Ligand-promoted reductive cleaning of iron-fouled membranes from submerged membrane bioreactors

Zhenghua Zhang[a,b], Mark W. Bligh[a], Xiu Yuan[a], T. David Waite[a,*]

[a] Water Research Centre, School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia
[b] Tsinghua-Kangda Research Institute of Environmental Engineering & Nano-Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, Guangdong, China

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ABSTRACT

Four pathways for cleaning of iron oxide-fouled membranes, namely i) proton (acid)-assisted, ii) ligand-promoted (citric acid), iii) reductive (ascorbic acid), and iv) ligand-promoted reductive (ascorbic acid-citric acid-mediated) were examined and their effectiveness were compared in this study. The cleaning effectiveness under oxic conditions followed the order: proton-assisted < ligand-promoted < reductive < ligand-promoted reductive. Iron oxide dissolution rate initially increased with increase of citrate concentration in the ascorbic acid-citric acid solutions but declined at higher citrate concentrations indicating that an intermediate citrate concentration was required for optimal cleaning. The mechanism of ligand-promoted reductive dissolution mediated by ascorbate and citrate was investigated through studies of dissolution behaviour under both oxic and anoxic conditions with citrate shown to have a mitigating effect on the consumption of oxygen, apparently by reducing the iron catalyzed oxidation of ascorbate. Kinetic modelling showed that the dynamics of dissolution could be reasonably well simulated with the inclusion of a surface > Fe(III)-citrate-Fe(II) ternary complex which facilitates the detachment of surface Fe(II). Use of dual reagents (ascorbic acid and citric acid) under oxic conditions is recommended for the cleaning of iron-fouled membranes in view of the extreme cleaning effectiveness though it is critical that cleaning conditions be carefully optimised.

1. Introduction

Coagulants such as ferric chloride and aluminium sulphate are widely used for achieving phosphorus (P) removal from effluents of traditional biological unit operations and are now also being used in MBR plants [1–4]. High levels of iron dosing with Fe: P molar ratios of 2–4 are typical of the Fe(III) dosages used in full scale MBR plants in Australia for facilitation of sufficient and consistent P removal (typically 0.01–0.3 mg/L in effluents) in view of the sensitivity of receiving waters to algal growth [5,6]. However, severe membrane fouling resulted from high levels of Fe with amorphous ferric oxyhydroxide (AFO) particles and gelatinous assemblages containing Fe(III) bound to polysaccharide materials particularly responsible for gel layer formation and pore blockage, necessitating the application of an effective membrane chemical cleaning regime to remove iron species from the membrane [7–10]. Chemical reagents such as acids (hydrochloric, sulfuric, citric, oxalic, etc.), bases (caustic soda), oxidants (hypochlorite and hydrogen peroxide) and other chemicals (chelating agents, surfactants, etc.) have been widely used to remove materials from irreversibly fouled membranes [11] though little attention appears to have

been given to which of these, if any, are well suited to the cleaning of iron oxide fouled membranes.

With regard to the dissolution of iron oxides, there are four general pathways in acidic aqueous suspensions: proton (acid)-assisted, ligand-promoted acid, reductive, and ligand-promoted reductive dissolution [12,13]. The first two pathways involve the adsorption of proton and ligand to the surface of iron oxides which results in weakening of the bonds in the proximity of a surface Fe(III) center followed by slow detachment of the surface Fe(III) to solution [12]. If the surface Fe(III) is reduced to surface Fe(II) by reductants, the detachment of surface Fe(II) into solution is much faster than that of surface Fe(III) due to the higher lability of the Fe(II)–O bond compared to the Fe(III)–O bond [12]. Reductive dissolution of Fe oxide minerals involves many steps, including reductant adsorption, electron transfer, detachment of oxidised reductant, and detachment of Fe(II) (the rate determining step) [14]. Previous workers have reported that the detachment of surface Fe(II) might be accelerated in the presence of a ligand with ligand-promoted reductive dissolution (i.e. ascorbate-EDTA; ascorbate-oxalate; dithionite-citrate) shown to be particularly effective in promoting fast dissolution of iron oxides [13,15,16], however, the mechanism

Nomenclature		EDTA	ethylenediaminetetraacetic acid
		f	percentage of undissolved iron on the membrane (%)
AFO	amorphous ferric oxyhydroxide	P	phosphorus
Asc	ascorbic acid (mM)	Fe(II)Cit	complex of Fe(II) and citric acid
Cit	citric acid (mM)	Fe(III)Cit	complex of Fe(III) and citric acid
C_0	the initial iron concentration on the membrane (mM)	>Fe(III)CitFe(II)	surface complex of Fe(III), citric acid and Fe(II)
C	the released iron concentration (mM)		

dominating such dissolution processes remains unclear.

Citric acid, a tricarboxylic acid that forms strong solution complexes with iron, is not particularly effective when used as a single cleaning agent for inorganics removal [17] while ascorbic acid, an effective Fe (III) reducing agent, has been shown to be especially effective in re- moving iron species from iron oxide-fouled membrane surface [10,18]. However, ascorbate-mediated reductive dissolution under oxic condi- tions is much diminished compared to that under anoxic conditions, apparently due to the catalytic oxidation of ascorbate via hetero- geneous re-oxidation of surface Fe(II) [18]. It has also been reported that the combination of a reductant and a strong chelating ligand is especially effective in promoting the dissolution of iron oxides due to the possible synergistic effects between these two agents [13]. For ex- ample, Banwart et al. [15] reported that in the presence of ascorbate, the adsorption of oxalate (a ligand capable of forming bidentate mononuclear surface complexes) leads to a significant increase in the rate of reductive dissolution of hematite even though the adsorption of oxalate displaces some of the ascorbate from the hematite surface. A similar synergistic effect of reductant and complexant has also been observed in the dissolution of goethite by dithionite and citrate or EDTA [16]. Therefore, it is reasonable to postulate that in a system with both ascorbic acid and citric acid, ligand-promoted reductive dissolution could also occur and be more effective than ascorbate-mediated re- ductive dissolution for iron oxides-fouled membranes.

In this study, we investigated proton-assisted (acid), ligand-pro- moted (citric acid), reductive (ascorbic acid), and ligand-promoted re- ductive (ascorbic acid-citric acid-mediated) cleaning of Fe(III)-based foulants from membranes used in submerged membrane bioreactors to which ferric chloride had been added for facilitation of phosphorus removal. Detailed investigations of the ascorbic acid-citric acid-medi- ated reductive cleaning of the iron-fouled membranes were undertaken under both oxic and anoxic conditions. Based on the findings of these studies, a kinetic model was developed as an aid to elucidating the key factors controlling the effectiveness of the dual reagent cleaning pro- cess. This model may also assist in determining the conditions that are optimal for removal of iron foulants in practical cleaning procedures.

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 (Fe/P molar ratio of 4) was dosed to facilitate phosphorus removal [9]. The small membrane module was operated at a constant flux of 30 L/ m^2 h (with no relaxation) for a period of two weeks 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
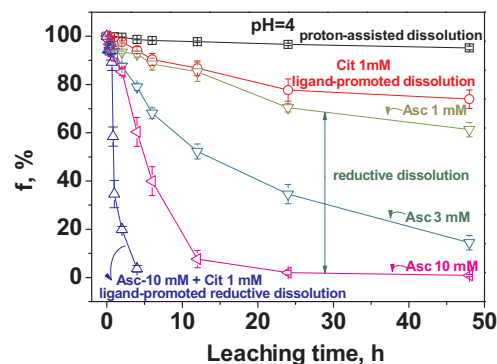

Fig. 1. Cleaning effectiveness of iron-fouled membranes at pH 4 with i) hydrochloride acid, ii) citric acid (Cit) at concentration of 1 mM, iii) ascorbic acid (Asc) at concentra- tions of 1, 3 and 10 mM, and iv) Asc-Cit at concentrations of 10 mM of Asc and 1 mM of Cit. Fraction (f) is representative of the percentage of undissolved iron on the membrane ($f = (C_0 - C)/C_0$, where C is the released iron concentration and C_0 is the initial iron concentration) as a function of leaching time.
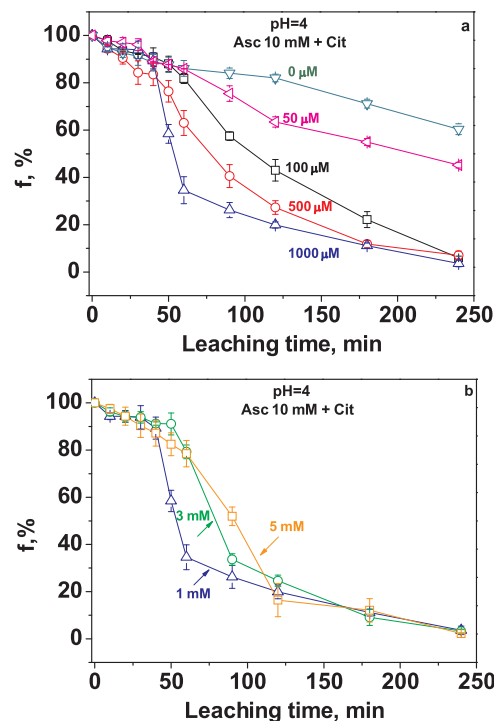

Fig. 2. Cleaning effectiveness of iron-fouled membranes at pH 4 in ascorbic acid (Asc)- citric acid (Cit) solutions with Asc concentration of 10 mM and Cit concentrations of 50, 100, 500, 1000 (a), 3000, 5000 μM (b). Fraction (f) is representative of the percentage of undissolved iron on the membrane ($f = (C_0 - C)/C_0$, where C is the released iron con- centration and C_0 is the initial iron concentration) as a function of leaching time.

immersed in 50 mL of one of the cleaning solutions from the following experimental configurations:

1. Hydrochloride acid; pH 4
2. Citric acid (Cit); pH 4; 1 and 10 mM