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Influence of phosphorus precipitation on permeability and soluble microbial product concentration in a membrane bioreactor

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HIGHLIGHTS

- MBR pilot-plant with flat sheet membrane fed by raw municipal wastewater was monitored for 2 years.
- Impact of coagulant dosing on flux, nutrient removal, SMP and filtration cake was evaluated.
- Coagulant dosing resulted in a significant decline in carbohydrates and protein concentrations.
- High PO_4-P, COD and NH_4-N removal efficiency was achieved over periods with coagulant dosing.
- The main contributors to inorganic fouling were compounds of elements Ca, Si and Fe.

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ABSTRACT

Many articles have been published on coagulant dosing in membrane bioreactors, though few have been long-term studies examining the treatment of real wastewater. This study summarises the results of a membrane bioreactor pilot-plant (flat sheet membrane, nominal pore size 0.03 μm) that treated real municipal wastewater for two-years. Both influence of phosphorus precipitation by ferric sulphate on membrane permeability (flux decrease) and soluble microbial product concentration (especially on carbohydrates and proteins) were monitored. Flux decrease over work cycles lasting several months without phosphorus precipitation were compared to two periods with precipitation. X-ray elemental diffractometry of the filtration cake showed differences in the main contributors to inorganic fouling, with decreases in Ca and Si during operation with coagulant addition, and an increase in Fe.

1. Introduction

A membrane bioreactor (MBR) includes a membrane separation process into the standard activated sludge process. Inclusion of this process eliminates the weakest link in activated sludge wastewater treatment, making effluent quality independent of biomass settling characteristics. MBRs have several important advantages over conventional activated sludge systems, including high effluent quality, ease of operation and high bacteria removal efficiency.

MBR technology currently faces a number of research and development challenges, however, including membrane fouling, high membrane cost and the need for pretreatment. Membrane fouling increases operational costs and shortens membrane lifetime (Yang et al., 2006). Further, as the MBR mixed liquor includes both living organisms and their metabolites, the fouling is more complex than that of a simple membrane separation processes (Bae and Tak, 2005). Studies aimed at minimising membrane fouling can be divided into several groups: (i) those focused on the characteristics of the mixed liquor that affect membrane fouling, including its morphological characteristics (Lee et al., 2003; Gómez

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Abbreviations: C, carbohydrates; COD, chemical oxygen demand; EPS, extracellular polymeric substances; F/M, food to microorganisms ratio; HS, humic substances; IR, internal recycle; L_p, permeability; MLSS, mixed liquor suspended solids; MLVSS, mixed liquor volatile suspended solids; MBR, membrane bioreactor; NH_4-N, ammonia nitrogen; NO_3-N, nitrate nitrogen; P, proteins; PES, polyethersulphon; PFS, polymeric ferric sulphate; PFC, polymeric ferric chloride; PO_4-P, phosphate phosphorus; SMP, soluble microbial products; SRT, sludge retention time; $Y_{obs.}$, observed biomass yield; $W_{org.}$, proportion of organic fraction; WWTP, wastewater treatment plant.

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et al., 2012); (ii) soluble microbial products – SMP and extracellular polymeric substances – EPS (Dvořák et al., 2011; Holba et al., 2012); and (iii) addition of flux enhancers, such as organic flocculants or inorganic coagulants (Dizge et al., 2011; Ngo and Guo, 2009).

The characteristics of activated sludge can be altered by dosing with organic flocculants, such as flux enhancers, or by addition of inorganic coagulants, such as aluminium or ferric salts (Le-Clech et al., 2006). While both aluminium and ferric coagulants are known to improve mixed liquor filterability (Wu et al., 2006), a decrease in oxygen uptake rate and inhibition of the activated sludge process have both been described by Surmacz-Gorska et al. (1996) following addition of aluminium salts. While the inhibiting effects of aluminium salts on release of phosphorus are characterised by chemical reactions, however, those affecting phosphorus uptake are influenced by biological effects (Liu et al., 2011). The influence of ferric salts on the nitrification process is negligible, with concentrations lower than 40 mg L^{-1} having no influence on simultaneous chemical precipitation of phosphorus (Liu et al., 2011).

Higher coagulation efficiency can be achieved using pre-polymerised coagulants such as polymeric ferric chloride – PFC (Jiang and Graham, 1998) or polymeric ferric sulphate – PFS; Wu et al. (2006) reporting PFS to be the most effective coagulant for membrane fouling control. Polymeric coagulants also have a positive effect on charge production and longer chain molecules, resulting in improved mixed liquor filterability; the optimal dose being defined Wu et al. (2006) as 1.05 mM Fe. Surplus polymeric coagulant, however, can lead to "colloidal restabilisation". Fe(III) compounds are known to bridge negatively charged EPS functional groups, and also to promote an increase in floc size, density and shear force resistance (Li, 2005). In the Czech Republic, however, non-PFS is widely applied as a coagulant, hence the same form was chosen for this study.

In this study, the main aims of coagulant dosing were to minimise phosphorus concentrations in MBR effluent and to investigate the impact of precipitation products on flux decline; in part as detailed mechanisms of membrane fouling caused by Fe(III) compounds have yet to be classified. While many articles have been published about coagulant dosing in MBRs, most are based on laboratory-scale studies using synthetic wastewater (Zhang et al., 2008) or from short-term (few days) operation of a pilot-plant (e.g. Yang et al., 2011). This paper summarises results gained through two-years of MBR pilot-plant operation (four operational periods), during which actual municipal wastewater originating from a large agglomeration in central Bohemia was treated. In addition to coagulant dosing, impact on membrane fouling, nutrient removal efficiency, SMP concentration fluctuations and changes in filtration cake quality was also monitored.

2. Methods

2.1. Experimental set-up and operation

The MBR pilot-plant, which has a total volume of 510 L was operated for two years alongside a conventional municipal wastewater treatment plant – WWTP (central Bohemia, Czech Republic), allowing raw wastewater to be used as a feed. At the beginning of each operational period, activated sludge from the WWTP settling tank was used for inoculation of the MBR. Mechanical pre-treatment of the raw municipal wastewater consisted of filtration through fine 3 mm screens only. Main influent characteristics are summarised in Tables 1 and 2. The MBR was divided into two parts, i.e. anoxic and oxic sections (volume ratio 25% and 75%, respectively); the oxic section being equipped with fine bubble aeration (mean oxygen concentrations are provided in Tables 1 and 2). The internal recirculation flow from aerobic to anoxic section was provided by airlift with average flow 5 L $\min^{-1}$. Excess sludge was withdrawn periodically – according to the biomass concentration in the system. Separation of activated sludge was undertaken using a polyethersulphon (PES) flat sheet ultrafiltration membrane (nominal pore size 0.03 μm, 6 m^2) immersed in the oxic MBR section. Filtration took place at a constant transmembrane pressure of 50 mbar, which resulted in a decrease in flux over time due to membrane fouling. The MBR was equipped with simultaneous phosphorus precipitation using a 41% solution of ferric sulphate; the solution being added to the mixed anoxic sections during the 3rd and the 4th operational periods. Basic pilot-plant operational characteristics are shown in Table 3.

2.2. Analytical methods

Both influent into and effluent from the MBR were tested for chemical oxygen demand (COD), ammonia nitrogen (NH_4-N), nitrate nitrogen (NO_3-N) and phosphate phosphorus (PO_4-P). In addition, mixed liquor suspended solids (MLSS) were assessed gravimetrically. All parameters were measured in accordance with standard methods for water and wastewater examination (APHA, 2005).

Total EPS concentration was calculated as the sum of concentrations for four EPS groups: carbohydrate, humic substances, protein and DNA. SMP were analysed in the supernatant obtained by gravitational sedimentation. EPS in activated sludge were quantified following thermal extraction according to Morgan et al. (1990). Carbohydrates content was analysed using the method of Dubois et al. (1956), with the exception that 5% phenol was applied instead of 80% (Raunkjær et al., 1994). Protein was measured spectrophotometrically using the method of Lowry et al. (1951); and HS were measured according to Sharma and Krishnan (1966). Revised values for protein and HS concentrations were obtained using the method of Frølund et al. (1995). DNA was analysed using the method of Burton (1956).

3. Results and discussion

3.1. Influence of ferric sulphate dosing on effluent quality

The primary objective of the MBR pilot-plant was to minimise nutrient concentration in the effluent and increase nutrient removal efficiency. The pilot-plant was initially operated over two periods of 165 and 175 days without ferric sulphate dosing. Chemical characteristics of the influent and effluent over these periods, including removal efficiencies, are shown in Table 1. Very high COD and NH_4-N removal efficiency was achieved over these two periods at 96.8% and 97.5%, respectively, for COD and 97.9% and 87.1%, respectively, for NH_4-N. On the other hand, removal of phosphorus (in the form of orthophosphate), e.g. by biomass incorporation was found to be inefficient, at 23.3% and 54.7%, respectively. This led to a decision to undertake coagulant dosing. Though aluminium salts are known to have a positive impact on decreasing filamentous bacteria (Tandoi et al., 2006), a ferric coagulant was chosen due to its higher optimal coagulation pH, as well as its wide application in the Czech Republic. A non-PFS was used, though this may have resulted in a lower impact on increase in activated sludge floc size and less improvement in filterability. The optimal dosage of ferric sulphate solution (12.4 mg Fe L^{-1}) was calculated based on the mean incoming concentration of PO_4-P and hydraulic retention times observed over the two previous periods. A similar optimal dosage was reported by Yang et al. (2011), based on several batch tests using different dosages of PFC (5, 10, 15 and 20 mg L^{-1} of Fe); the final optimal dosage concentration being