Impact of iron dosing of membrane bioreactors on membrane fouling

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HIGHLIGHTS

- Examination of impact of dosing of Fe(III) salt on resultant supernatant Fe(III) speciation.
- Assessment of implications of supernatant Fe(III) speciation on membrane fouling.
- Analysis of extent of Fe redox transformations following dosing of Fe(III) salt and assessment of impact on membrane fouling.
- Deductions concerning likely mechanism(s) of colloidal iron oxyhydroxide formation.

ARTICLE INFO

ABSTRACT

Flux decline in bench scale membrane bioreactors (MBRs) configured for chemical phosphorous removal using ferric chloride increased as the molar Fe to P ratio increased from 2 to 4 and was strongly dependent on the valence state of the low concentrations of filterable iron present in the supernatant. MBRs operating without pH control over the pH range 5.1–7.1 exhibited variable but generally higher concentrations of dissolved and colloidal (<0.8 μm filterable) iron in the supernatant of the anoxic zone (1.18–26.43 μM) than in the aerobic and membrane chambers (0.18–6.72 μM). At pH 5.1, 97% of the iron suspended in the anoxic chamber was present as Fe(II). In contrast, the concentration of iron was relatively uniform in the three chambers of the MBRs (3.2 ± 0.4 μM) when pH was controlled by caustic addition. Under pH-controlled conditions, 70–80% of the iron in the supernatant was in the form of soluble (<0.2 μm) Fe(II) rather than Fe(III). While dosing of the MBRs with a moderate concentration of ferric chloride (Fe/P molar ratio of 2) led to effective phosphorus removal and minimal enhancement in extent of fouling, a higher ferric chloride dose (Fe/P = 4) gave little improvement in P removal and led to severe membrane fouling. While Fe(III) dosing is an effective strategy for P removal provided sufficient Fe is added, the dangers of overdosing are severe with careful optimisation of dose clearly required in order to avoid debilitating membrane fouling.

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1. Introduction

Ferric chloride is commonly used in municipal wastewater treatment as an aid to odour control as well as phosphorus removal [1,2]. Theoretically, one mole of iron is required to precipitate one mole of phosphorus with the resulting mineral, strengite ($FePO_4 \cdot 2H_2O$), exhibiting a minimum solubility at pH 5.3 [3]. However, significant differences between theory and practice have been observed with values of the Fe to P molar ratio between 1 and 7.5 reported to achieve maximum phosphorous removal in wastewater treatment plants [4]. Rittmann and McCarty state that the optimal 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 in order to produce an effluent with 1 mg P/L [5]. This is because the phosphorous removal efficiency is not only affected by the influent characteristics and discharge limit but also by operating conditions (such as pH, temperature, reactor configuration and micro-organisms present) [1,6]. These factors influence the forms of Fe and P species present and the affect the rate and extent of transformation between these species [3,7–10]. For example, on initial addition of an inorganic ferric (Fe(III)) salt to the mixed liquor, Fe(III) may form amorphous ferric oxyhydroxide (AFO) precipitates which subsequently may adsorb phosphate, organic compounds such as soluble microbial products (SMP) and other dissolved constituents. Whether this process involves iron oxyhydroxide nucleation and particle formation followed by adsorption of constituents such as phosphorus to oxyhydroxide surface sites or results in coprecipitation of iron and phosphorus will depend

upon the precise conditions of pH and local concentrations of sorbing species [11,12].

It is also possible that, rather than precipitating, dissolved ferric ions may form a complex with soluble microbial products [10]. The formation of these species will be determined by the strength of association between $Fe(III)$ and particular organic functional groups and the concentration of compounds containing these functional groups present in the supernatant. Active uptake of a portion of the added iron by the consortium of organisms present will occur as will association of iron oxyhydroxide particles with organism surfaces [13]. Reduction of $Fe(III)$ species to ferrous ($Fe(II)$) forms may occur if the ferric salt is added to the anoxic zone of the MBR given the low redox potential ($E_h < -0.2$ mV) of this zone and the likely presence of reducing moieties such as hydroquinones with the subsequent possible formation of vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O(s)$) [14]. In some instances, ferrous iron rather than ferric iron is added because of the lower cost of ferrous compared to ferric salts though oxidation of the added $Fe(II)$ will be necessary in this case for effective removal of phosphorus [15]. A schematic of the various iron transformation processes that might be expected to occur on addition of either ferric or ferrous salts to a membrane bioreactor is provided in Fig. 1.

While use of submerged membrane bioreactor technology has risen dramatically over the last ten years, there has been only limited investigation of the variety of reactions that can occur on addition of coagulants to membrane bioreactors and the impact of this addition on phosphorous removal and membrane fouling. In contrast to chemical phosphorous removal in conventional activated sludge (CAS) systems where the inorganic salts are typically added downstream of the activated sludge process but upstream of tertiary filters, in MBR processes iron or aluminium salts are typically added to the mixed liquor. Consequently, the logistics and control of chemical addition along with the mechanics and efficiency of the chemical phosphorous removal process are more complex in the MBR process compared to the CAS process. The addition of inorganic salts such as ferric chloride for phosphorus removal is almost certain to influence the properties of the mixed liquor and hence the extent of membrane fouling. Indeed, it is now recognised that it is the colloidal and soluble microbial products (SMP) present in the mixed liquor that are principally responsible for membrane fouling as these products have comparable size to the membrane pores and also exhibit a tendency to form impermeable gels on the membrane surface [16–20]. While there has been some investigation of the interaction of coagulants with these colloidal and soluble microbial products [21–25], most of these studies have been of a relatively low dosage which is not sufficient for phosphorus removal and with limited insight gained into the nature of the Fe-SMP entities formed or their impact on membrane fouling. Understanding the interactions of high amounts of iron with organics present in the membrane bioreactors is particularly important for the operation of MBRs in Australia. Severe membrane fouling has been observed in a full-scale MBR plant where an Fe:P molar ratio of 4.8:1 was used for both odour control and phosphorus removal to meet the stringent discharge limit. As such, the aim of this paper is to investigate the speciation and transformation of iron in different chambers of laboratory scale membrane bioreactors to which molar ratios of Fe to P typically present in Australian wastewater treatment plants have been added and to
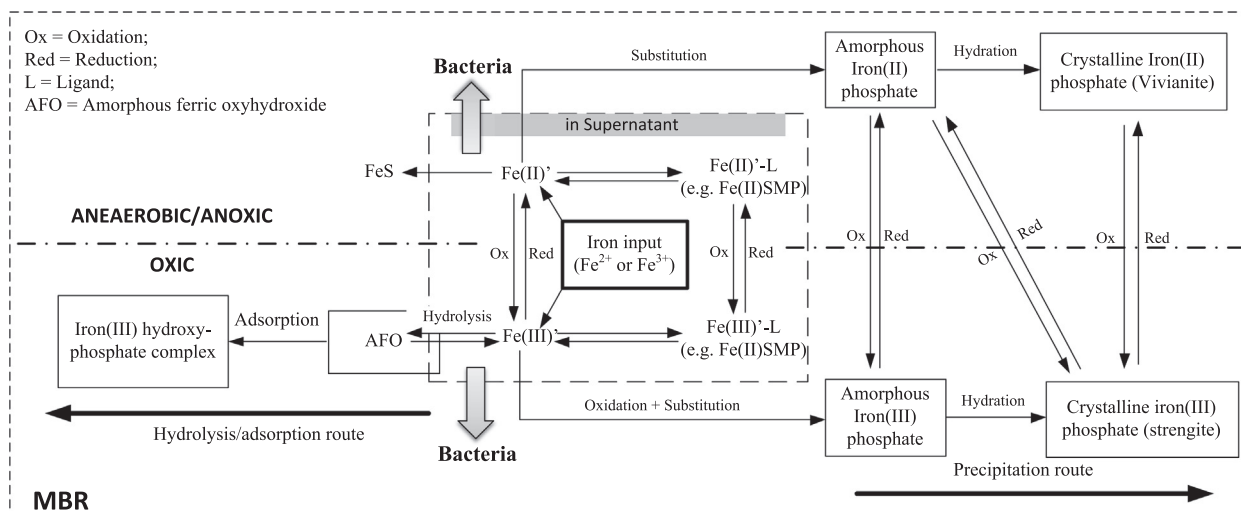

Fig. 1. Schematic of key chemical transformations that may occur on addition of iron to a membrane bioreactor.