operators of MBR plants as it results in increased power and chemical consumption and decreased membrane life. As such, an effective cleaning strategy is critical to both day-to-day performance and overall treatment cost.

Possible contributors to membrane fouling are typically considered to include 1) a cake layer that is loosely associated with the membrane surface, 2) a more impermeable gel layer that is more tightly bound to the membrane surface, and 3) blocking of membrane pores by particulates small enough to be transported into the membrane. Mixed liquor suspended solids (MLSS), soluble microbial products (SMP) and extracellular polymeric substances (EPS) are the most significant contributors to membrane fouling in MBRs [2–8]. The cake layer on the membrane surface is mostly formed by biomass flocs since they are generally much larger than

the membrane pore size while gel layer formation and pore blocking are normally associated with SMP and EPS since they may attach to and then accumulate on the membrane surface [5,7,9,10] and their sizes are typically comparable to or even smaller than those of the membrane pores [8,11].

Both physical cleaning and chemical cleaning strategies are usually adopted in routine MBR operation. Physical cleaning techniques include use of intermittent filtration involving regular, short (typically on the order of one minute) "relaxation" periods (during which no filtration takes place enabling bubbling to more effectively remove any accumulated deposits on the membrane surface) and less frequent rinse and backwash procedures. While fouling associated with the presence of a cake layer on the membrane surface can be reduced by physical cleaning, chemical cleaning is required for reduction in fouling associated with the presence of a gel layer and blocked pores [2]. Sodium hypochlorite (NaOCl) and citric acid are the prevalent chemical cleaning agents recommended by the main MBR suppliers [2] with NaOCl considered effective in removal of organic foulants and citrate considered effective in removal of inorganic foulants.

In order to prevent eutrophication of receiving water bodies, low total phosphorus (TP) concentrations (typically of 0.01–0.3 mg/L) in wastewater effluents are mandated in many countries. Coagulants such as ferric chloride and aluminium sulphate are widely used for achieving P removal from effluents from traditional biological unit

operations and are now also being used in MBR plants [12–15]. While addition of coagulant following biological treatment, with a separate secondary clarification step, provides good control over the process, addition of the coagulant directly to the MBR vessel provides many advantages, particularly in terms of reduced footprint and associated costs.

While dosing with ferric chloride directly to the MBR vessel has been shown previously to improve filterability [16–18], the objective of dosing in those studies was to improve floc characteristics with Fe dosing levels too low for any effective removal of P. At higher levels of Fe dosing required to effect P removal [19], there is the potential to significantly increase problems with fouling due to the rapid and extensive formation of colloidal iron oxides [20]. Typically, the metal-salts dosage is 1.5–2.5 times the stoichiometric amount with a practical mole ratio of Fe to P of 2:1 required to treat wastewater with 10 mg P/L and provide an effluent with 1 mg P/L [21]. An even higher dosage of iron salts is usually required in Australian full scale MBR plants to ensure sufficient and consistent removal of phosphorus below 0.1–0.3 mg/L [22] though severe membrane fouling might be expected at such high dosages. As such, understanding the fouling performance at high Fe dosages is particularly important for the operation of MBRs to which strict P discharge limits apply.

As shown by Wang and Waite [20], most of the iron added to MBRs is retained in the sludge with over 60% converted to highly insoluble ferric oxyhydroxide and the rest associated with the biomass, a portion of which will deposit on the membrane surface in the form of a cake layer. Dissolved organic molecules may form soluble (or possibly macromolecular) complexes with Fe(III) (depicted as Fe(III)SMP by Wang and Waite [20]) which, particularly in the presence of divalent ions such as Ca^{2+}, may associate on the membrane surface as a gel layer. Organics may also stabilise amorphous ferric oxide (AFO) in colloidal form with this material presumably able to penetrate but ultimately clog membrane pores.

While citrate is recognised as a strong Fe(III)-binding ligand and may promote removal of Fe(III)-containing gels and oxides from the membrane surface and pores via ligand-promoted dissolution, reductive dissolution using agents such as ascorbic acid (Asc) or dithionite might be expected to be more effective given the relative rates of ligand-promoted versus reduction-promoted dissolution [20,23–28]. In terms of the standard reduction potential, both Asc (0.06 V) [29] and dithionite (−0.66 V) [30] have much lower reduction potential than that of Fe(III) (0.77 V) [31] though the actual reduction potentials in the wastewater environment will depend very much on speciation and concentration

with pH likely to play an important role. To date, however, no systematic studies on the efficacy of such Fe(III) reductants for the cleaning of iron-fouled membranes have been reported.

In this study we investigated the effectiveness of different strategies for the chemical cleaning of membranes that had been fouled under a dosing regime where ferric chloride had been added for the purpose of maximising phosphorus removal. Traditional strategies using sodium hypochlorite and citric acid were compared to the use of the reductants ascorbic acid (Asc) and sodium dithionite for the removal of Fe(III) based foulants from the membranes. Hydraulic performance of the MBRs is first reported where severe Fe-related gel layer fouling and/or pore blocking subsequent to Fe(III) dosing, indicating the necessity of chemical cleaning, were observed. The impact of parameters such as concentration and pH in determining the effectiveness of the cleaning regimes was investigated through studies on small membrane modules. From these results, optimal protocols for cleaning of the large modules were developed. The effectiveness of various cleaning strategies was assessed by analysing and comparing Fe removal and the associated membrane resistance.

2. Materials and methods

2.1. Membrane bioreactors

Three bench-scale MBRs with a working volume of 30 L each were operated at 22 °C, a mixed liquor suspended solid (MLSS) concentration of 8 g/L, a hydraulic retention time (HRT) of 10 h and a solids retention time of 30 days for five months (> 4 SRT's) before ferric chloride was continuously added to two of the reactors (the third was maintained as a "no iron addition" control). Each MBR contains an anoxic zone (6 L), an aerobic zone (18 L) and a membrane compartment (6 L) separated by baffles (Fig. 1). Two identical modules of reinforced polyvinylidene fluoride (PVDF) hollow fiber membranes with nominal pore size 0.2 μm and total surface area 0.2 m^2 (Beijing Origin Water, China) were arranged in a vertical configuration within the bioreactors. The membranes operated at a flux of 16.7 L/m^2 h under continuous coarse bubble aeration in 10 min filtration cycles consisting of 9 min of filtration and 1 min of relaxation. Transmembrane pressure (TMP) was continuously monitored by pressure transducers and the data recorded using Labview® (National Instruments, USA). The operational parameters for the MBRs are described in detail in the Supporting information (Table s1). Filtration was interrupted
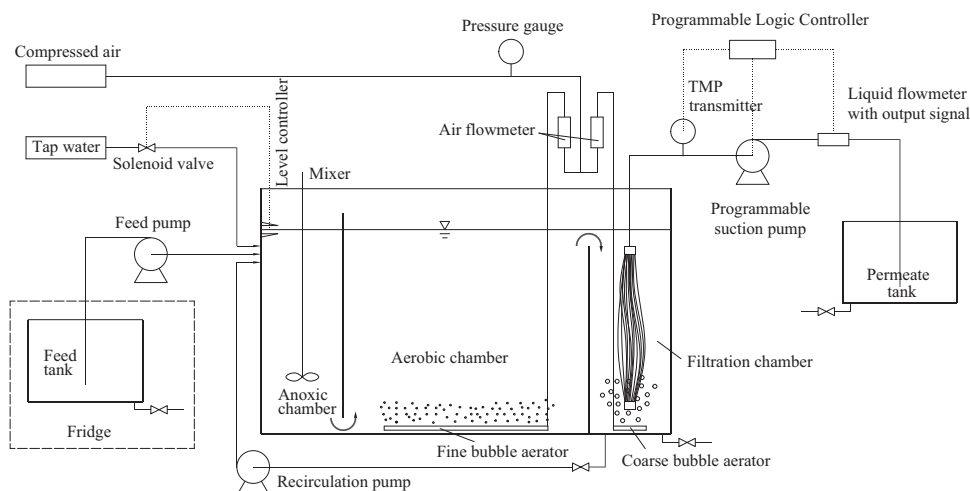

Fig. 1. Schematic diagram of the bench-scale MBR system.