Chemical equilibrium model to investigate scaling in moving bed biofilm reactors (MBBR)

Vasan Sivalingam[1]   Osama Ibrahim [1]   Sergey Kukankov[1]   Babafemi Omodara[1]   Eshetu Janka[1]   Shuai Wang[2]   Carlos Dinamarca[1]   Hildegunn HH [1]   Rune Bakke[1]

[1]Department of Process, Energy and Environmental Technology, University of South-Eastern Norway, Norway, `eshetu.j.wakjera@usn.no`

Biowater Technology AS, Norway, `sw@biowatertechnology.com`

Abstract

Moving bed biofilm reactor (MBBR) is a robust, flexible and compact technology for treatment of medium to high strength wastewater. However, while treating wastewater with high concentration of ammonium, phosphorus and metal ions, scaling on the biofilm carriers can occur, causing biofilm carriers to sink the bottom of reactors. That leads to less carrier motion, higher energy consumption and deteriorated mass transfer, causing lower process efficiency and increased operational cost. This can be a major MBBR operational challenge for certain types of wastewater. In this study, scaling on biofilm carriers in an MBBR reactor treating reject water from anaerobically digested wastewater sludge was investigated. The 67 L reactor was operated at 16 h hydraulic retention time (HRT) for over 250 days. The metal ion concentrations in the reject wastewater in and out of the MBBR were analyzed using microwave plasma-atomic emission spectroscopy (MP-AES). The chemical equilibrium simulation tool -- Visual MINTEQ 3.1 was applied to determine the possible mineral precipitates. The measured concentrations of Mg^{2+}, Ca^{2+}, Fe^{3+}, NH_4-N, PO_4^{3-}, SO_4^{2-} and alkalinity from the inlet and outlet of the reactor were used as inputs to the model. Dry biomass and precipitates from biofilm carriers were digested by a DigiPREP digestion system and element analysis performed using MP-AES for simulated data validation. The results show that Fe^{3+} and Ca^{2+} had the highest potential to form mineral precipitates and scaling on the biofilm carriers. Hematite, Maghemite, Hydroxyapatite, Geothite and Magnesioferrite were the first five predominant forms of mineral precipitates, in the pH range from 6.0 to 9.0. The saturation indices (SI) of these five minerals increased with pH, implying that measures to lower pH may reduce the problem. Digested biomass composition and inorganic solid analysis confirmed that calcium is the major cause for scale formation on the biofilm carriers. Crystal formations in the biofilms were confirmed by optical microscopy images.

Keywords: Visual MINTEQ, scaling, moving bed biofilm reactor, reject water

1 Introduction

Scaling on biofilm carriers is a major problem in moving bed biofilm reactors (MBBR) treating wastewater with high concentration of ammonium, phosphorus and metal ions. Scale formation occurs, e.g., in treatment of reject water from sludge digestion. When sludge is digested anaerobically, ammonia and soluble orthophosphate will be released from the sludge and end up in the reject water when such sludge is dewatered, and, in the presence of magnesium, calcium or ferric ions, could result in crystallization of inorganic salts. The amount of active biomass is an important factor in assessment the performance of MBBR, and the biomass growth chiefly depends on the designed carrier's effective surface area (ESA). During the MBBR operation, ESA can decrease because of excess biofilm biomass accumulation so that the area of biofilm exposed to the liquid (EBA) decreases. Surplus biofilm thickness may thereby have negative effect on the reactor's efficiency by reducing EBA and mass transfer and also by increasing carrier weight (Ødegaard, 2006; Piculell, 2016).

Crystallization can happen when a solution is supersaturated. This occurs when the solute concentration surpasses the equilibrium and nucleation occurs due to high free energy. Saturation index (SI) is an important parameter for determination of the probability for mineral precipitation. SI is a logarithmic ratio between ion activity product (IAP) and equilibrium constant (K_{sp}) in the wastewater treatment process (Sharp *et al.*, 2013)

$$SI = \log \frac{IAP}{K_{sp}} \qquad (1)$$

IAP (ion activity product) is quantified as a product of all comprised ion concentrations which should be measured as soluble ions. Ionic strength (I) depends on dissolved solids concentrations and can be calculated from (2).

$$I = \frac{1}{2} \sum Z_i^2 \, C_i \qquad (2)$$

Where, Z_i is the valency of the ion and C_i is the concentration. Ionic strength for wastewater is in the range of 0 to 0.2. If the composition of wastewater is unknown, it can be approximated as the dissolved solids [g/L] x 2.5 x $10^{-5} \times 2.5 \times 10^{-5}$ .Debye-Huckel method

uses mean ionic activity (γ) for activity correction as follows (Cellen, 2010):

$$\log \gamma = -0.5Z^2 \frac{\sqrt{I}}{1+\sqrt{I}} \qquad (3)$$

Visual MINTEQ 1.3 is based on Equations 1-3 and is one of the most used chemical equilibrium simulation tool to determine possible mineral speciation and estimate its solubility at chemical equilibrium. Visual MINTEQ is a simulation tool which can be used to compute the equilibrium composition of dilute aqueous solutions. It is a Windows version of MINTEQA2 equipped with inclusive thermodynamic data to estimate speciation, solubility and equilibrium of minerals in the solutions. It was found to be a good simulation tool in several studies which have been implemented in different versions of Visual MINTEQ to predict and control of possible mineral precipitations in wastewater. Jia (2014), applied Visual MINTEQ 3.0 to analyze the formation of struvite from sludge dewatering effluent from Bolivar wastewater treatment plant in south Australia. Visual MINTEQ 2.23 was used of struvite formation in a wastewater treatment by (Çelen *et al.*, 2007; Çelen and Türker, 2010) to estimate the required modifications for phosphates precipitation in liquid swine manure. Chand (2018), investigated the struvite formation possibility from anaerobically digested sludge by calculating the values of saturation indices with help of Visual MINTEQ 1.3.

In our study, the model is applied with the objective to investigate the possible precipitates in moving bed biofilm reactors (MBBR) treating reject water. The model calculations were done mainly based on chemical element's concentrations of magnesium, phosphorous, ammonium, iron and calcium. The Debye-Huckel method was use for activity corrections during model setup for precipitation prediction (Jia, 2014). Specified temperature, alkalinity and pH values were used for determination of saturation index (SI).

2 Materials and methods

A moving bed biofilm reactor (MBBR) was installed on the lines of reject water directed to main wastewater inlet as shown in Figure 1. The MBBR has a dimension of LxBxH=0.35x0.35x0.55m (effluent level) with a working volume of 67 L. It was filled with bio carriers to a filling degree of approximately 70 % of the reactor volume. The bio carriers, BWT S® (Biowater Technology AS), made of high-density polyethylene (HDPE) with dimensions of 14.5x18.5x7.3 mm and protected surface area of 650 m^2/m^3, were used as biofilm attaching substratum. The reactor was fed by centrifuged effluent from anaerobic sludge digestion. Since the centrifuge works intermittently (i.e., 6-9 hours during week days) the reject wastewater is stored in an intermediate bulk container (IBC) onsite to ensure that there is constant supply of feed into the reactor. The

reactor was continuously aerated with air flow 26 ± 2 L/min.
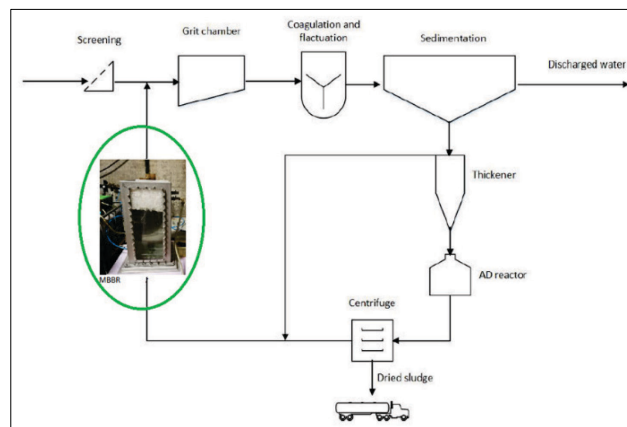
Figure 1. Flow diagram of Knarrdalstrand municipal wastewater treatment plant, Porsgrunn showing the MBBR position.

At the beginning, carriers moved freely in the MBBR reactor as intended but gradually carriers started to sink after strong biofilm growth and eventually settled permanently with heavy scaling on the bottom of the reactor after ~200 d of operation (Figure 2)

2.1 Sampling and wet chemical analysis

Samples of influent and effluent were collected two times per week and various chemical analyses such as ammonium, total chemical oxygen demand (CODt), soluble COD (CODs), total suspended solids (TSS), volatile suspended solids (VSS), PO_4-P and Alkalinity were carried out. The analyses were performed based on the standard methods according to APHA (1995).

2.2 Element analysis by Microwave plasma atomic emission spectroscopy

Microwave plasma atomic emission spectroscopy (MP-AES 4210) was used to estimate the total ion concentrations for elements, Ca, Fe, Mg, P and Al in the reject water. MP-AES provides analytical techniques to determine the elemental composition of samples by surveying their electromagnetic spectrum or mass spectrum. MP-AES uses nitrogen extracted from air by nitrogen generator to form plasma. Axial magnetic and radial electrical fields strengthen the nitrogen plasma. The sample aerosol was injected into plasma and the axial emission was directed into scanning monochromator. The different elements have a different wavelength. The emissions of selected wavelength range are reflected on high efficiency charge coupled device (CCD) detector.
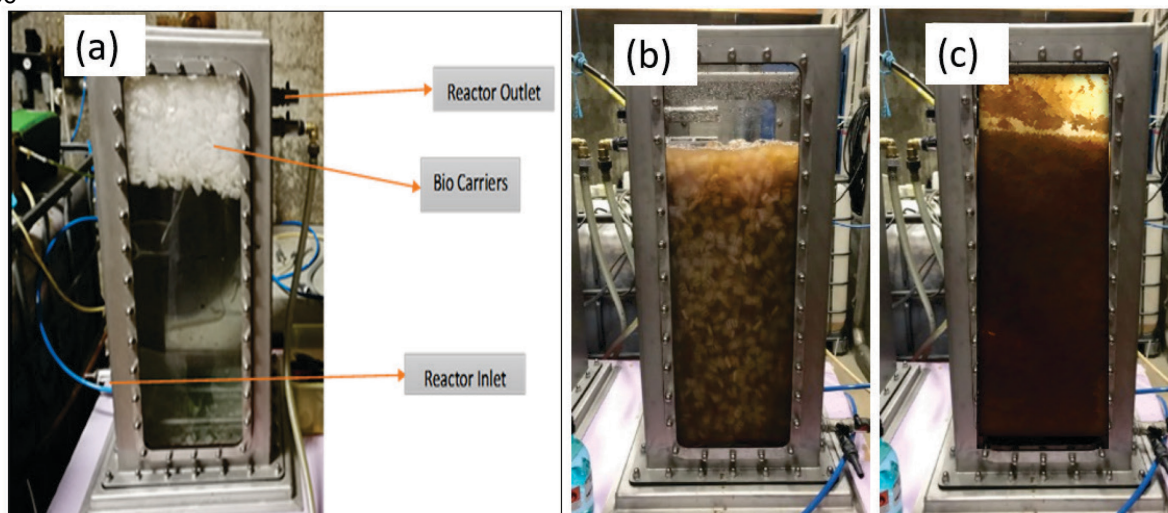
Figure 1. MBBR reactor setup with BWTS® carriers (a-MBBR with newly filled carriers, b- MBBR in good condition with freely moving carriers, c- MBBR with settled carriers.

2.2.1 Liquid sample preparation for element analysis

Samples from influent and effluent of the reactors were centrifuged, filtered and then diluted with 2% nitric acid (HNO_3) to 100 and 1000 dilution factors. Subsequently, the samples were measured by the MP-AES instrument for the elements Ca, Fe, Mg and P. Agilent Technologies ICP-OES Calibration Solution was used for wavelength calibration and Sigma-Alorich Periodic table mix 1 was used for wastewater standard calibration.

2.2.2 Quantification of biomass on carriers

Five carriers (N) were taken from the MBBR reactor, placed on an aluminum plate and dried at 105°C for 24 h and cooled down for 10 min in the desiccator. Then dried carriers were weighted (m_1). After that, carriers were soaked into hypochlorous acid (HOCl) for 2 hours, biomass was brushed and washed out by tap water. Again, the cleaned carriers were dried at 105°C for 24 h and weighted (m_2). Eventually, biomass per carrier m was calculated as mentioned in (4).

$$m = \frac{m_1 - m_2}{N} \qquad (4)$$

Biomass per unit protected surface area was calculated according to (5).

$$W = m \cdot \frac{V_C}{A} \qquad (5)$$

Here:
W: Biomass per unit surface area (g/m^2)
m : Biomass per carrier (g/piece)
V_C: Number of carrier pieces per volume ($piece/m^3$)
A: Protected surface area (m^2/m^3)

2.2.3 Solid sample preparation for element analysis

A DigiPREP Digestion System was used to digest organic materials included in dried sample of sludge and carrier's biomass. The DigiPREP Digestion System involves a microwave – assisted acid digester (MAAD) equipped with a touch-screen controller, Digi- tubes and

filters. Samples from sludge and carriers were dried for at least 10 hours in an oven at 105°C, then the carriers were rubbed off. Dried samples of mass 0.5 g were digested with 10 mL concentrated HNO_3 (69% v/v) in special digested tubes placed in a MAAD. Digested samples were cooled and then filtered with 1.2-1.5µm pore size glass filter. Thereafter, samples were diluted up to 50 mL with distilled water. Again, the diluted samples were diluted with 2 % HNO_3 up to 100 and 1000 dilution factor. Subsequently, the samples were measured by MP-AES.

2.3 Model inputs

Metal ion concentration, temperature and pH were the main inputs for Visual MINTEQ simulations. These parameters were varying over the time, therefore average values were used as input for the model. The average temperature was set to 16.5°C and pH was attempted to be kept constant at value8.2. The ion concentration inputs are given in Table 1. Ionic strength was let it to be calculated by model itself based on Debye-Huckel activity model.

**Table 1.** Input ion concentrations for Visual MINTEQ simulations.

Elements	Concentration (mg/L)
Mg^{2+}	35
Ca^{2+}	700
Fe^{3+}	15
NH_4^+	440
$P(PO_4)$	40
SO_4^{2-}	4

2.4 Crystal observation in solid samples

The presence of crystals in biomass and sludge samples was investigated by stereo microscope Nikon SMZ745 and fluorescence microscope Olympus IX70. Both microscopes are equipped with cameras to capture the pictures of biomass at 20x and 40x magnification.

3 Results and Discussion

The effective biofilm thickness is crucial to maintain efficient mass transfer between biofilm and bulk liquid phase. Excessive biofilm accumulation and scaling on the bio-carriers was observed over the study period. For instance, the average values of biomass on carrier per unit surface area exceeded 135 g/m^2 temporarily and stabilized in the range of 90-120 g/m^2 as shown in Figure 3.
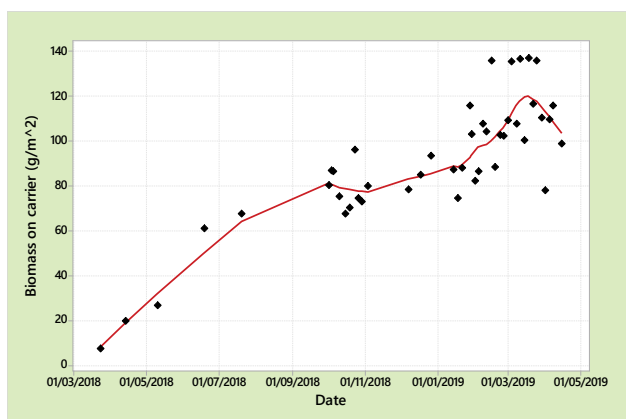
Figure 3. Biomass accumulation on carrier in MBBR reactor over the time (01.03.2018 – 01.05.2019).

Due to the increasing biofilm density it was observed that freely moving carriers started to settle and the effectiveness of the process in removing organics deteriorated (data not shown).

Table 2. Saturation indices for possible mineral precipitates in MBBR reactor, found in simulation result.

Mineral	Saturation Index
Hematite	21.6
Hydroxyapatite	18.1
Magnesioferrite	15.8
Maghemite	14.5
Goethite	9.6
Lepidocrocite	9.1
Ferrihydrite (aged)	7.2
$Ca_3(PO_4)_2$ (beta)	6.9
$Ca_4H(PO_4)_3:3H_2O(s)$	6.9
Ferrihydrite	6.7
$Ca_3(PO_4)_2$ (am2)	5.5
Strengite	4.2
$Ca_3(PO_4)_2$ (am1)	2.8
$CaHPO_4(s)$	1.1
$CaHPO_4:2H_2O(s)$	0.8
Struvite	0.4

The chemical equilibrium model has shown several possible precipitates on the biofilm carriers that may

have caused the high biofilm density and carrier settling (Table 2). The results show that Fe^{3+} and Ca^{2+} ions had the highest potential to form mineral precipitates and scaling on the biofilm carriers. Among other diverse forms of precipitates, Hematite, Hydroxyapatite, Magnesioferrite, Maghemite, and Goethite were the most predominant forms of mineral precipitates, with saturation indices (SI) of 21.6, 18.1, 15.8, 14.5, and 9.6, respectively. Digested dried sample of sludge and carrier's biomass had 37 % and 28 % mass percentage of calcium, respectively. pH had effects on the precipitates' SI in the pH range from 6.0 to 9.0 are shown in Figure 4.

Struvite was not one of the major precipitates in this study because it has low saturation index 0.4 (Table 2
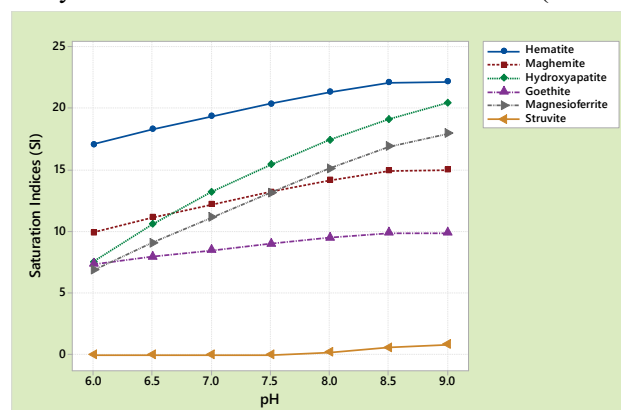
Figure 4. The saturation indices variation with pH for the predominant mineral precipitates predicted by the model.

and Figure 4). Struvite is magnesium ammonium phosphate and it normally precipitates when the ion concentration of magnesium, ammonium and phosphate are over saturated and the molar ratio is 1:1:1 (Tansel *et al.,* 2018*)*.

The simulations have shown that pH has significant effect on the amount and type of precipitants on the biofilm carriers. Hematite, Maghemite, Hydroxyapatite and Magnesioferrite precipitation increased most with increase in pH. Goethite and Struvite were not much influenced by pH with a slight increase in struvite when the pH was above 8 (Figure 4). pH in the range of 7 to 11 is generally known to be conducive for the formation of struvite, calcium phosphate and calcium carbonate and the crystallization rate decreases when the pH drops below this 7 to 11 range (Daneshgar *et al*., 2018). The aeration process in the MBBR reactor may have increased pH by CO_2 stripping and by biological reactions (Organics consumption, NH4 increase etc.). The measured inlet pH in this study was ~ 7.5 and the reactor pH was ~ 8.2, respectively.

Several studies have shown that crystallization occurs in biofilms when the bulk liquid solution contains more dissolved solute than the equilibrium saturation values. The ions involved in scale formation have intricate interaction and different crystals could be formed

depending on the system condition such as ionic concentrations, temperature and pH (Harker *et al.*, 2013).

A microscopic image of the observed crystals formed in the biofilm carriers is shown in Figure 5.
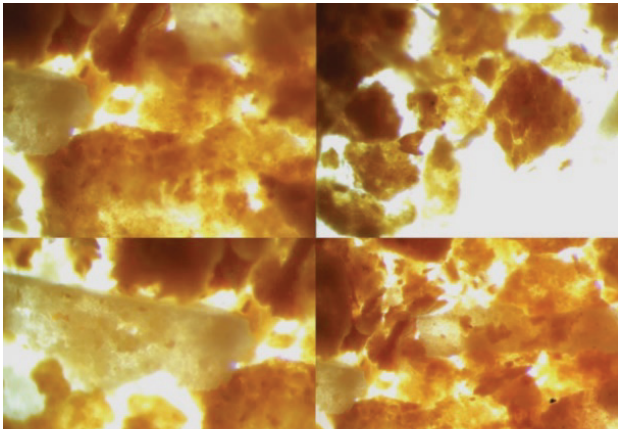
Figure 5. Microscopic observation of crystals on the biofilm carriers. The crystals were the precipitates after washing the biofilm carriers. Image is taken by stereoscopic zoom microscope with C-W10XB adjustable 10x/22mm wide field eyepieces and auxiliary objective AL-2x.

The simulation result has showed that, the major proportion of the crystal is a combination of either iron or calcium precipitates. Comparing the microscopic image with other studies of scanning electron microscope the struvite crystallization was significantly low. Since the reject wastewater contains large amount of calcium, it might inhibit the struvite crystallization. Similar studies have indicated that calcium has effect on struvite crystallization at different magnesium to calcium molar ratios (Hao *et al.*, 2008). When the molar ratio of calcium is high, the formed crystal shows transformation in morphology different from struvite.

4 Conclusions

Scaling on biofilm carriers of moving bed biofilm reactor (MBBR) is a major problem during treatment of reject wastewater, as it makes biofilm carriers heavy so that they sink to the reactor bottom. The study has confirmed that high concentration of ammonium, phosphorus and metal ions creates scaling on the biofilm carriers.

The chemical equilibrium simulation tool Visual MINTEQ 3.1 is a useful tool to predict which mineral precipitates can occur in wastewater treatment process, to what extent they may form and factors influencing their formation.

The pH and ionic concentration of metal ions play significant roles in the formation of different crystals. In this study, Fe^{3+} and Ca^{2+} had the highest potential to form mineral precipitates and scaling on the biofilm carriers. Among possible forms of precipitates Hematite, Hydroxyapatite, Magnesioferrite,

Maghemite, and Goethite were the most predominant in order of their saturation indices (SI). pH control, generally by lowering pH, appears to be the most realistic way to limit scaling.

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