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Ascorbic acid-mediated reductive cleaning of iron-fouled membranes from submerged membrane bioreactors

Zhenghua Zhang, Mark W. Bligh, T. David Waite*

Water Research Centre, School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

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ABSTRACT

The ascorbic acid (Asc)-mediated cleaning of iron-fouled membranes from submerged membrane bioreactors (MBRs) dosed with iron salts for facilitation of phosphorus removal is investigated here with the cleaning process, involving the reductive dissolution of iron oxides on the membrane surface and within membrane pores, conducted under both oxic and anoxic conditions and in the presence of 1,10-phenanthroline, a strong Fe(II)-binding ligand. A significant reduction in cleaning effectiveness was observed when oxygen was present with kinetic modelling of key processes operating in this system indicating that the reduced effectiveness could be attributed to the Fe(III)-catalysed oxidation of ascorbate with Fe(III) being replenished by the relatively rapid heterogeneous oxidation of Fe(II). While either removal of oxygen or addition of Fe(II)-binding agents such as phenanthroline are effective in preventing the Fe(III)-catalysed oxidation of ascorbate, cleaning of iron oxide-fouled membranes under oxic conditions with frequent replenishment of freshly prepared Asc is recommended as a reasonable balance between cleaning effectiveness and cost.

1. Introduction

In order to prevent eutrophication of receiving water bodies, low total phosphorus (P) 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 [1–4].

High levels of Fe dosing are required for effective P removal with Fe:P molar ratios of 2–4 [5] typical of the Fe(III) dosages used at full scale MBR plants in Australia and other countries where low phosphorus targets are commonly prescribed in view of the sensitivity of the receiving waters to algal growth [6]. However, the addition of high levels of Fe to the bioreactors significantly increases problems with fouling, particularly over long term operation due to the rapid and extensive formation of colloidal iron oxides and their associations with other constituents [7–10]. Amorphous ferric oxyhydroxide particles (AFO) and gelatinous assemblages containing Fe(III) bound to polysaccharide materials are responsible particularly for gel layer formation and/or pore blocking, indicating the necessity of chemical cleaning [8–10]. However, it has been reported that the prevalent chemical cleaning agents, sodium hypochlorite and citric acid, are not particularly effective in removing iron species from the membrane surface [10].

Ascorbic acid (Asc) is recognised to be particularly effective in reducing the ferric iron (Fe(III)) present in iron oxyhydroxide particles to the more soluble ferrous (Fe(II)) form [11–13]. While the results of these studies suggest that ascorbic acid could be an effective cleaning agent for iron oxide-fouled membranes, the studies were undertaken under anoxic conditions and/or were focussed only on the initial phase of dissolution [11–13]. In terms of chemical cleaning of iron-fouled membranes, significantly longer dissolution times (12–48 h) than used in these studies [11–13] are likely to be needed to ensure effective foulant removal [10]. Additionally, use of oxic rather than anoxic conditions would be far preferable in view of the difficulty (and associated cost) of oxygen removal. Indeed, results of preliminary studies of the use of ascorbic acid as a cleaning agent for iron oxide-fouled membranes reveal that the process is much less effective in the presence compared to the absence of oxygen though the exact reason for the deleterious effect of oxygen is unclear [10]. In view of this, further insight into the processes operating during the ascorbate-mediated reductive dissolution process is required in order to optimise the Asc cleaning of iron-fouled membranes.

In this study, we investigate the ascorbic acid-mediated reductive cleaning of Fe(III)-based foulants from membranes used in submerged membrane bioreactors to which ferric chloride had been

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* Corresponding author. Tel.: +61 293855059; fax: +61 293138341.
E-mail address: d.waite@unsw.edu.au (T.D. Waite).

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added for facilitation of phosphorus removal. Investigations of the ascorbic acid-mediated cleaning of iron-fouled membranes were undertaken over a range of conditions including oxic dissolution, oxic dissolution with near constant ascorbate concentration, anoxic dissolution and oxic dissolution in the presence of phenanthroline. Based on the findings of these studies, a kinetic model of the major processes operating in the ascorbic acid-mediated dissolution of iron oxides is developed enabling quantitative description of the rate of Asc membrane cleaning under oxic conditions.

2. Materials and methods

2.1. Formation of iron-fouled small membrane modules

Accelerated fouling and cleaning studies were conducted using a small membrane module containing four polyvinylidene fluoride (PVDF) hollow fibre membranes (Beijing Origin Water, China) with nominal pore size 0.1–0.3 μm, diameter 0.24 cm, length 15 cm and total surface area 0.0044 m^2. The small module was oriented vertically in the membrane bioreactor to which a 37.2 mM ferric iron solution was dosed to facilitate phosphorus removal (Fe/P molar ratio of 4) [10]. The small membrane module was operated at a constant flux of 30 L/m^2.h (with no relaxation) for a two week period before cleaning studies were undertaken.

2.2. Cleaning studies of iron-fouled membranes

After operation for two weeks, the fouled membranes were rinsed with MQ water and then cut into a number of 5 cm length pieces and immersed in 50 mL of Asc cleaning solutions at different concentrations and different conditions as follows:

(1) under oxic condition;
(2) under oxic condition with near constant ascorbate concentration;
(3) under anoxic condition; and
(4) under oxic condition in the presence of phenanthroline

Note that “oxic condition” is meant to convey that the cleaning solutions are open to the atmosphere and, as such, contain oxygen while “anoxic condition” indicates that the solutions are closed to the atmosphere and have been sparged of residual oxygen. Dissolved oxygen concentrations in both the oxic and anoxic cases were determined using a dissolved oxygen probe. Solutions were, in all cases, unstirred with the pH of the Asc solutions carefully controlled at 4 with an appropriate buffer (sodium acetate (8.2 mM)/acetic acid (1.8 mM)). We confirmed that the sodium acetate/acetic acid buffer negligibly influences the iron oxyhydryoxide foulant with less than 2% removal of iron from the iron-fouled membrane surface after 12 h reaction. Also, very similar cleaning performance was observed with both the non-complexing buffers 1,4-diethylpiperazine and sodium acetate/acetic acid as shown in Fig. S1. Aliquots (5 mL) of the membrane-leachate solution were removed after various intervals of immersion for measurement of total Fe by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Agilent 7300, USA). After Asc cleaning, each fouled membrane was immersed for a further 24 h in 50 mL of 300 mM sodium dithionite in order to remove any residual iron remaining on the membrane. Based on this technique, a measure of the initial iron concentration on each membrane (C_0) was taken to equal the iron concentration in the wash solution after Asc cleaning plus the residual iron concentration in the dithionite wash solution. The cleaning effectiveness of different agents was quantified by comparing the undissolved iron fraction on the membrane (f) ($f=(C_0-C)/C_0$, where C is the released iron concentration and C_0 is the initial iron concentration).

2.2.1. Dissolution under oxic condition

The membrane pieces were immersed in ascorbic acid solutions with concentrations of 1, 2, 3, 5, 10 and 20 mM at controlled pH 4 for periods of up to 48 h.

2.2.2. Dissolution under oxic condition with near constant ascorbate concentration

Freshly prepared ascorbic acid solutions with concentrations of 1 and 10 mM at controlled pH 4 were applied for periods of up to 6 h. At each leachate analysis time (10, 20, 30, 40, 50, 60, 90, 120, 240 and 360 min), the Asc solution was replaced with fresh solution such that the Asc concentration was maintained approximately constant.

2.2.3. Dissolution under anoxic condition

Ascorbic acid solutions with concentrations of 1, 2, 3, 5, 8, 10 and 20 mM at controlled pH 4 were applied for periods of up to 6 h. Asc cleaning solutions were bubbled with argon gas for 10 min before membrane immersion with bubbling continued during the cleaning experiments in order to ensure the removal of oxygen.

2.2.4. Dissolution under oxic condition in the presence of phenanthroline

1,10 Phenanthroline is a strong Fe(II) binding ligand with three molecules of phenanthroline chelating a single Fe(II) molecule [14]. 1 mM of 1,10 phenanthroline, which is in excess of the iron concentration in the Asc cleaning solutions (20–200 μM), was included in the pH 4 1 mM and 10 mM Asc cleaning solutions in order to assist in elucidation of the Asc dissolution mechanism.

2.3. Specific surface area (in m^2 g^{-1}) measurement of iron oxyhydroxides on the membrane by BET analysis

The surface area, pore volume and pore size of 5 cm pieces of one fresh membrane and two identical iron-fouled membranes after Milli-Q water rinse were determined using a nitrogen adsorption analyser (Micromeritics Tristar, USA) with the adsorption/desorption nitrogen isotherms (Fig. S2) analysed using the BET model. Samples were pre-treated by heating the membranes at 30 °C overnight under vacuum. After the BET analysis, the same fouled membrane was immersed in 10 mL of 300 mM sodium dithionite for 24 h in order to remove the iron remaining on the membrane and the iron concentration determined by ICP-AES.

2.4. Kinetic modelling

The MS-Excel based modelling programme Kintecus [15] was used to fit a kinetic model to the experimental data.

3. Results

3.1. Dissolution of iron-fouled membranes under various conditions

Under oxic conditions, the percentage of iron dissolved from the membrane increased with increase in ascorbic acid concentration with essentially complete dissolution of iron from the membrane observed after 20–30 h at the higher Asc concentrations though only partial dissolution, even after 48 h, occurred at lower Asc concentrations (Fig. 1). As shown in Fig. 2, a significant increase in proportion of Fe dissolved was observed when the ascorbic acid was frequently replenished. Similarly, greater cleaning effectiveness with higher dissolution rates at particular Asc concentrations are observed under anoxic conditions than was the case in the presence of oxygen (Fig. 3). The rate and extent of oxic dissolution was found to be substantially higher in the presence of