

Article

The Use of Natural Minerals in a Pilot-Scale MBR for Membrane Fouling Mitigation

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Abstract: This study examines the effect of bentonite and zeolite concentration (0.25–5 g/L) on the membrane fouling of a fully automated, pilot-scale membrane bioreactor (MBR) treating high-strength synthetic municipal wastewater. Reversible fouling was estimated by sludge filterability measurements and irreversible fouling was estimated by the reduction of the carbohydrate fraction of soluble microbial products (SMP_c), which are considered to be significant MBR foulants. Both minerals were added to biomass samples (during batch-mode experiments) which were obtained from the system's aeration tank. Results showed that the optimal bentonite and zeolite concentrations were 3.5–4 g/L and 2.5–3.5 g/L, respectively. Interestingly, above these values, the addition of both minerals increased the examined fouling indices, i.e., the measured filterability times and the SMP_c concentration, implying that they might act as foulants at high concentrations. Optical microscopy images of the biomass samples showed that the addition of minerals at the optimal concentrations did not affect significantly filamentous microorganisms, since filament index (FI) was practically unaffected (~2). Finally, regarding the system's treating performance, it was found that the pilot-scale MBR can operate successfully with high-strength synthetic municipal wastewater, since remarkable behaviour was exhibited in terms of organics (BOD₅, COD) and ammonium (NH₄⁺-N) removal (>98%).

Keywords: membrane bio-reactor (MBR); membrane fouling; soluble microbial products (SMP); adsorption agents; natural minerals; bentonite/zeolite addition

1. Introduction

In recent decades, membrane bioreactor (MBR) technology has been widely used for municipal and industrial wastewater treatment, and for water reuse applications as well. Unlike the conventional activated sludge process (ASP), which employs a gravity-based clarifier (or settling tank) for the biomass separation, membrane bioreactors combine the wastewater biological treatment in the aeration tank with membrane filtration. As a result, the most significant advantages of the MBR technology over the conventional ASP include superior effluent quality, reduced reactor volume and footprint, less production of excess sludge, operation which is unaffected by possible poor sludge settling problems (bulking), and sufficient disinfection properties due to the ability of membranes to retain effectively most microorganisms.

However, membrane fouling still remains the major problem of the MBR technology, preventing its widespread application for full-scale municipal or industrial wastewater treatment. Among a wide range of cutting edge methods (e.g., the addition of coagulants or bio-film carriers, application of electrical field, ultrasound or ozone, quorum quenching, membrane surface modifications, etc.), the use of adsorbents is a novel strategy which has been implemented for membrane fouling control over the last few years [1–4]. Adsorbents provide a large surface area for the adsorption of materials

which are present in wastewater and water. In MBRs, adsorbents offer the potential to adsorb organic substances, notably extracellular polymeric substances (EPS) or soluble microbial products (SMP), hence reducing membrane fouling propensity. Powdered or granular activated carbon (PAC or GAC, respectively) is the most widely applied adsorption agent in MBRs for this purpose. Hu et al. (2017) [5] developed a PAC-dynamic membrane bioreactor in order to treat domestic wastewater by dosing with 3 g/L PAC and showed that filtration behaviour was significantly improved. Fang et al. (2012) [6] studied the way that the trans-membrane pressure (TMP) rise is delayed by the addition of PAC in an MBR. They observed that TMP increased steadily and reached 0.016 MPa on the 6th day of operation without PAC, while it increased and reached 0.015 MPa on the 10th day when PAC was added. Lin et al. (2011) [7] demonstrated that the total membrane resistance of a PAC-assisted MBR was lower than that of a conventional MBR operating without the addition of PAC. Wu et al. (2017) [8] investigated the mechanical scouring behaviour of GAC particles with sizes ranging from 0.9 to 4.6 mm and showed that they improved permeate flux and reduced cake layer resistance. Johir et al. (2013) [9] studied the effect of different particle sizes of GAC on membrane performance in a submerged MBR and observed that the total membrane resistance was reduced by 60%. In general, the addition of PAC results in the absorption of EPS, SMP or colloids which are present in the mixed liquor and, thus, mitigate mainly irreversible fouling, i.e., fouling which can be removed after the application of a chemical cleaning method on the membrane (soaking of the membrane in solutions of NaOCl, citric acid, etc.). Similar to PAC, the adsorption ability of GAC is remarkable, however, it is usually added to produce scouring on the membrane surface and results in the mitigation of reversible fouling, i.e., fouling which can be removed after the application of a physical cleaning method on the membrane (relaxation, backwashing, aeration, etc.) [10,11].

Nevertheless, few research studies focus on the use of alternative adsorption agents, such as zeolite, bentonite, or other natural minerals in their powdered form. Damayanti et al. (2011) [12] used zeolite, PAC and *Moringa oleifera* in order to mitigate fouling in a lab-scale submerged MBR which treated palm oil mill effluent (POME). At the optimum dosages of 4, 8, and 12 g/L, SMP removal rates were 58%, 42%, and 48% for PAC, zeolite, and *Moringa oleifera*, respectively. Yuniarto et al. (2013) [13] also employed zeolite and PAC for bio-fouling mitigation in a lab-scale submerged MBR for treating diluted POME for a period of 70 days. Their addition increased critical flux and significantly lowered TMP in long-term operation. In addition, it was found that both PAC and zeolite improved effluent quality in terms of COD removal and residual colour compared to a control MBR without adsorbents. Rezaei and Mehrnia (2014) [14] found that the addition of the zeolite improved sludge properties (22.5% increase of MLSS, 7% more accumulation of large particles) and resulted in the reduction of SMP concentration (50%) and TMP (66%). Malamis et al. (2014) [15] conducted batch-mode filtration experiments in order to examine the possible impact of three natural minerals (zeolite, bentonite, and perlite), three coagulation agents (ferric chloride, alum, and polyaluminium chloride), and a cationic polymer (MPE50) on the reduction of membrane fouling in a pilot-scale MBR. The use of additives increased membrane permeability and fouling mitigation followed the order MPE50 > polyaluminium chloride > ferric chloride > alum > zeolite > bentonite, while perlite increased fouling. Results also showed that they reduced the colloidal substances of sludge, however their effect on SMP was not investigated.

The present study examines the effect of two natural minerals, namely bentonite and zeolite, on membrane fouling of a fully automated pilot-scale MBR treating high-strength synthetic municipal wastewater. To the author's best knowledge, little information on the comparative study and influence of these minerals on membrane fouling is provided in literature regarding the improvement of sludge filterability and the reduction of SMP_c concentration, i.e., the concentration of the carbohydrate fraction of SMP (SMP_c). This work focuses on the effect of bentonite and zeolite powders on sludge filterability and on the concentration of SMP_c , which deserves further attention due to its crucial role in most MBR treatment systems: carbohydrate SMPs are considered to be the most significant 'foulants', i.e., the primarily responsible substances which cause membrane fouling. Additionally, optical microscopy is implemented for the first time in order to examine the short-term effect of the

minerals on the filament index (FI), which is a measure of the number of filamentous microorganisms in the activated sludge and, consequently, of its settling and fouling propensity.

2. Materials and Methods

2.1. Pilot-Scale MBR Operation

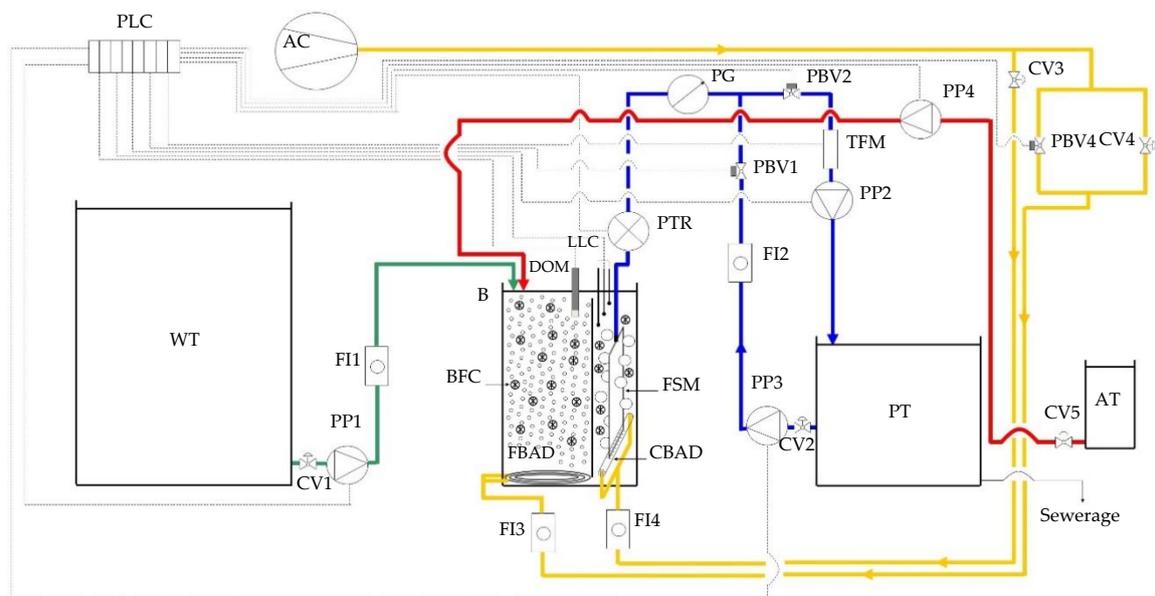
The experimental pilot-scale set-up consists of three sub-units: (a) wastewater feed unit, (b) (submerged membrane) bioreactor, which is divided into the aeration chamber and the membrane chamber, and (c) permeate collection unit (Figure 1). The system also includes a fourth unit (additive tank, denoted as AT in Figure 1), allowing for the in-line, continuous addition of additive suspensions directly to the bioreactor in operation. The in-line continuous addition of bentonite and zeolite suspensions is scheduled to be conducted shortly after the completion of the batch-mode experiments, and thus its study is beyond the scope of the present work.

The bioreactor is initially inoculated with activated sludge, which is received from the recirculation channel of the urban wastewater treatment plant of Thessaloniki city (located in the area of Sindos, near to Gallikos River). Then, the system is operated continuously in order to achieve steady-state condition. In the second stage, bentonite and zeolite powders are added in a series of batch-mode experiments. During these experiments, both minerals are added as a single drop mode in mixed liquor samples which are obtained from the aeration tank of the pilot plant on a daily basis. The drop mode addition of each examined mineral in the samples takes place instantly; however, the samples were tested for the major control parameters (i.e., filterability, SMP_c concentration and filamentous bacteria content—see also Sections 2.2–2.4, respectively) only after 10 min of mild magnetic stirring, in order to allow biomass and additives to interact properly within a sufficient time.

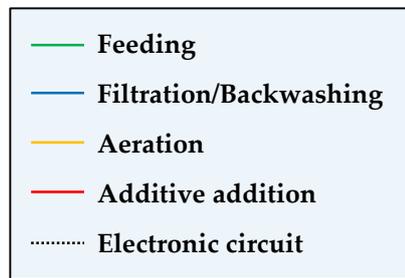
The bioreactor is fed with synthetic wastewater, which simulates a high-strength municipal wastewater (with BOD₅ around 1000 mg/L), under the following operating conditions: SRT = 20 d, HRT = 13 h, F/M ratio = 0.21 kg BOD₅/kg MLVSS·d, and J = 15 LMH. In order to maintain an SRT of 20 d, the MLSS concentration is kept constant at 7–8 g/L. The wastewater is led by a peristaltic pump to the bioreactor, where the concentration of the dissolved oxygen (DO) is controlled by a DO-meter in the range of 2–3 mg/L. The COD: N: P ratio of the synthetic wastewater is 100: 14: 3. Its composition is based on the standard one proposed by the Organization for Economic Co-operation and Development [16] for performing relevant biological wastewater treatment laboratory experiments. However, the concentrations of the components (peptone water, meat extract etc.) of the applied wastewater are selected to be much higher ($\times 10$) than those proposed by the OECD guidelines, in order to obtain a satisfactory F/M ratio (approximately 0.2) (Table 1). The air needed for the biomass aeration (and bio-oxidation of pollutants) and for the cleaning of the applied membrane is supplied by an air compressor, the pressure of which is appropriately reduced to the desired value by means of an air pressure reducer. Gas and liquid flow rates are measured by gas and liquid flow meters, respectively, while level sensors are used in order to control the level of the mixed liquor in the membrane tank. The permeate is withdrawn from the upper-end of the membrane by another peristaltic pump, while a high-resolution pressure transmitter is placed in the outlet of the membrane in order to record the TMP. The permeate collection unit is the final recipient of the produced permeate. A flat sheet, microfiltration membrane with a pore size of 0.4 μm and an effective area of 0.11 m^2 is employed, while one-minute relaxation steps are regularly performed every 9 min of filtration. The effect of both minerals on reversible fouling reduction potential is assessed in terms of sludge filterability tests, according to the standard time-to-filter (TTF) method, while irreversible fouling reduction potential is assessed in terms of SMP_c removal, after the appropriate analytical determination of SMP_c . Additionally, optical microscopy images of the mixed liquor samples are obtained in order to examine the short-term effect of the minerals on the filament index (FI), which is a measure of the population of filamentous microorganisms in the sludge, and consequently of its settling and fouling propensity.



(a)



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|---------------------------------|------------------------------------|
| WT: Wastewater Tank | CBAD: Coarse Bubble Air Diffuser |
| CV: Control Valve | PTR: Pressure Transducer |
| PP: Peristaltic Pump | PG: Pressure Gauge |
| FI: Flow Indicator | PBV: Pneumatic Ball Valve |
| B: Bioreactor | TFM: Turbine Flow Meter |
| DOM: Dissolved Oxygen Meter | PT: Permeate Tank |
| BFC: Bio-Film Carriers | AT: Additive Tank |
| FBAD: Fine Bubble Air Diffusers | AC: Air Compressor |
| LLC: Liquid Level Controllers | PLC: Programmable Logic Controller |
| FSM: Flat Sheet Membrane | |



(b)

Figure 1. (a) Pilot-scale MBR; (b) Schematic of the pilot-scale MBR.

2.2. Filterability Tests by Applying the TTF (Time-To-Filter) Method

The time-to-filter (TTF) method is a well-established method [17,18], which can be used as an easy and relatively rapid way to assess sludge filterability. A 90-mm Buchner funnel is used with Whatman

#1, #2, or equivalent filter papers. A short description of the procedure is as follows: after pouring 200 mL of mixed liquor on the Buchner funnel, the time required to obtain 100 mL of filtrate is recorded at the vacuum pressure of 510 mbar (designated as TTF). Low TTF values indicate high sludge filterability, whereas high TTF values indicate low sludge filterability.

Table 1. Composition of synthetic municipal wastewater.

Substance	Synthetic Wastewater According to OECD Guidelines Concentration, mg/L	Synthetic Wastewater Used in the Experiments	Physical/Chemical Parameters of the Synthetic Wastewater Used in the Experiments ¹
Peptone	160	1600	
Meat extract	110	1100	BOD ₅ = 1102 ± 28 mg/L
Urea	30	300	CO = 1983 ± 54 mg/L
K ₂ PO ₄	28	280	TN = 268 ± 26 mg/L
NaCl	7	70	NH ₄ ⁺ -N = 189 ± 18 mg/L
CaCl ₂ ·2H ₂ O	4	40	NO ₃ -N = 1.6 ± 0.1 mg/L
MgSO ₄ ·7H ₂ O	2	20	PO ₄ ³⁻ -P = 49 ± 5.2 mg/L

¹ Average of 30 replication of measurements.

2.3. SMP_c Concentration Measurements by Applying the Phenol-Sulfuric Acid Method

The carbohydrate fraction of the SMPs is extracted by the following procedure: mixed liquor samples are daily obtained from the bioreactor and centrifuged in order to separate the solid biomass. Then, the phenol-sulfuric acid method [19], which is the most widely used colorimetric method for the determination of carbohydrate concentration in aqueous solutions, is applied in the supernatant for the determination of the carbohydrate fraction of SMPs. The principle of this method is that carbohydrates, when dehydrated by reaction with concentrated sulfuric acid, produce furfural derivatives. Further reaction between furfural derivatives and phenol develops a detectible color. A short description of the standard procedure is following: 1 mL of a carbohydrate solution is mixed with 1 mL of wt. 5% aqueous solution of phenol in a test tube. Subsequently, 5 mL of concentrated H₂SO₄ are added rapidly to the mixture. After allowing the test tubes to stand for 10 min, they are vortexed for 30 s and placed for 20 min in a water bath at room temperature for color development. Then, light absorption at 480 nm is recorded on a spectrophotometer. Reference solutions are prepared in identical manner as aforementioned, except that the 1 mL of carbohydrate is replaced by glucose. A Hitachi UV/Vis double-beam spectrophotometer is used for these measurements.

2.4. Determination of the Filament Index (FI) by Applying Optical Microscopy

The Axio Lab.A1 light microscope (Carl Zeiss), equipped with a microscopy camera (AxioCam ERc 5s Rev.2), is used to determine the filament index (FI) of the mixed liquor samples before and after the addition of bentonite and zeolite powders. The ZEN lite software is employed in order to process and analyse the obtained images. The FI is determined according to the method which is proposed by Eikelboom (2000) [20]. A scale of 0–5 is used from none to infinite filaments. Between the consecutive FI classes, there is a difference of approximately a factor of 10. The FI is determined by comparing the microscopic images of the sludge, at a low magnification, with a series of reference photos of the various FI classes. The mixed liquor receives the FI value of the photo which best corresponds to the number of filamentous microorganisms in the microscopic image. When FI = 1 or 2, the effect of filamentous microorganisms on the settling velocity of the sludge is slight. When FI = 3, the settling properties are often significantly deteriorated and when FI > 3 bulking usually occurs.

3. Results and Discussion

3.1. Effect of Bentonite and Zeolite on Membrane Fouling

In this section, the effect of bentonite and zeolite on reversible and irreversible fouling reduction potential is examined. Both minerals were not continuously added in the bioreactor (continuous-flow addition experiments), but as a single drop in mixed liquor samples which were obtained from the aeration tank of the MBR operating pilot-scale unit on a daily basis (batch-mode experiments). With this process ('screening'), it is possible to test and compare a wide range of different concentrations of bentonite and zeolite, in order to determine the optimal ones, and subsequently, to employ them in real field conditions. The screening process has been successfully employed for the selection and addition of different types of coagulation agents as well [21].

Results are presented in terms of the ratios $TTF_{add}/TTF_{no\ add}$ and $SMP_{add}/SMP_{no\ add}$ (where the subscripts 'add' and 'no add' stand for 'additive' and 'no additive' and refer to either bentonite or zeolite powder). More specifically, $TTF_{bent}/TTF_{no\ bent}$ and $TTF_{zeol}/TTF_{no\ zeol}$ are the ratios of the TTF recorded after the addition of bentonite or zeolite, respectively, in the mixed liquor sample, to the TTF recorded before this addition (i.e., the respective blank measurement). It is evident that the lower this ratio is, the more the sludge filterability is enhanced. Similarly, $SMP_{bent}/SMP_{no\ bent}$ and $SMP_{zeol}/SMP_{no\ zeol}$ are the ratios of the SMP_c concentration after the addition of bentonite or zeolite, respectively, in the mixed liquor sample, to the SMP_c concentration before this addition (i.e., the respective blank measurement). In the same way, the lower this ratio is, the more effective the tested concentration becomes in terms of SMP_c removal. The effect of bentonite and zeolite on sludge filterability and SMP_c removal was examined at many different concentrations (0.25–5 g/L). The choice of these concentrations was based upon the relevant literature, since most adsorption agents which are used for fouling mitigation in MBRs are employed at similar concentrations [5,13,15]. It has been also reported that the effect of an additive on fouling can be either positive or negative, depending on the employed concentration (low or high). Therefore, the examined concentration range was split in two sub-ranges in the presented figures, i.e., low concentration (0.25–2.5 g/L) and high concentration sub-range (2.75–5 g/L). This separation also allows for the better comparison between the low and high additive concentrations.

Figures 2 and 3 show how $TTF_{bent}/TTF_{no\ bent}$ and $TTF_{zeol}/TTF_{no\ zeol}$ ratios change with the increase of bentonite and zeolite concentration, respectively, allowing for the determination of the optimal concentrations for mitigating reversible fouling.

As shown in Figure 2a, the addition of bentonite at low concentrations (0.25–2.5 g/L) did not affect ratio $TTF_{no\ bent}/TTF_{no\ bent}$. More specifically, bentonite concentration at the 0.25–2.25 g/L range was found to reduce slightly the sludge filterability and only when its concentration reached 2.5 g/L, could a notable decrease of the ratio $TTF_{no\ bent}/TTF_{no\ bent}$ (almost 10%) be observed. However, the anti-fouling potential at this concentration (2.5 g/L) still cannot be regarded as reliable, since the concentration values, which precede or follow (i.e., 2.25 and 2.75 g/L), did not substantially reduce the ratio $TTF_{no\ bent}/TTF_{no\ bent}$. On the contrary, sludge filterability was significantly increased, when the bentonite concentration was ranged between 3–4 g/L (Figure 2b). At concentrations 3, 3.25, 3.5, 3.75, and 4 g/L, the ratio $TTF_{no\ bent}/TTF_{no\ bent}$ was significantly reduced and the reduction reached almost 20% for most concentrations. Therefore, the concentration of bentonite 3.5 ± 0.5 g/L can be characterized as optimal in terms of sludge filterability enhancement. In contrast, the influence of zeolite on ratio $TTF_{no\ zeol}/TTF_{no\ zeol}$ and on sludge filterability was very low. At the lower examined concentrations (i.e., 0.25–2.5 g/L) (Figure 3a), the ratio $TTF_{no\ zeol}/TTF_{no\ zeol}$ was practically unaffected by the addition of zeolite. The same applies for the higher zeolite concentrations (i.e., 2.75–5 g/L) (Figure 3b), with the exception of 3–3.5 g/L, which slightly reduced the measured TTF times. Nonetheless, this decrease was very low. Thus, it can be stated that the addition of zeolite at the examined concentration range (0.25–5 g/L) does not significantly affect sludge filterability.

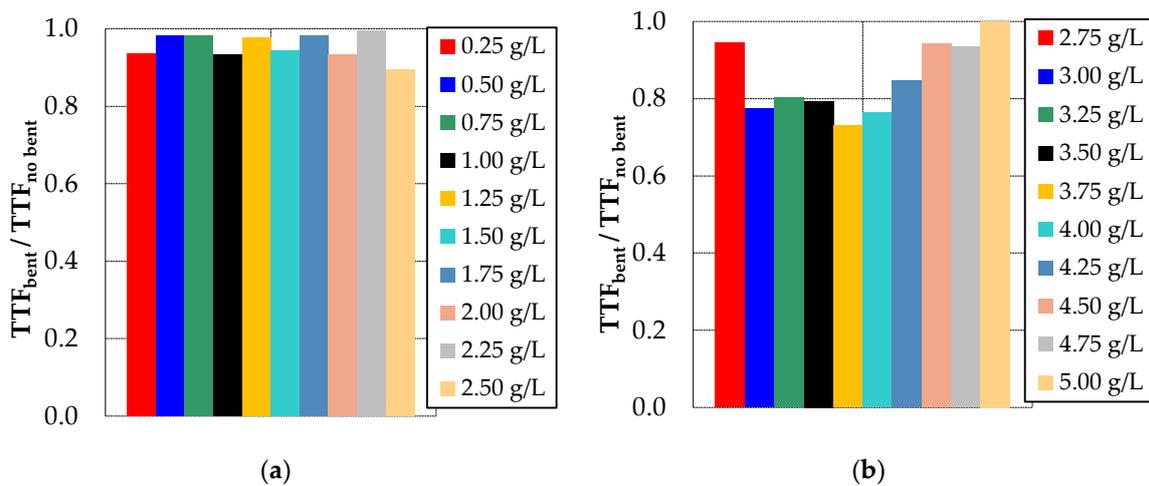


Figure 2. Effect of: (a) low (0.25–2.50 g/L) and (b) high (2.75–5 g/L) bentonite concentration on the ratio $TTF_{bent}/TTF_{no\ bent}$ for the estimation of reversible fouling reduction potential.

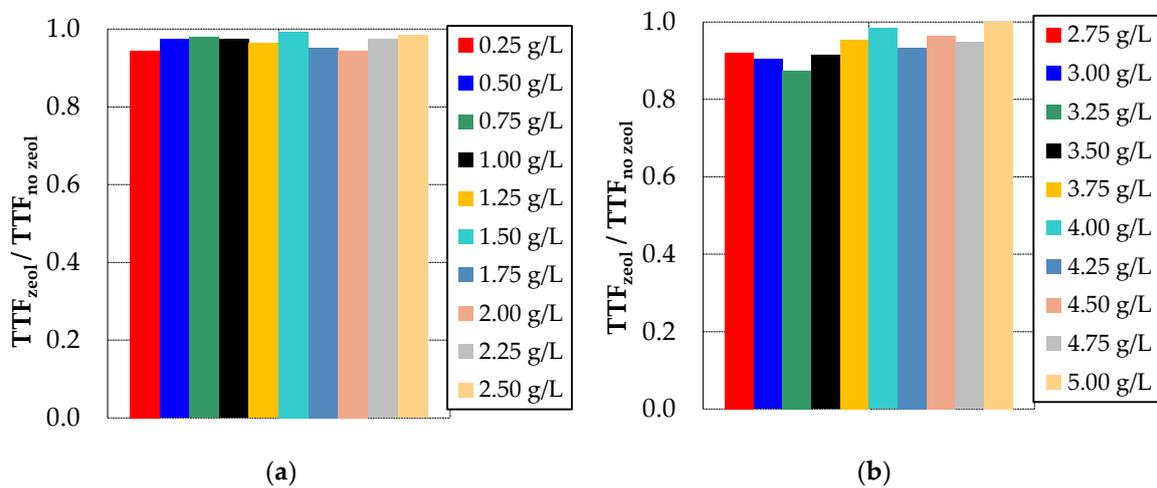


Figure 3. Effect of: (a) low (0.25–2.50 g/L) and (b) high (2.75–5 g/L) zeolite concentration on the ratio $TTF_{zeol}/TTF_{no\ zeol}$ for the estimation of reversible fouling reduction potential.

Figures 4 and 5 show how $SMP_{bent}/SMP_{no\ bent}$ and $SMP_{zeol}/SMP_{no\ zeol}$ ratios change with the increase of bentonite and zeolite concentration, respectively, allowing for the determination of the optimal concentrations for mitigating irreversible fouling.

As shown in Figure 4a, the addition of bentonite at the lower concentration range (0.25–2.5 g/L) did not affect substantially the SMP_c concentration, since the ratio $SMP_{no\ bent}/SMP_{no\ bent}$ was maintained at rather low values. The effect of bentonite remained almost negligible also at 2.75 g/L addition. However, as the concentration was increased, the ratio $SMP_{no\ bent}/SMP_{no\ bent}$ was decreased (Figure 4b). This decrease was more significant at the 3.5–4.5 g/L concentration range, when the reduction of SMP_c concentration was found to be more than 20%. At the concentrations 4.5–5 g/L, the ratio $SMP_{no\ bent}/SMP_{no\ bent}$ was found to be still relatively low; however, it starts to adopt an anodic trend, suggesting that the higher bentonite concentrations do not further reduce the SMP_c concentration. It is interesting to notice that the optimal concentration range for the SMP_c removal (i.e., 3.5–4.5 g/L), is very close to the optimal concentration range, regarding the sludge filterability improvement (i.e., 3–4 g/L, Figure 2b). The addition of zeolite to biomass samples at the lower concentrations examined (i.e., 0.25–1.5 g/L) did not influence the SMP_c concentration (Figure 5a). However, as zeolite concentration was increased, the ratio $SMP_{no\ zeol}/SMP_{no\ zeol}$ was decreased, and the reduction was maximum (almost 20%), when zeolite addition was 3 g/L (Figure 5b). Above this value, the ratio $SMP_{no\ zeol}/SMP_{no\ zeol}$ started to increase. Similar to what was observed for bentonite, the lowest

values of $SMP_{no\ zeol}/SMP_{no\ zeol}$ and $TTF_{no\ zeol}/TTF_{no\ zeol}$ ratios were observed at similar concentrations (2.5–3.5 g/L and 3–3.5 g/L, respectively).

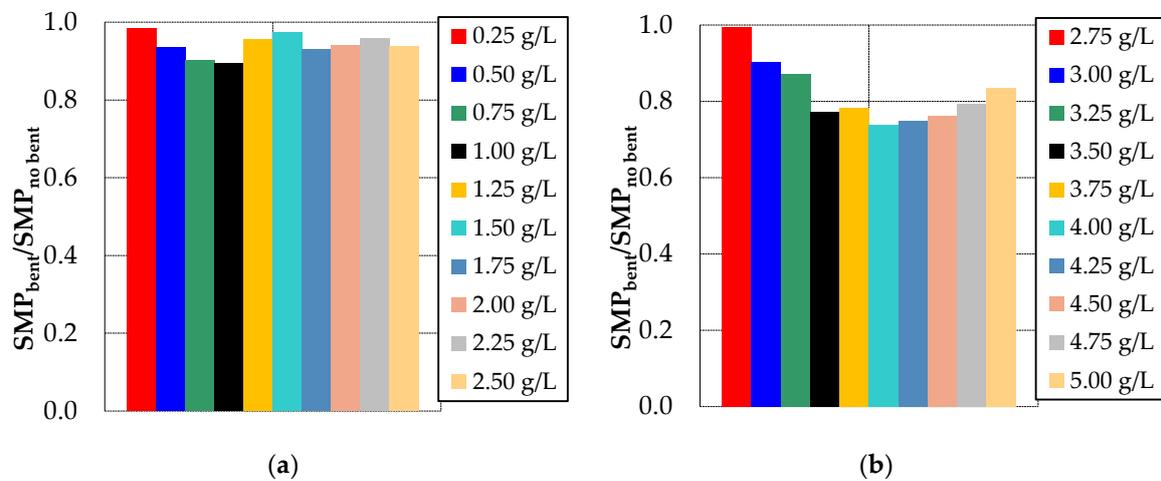


Figure 4. Effect of: (a) low (0.25–2.50 g/L) and (b) high (2.75–5 g/L) bentonite concentration on the ratio $SMP_{bent}/SMP_{no\ bent}$ for the estimation of irreversible fouling reduction potential.

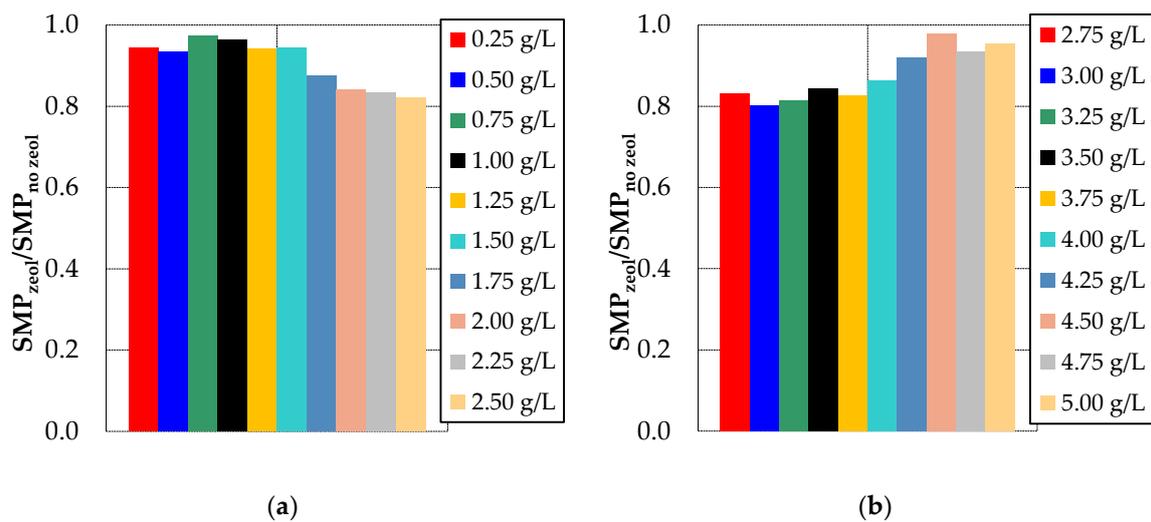


Figure 5. Effect of: (a) low (0.25–2.50 g/L) and (b) high (2.75–5 g/L) zeolite concentration on the ratio $SMP_{zeol}/SMP_{no\ zeol}$ for the estimation of irreversible fouling reduction potential.

Figure 6 shows the effect of all tested bentonite and zeolite concentrations on both ratios $TTF_{add}/TTF_{no\ add}$ and $SMP_{add}/SMP_{no\ add}$ allowing for the better comparison and determination of optimal concentrations for the estimation of reversible and irreversible fouling reduction potential. As shown, the concentrations of bentonite and zeolite which reduce most the aforementioned ratios are 3.5–4 g/L and 2.5–3.5 g/L, respectively. These concentrations can be characterized as optimal and are likely to reduce total fouling in the pilot-scale MBR if they are added continuously in the bioreactor. Interestingly, above these concentrations, ratios $TTF_{add}/TTF_{no\ add}$ and $SMP_{add}/SMP_{no\ add}$ increase with the increase of additive concentration, suggesting that both minerals might act as foulants if added at high concentrations (over the maximum tested concentration of 5 g/L). This is in accordance with Skouteris et al. (2015) [10] and Yang et al. (2012) [22] who state that overdosing with an additive (in their studies, PAC) may fail to reduce membrane fouling because of its potential to become a foulant itself, either through the formation of a cake layer on the membrane and/or by blocking the membrane pores.

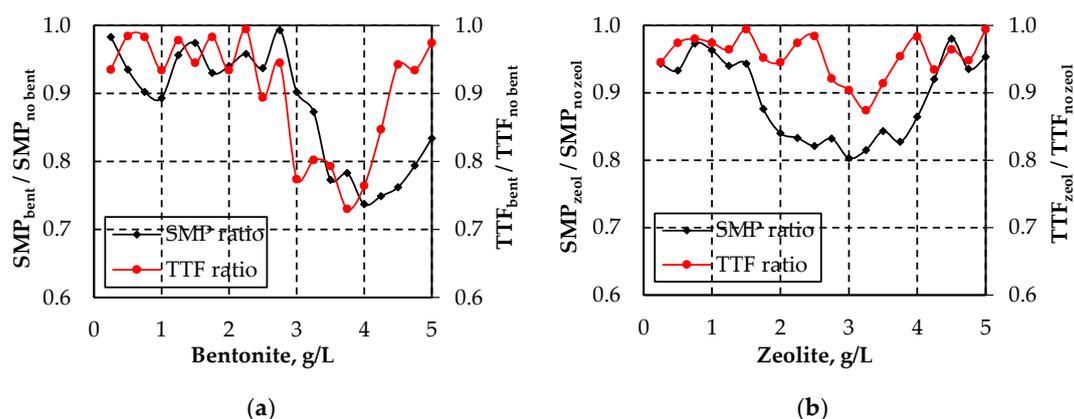


Figure 6. Effect of: (a) bentonite and (b) zeolite concentration on reversible and irreversible fouling reduction potential.

3.2. Optical Microscopy Images

It is reported that the entrapment of zeolite in the microorganisms of activated sludge, especially nitrifiers, can increase the size of microbial flocs and result in enhanced settlement [23]. Recently, it was also found that the adjustment of the population of filamentous bacteria can reduce membrane fouling in MBRs [24]. Aiming to determine if the addition of bentonite and zeolite influence the number of filamentous microorganisms and, therefore, the settling capacity and fouling propensity of the MBR biomass, optical microscopy images were taken before and after the addition of both minerals to the mixed liquor samples at their optimal concentrations (Figure 7). As shown in Figure 7a, the number of filamentous microorganisms is relatively low before the addition of bentonite or zeolite (blank measurement), corresponding to a FI~2. Figure 7b–f reveal that the addition of bentonite and zeolite did not affect significantly the population of filamentous microorganisms and the obtained images present almost the same profile. This is rather expected since the short-term nature of the batch-mode experiments does not favour the development of filamentous bacteria in the biomass that will entrap mineral particles, and thus increase the size of bio-flocs.

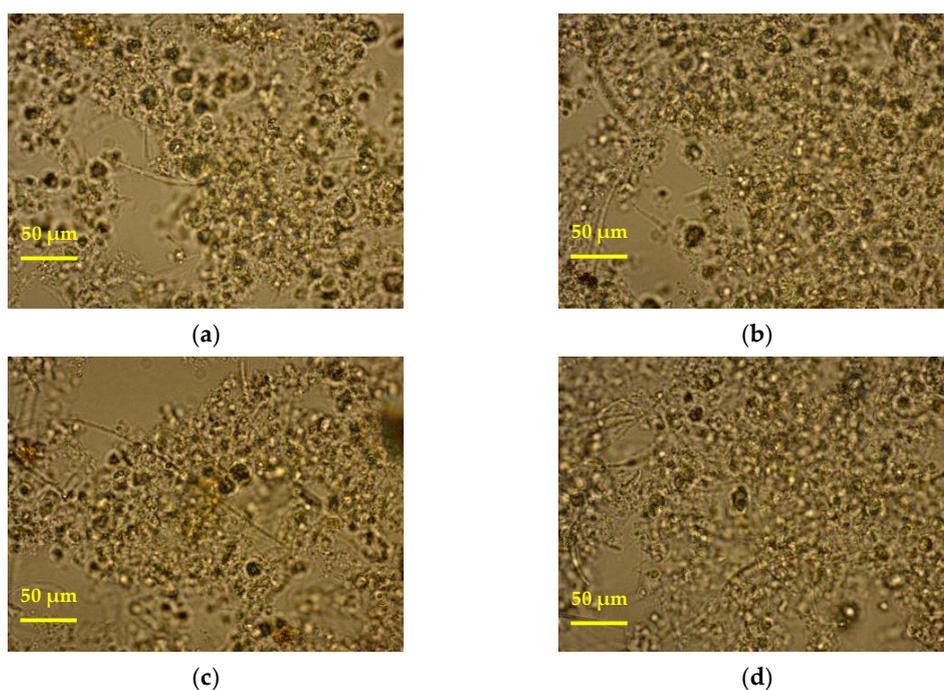


Figure 7. Cont.

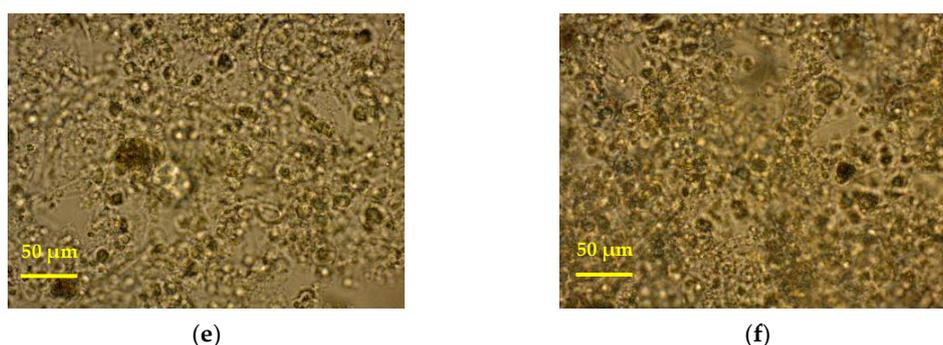


Figure 7. Optical microscopy images of the mixed liquor as seen through the Light Sheet Microscope for: (a) zero concentration of zeolite and bentonite (blank measurement), (b) 3.5 g/L bentonite, (c) 4 g/L bentonite, (d) 2.5 g/L zeolite, (e) 3 g/L zeolite and (f) 3.5 g/L zeolite.

3.3. Pilot-Scale MBR Performance

Although the primary objective of the present study is membrane fouling mitigation in MBR systems with the addition of bentonite and zeolite powders, the most important effluent quality parameters of the pilot-scale MBR were also measured in order to estimate its environmental impact. Effluent samples were collected and analyzed on the same days of the week and at the same time of day in order to minimize the impact of weekly or daily variations. The key contaminants demanding removal from municipal wastewaters usually comprise, roughly in order of importance, suspended solids (SS), organic matter and ammonia ($\text{NH}_4^+\text{-N}$), since most of the total nitrogen (TN) in domestic sewage is present in this form [25,26]. It is understood that the concentration of suspended solids in the effluent of the pilot-scale MBR was almost zero, since no solids were added for the preparation of the synthetic wastewater which was used during the experiments. Organic matter content was assessed in terms of BOD_5 and COD removal. As shown in Figure 8, the removal rates of BOD_5 , COD and $\text{NH}_4^+\text{-N}$ were above 98%, indicating a remarkably high effluent quality for the examined pilot-scale MBR. Although this is quite expected due to the synthetic nature of the employed wastewater, study of the fundamental effluent quality parameters (suspended solids, organic matter and ammonia) is always of utmost importance and should be given appropriate attention. It is believed that the key element for the wider application of the MBR technology can be the gradual enforcement of strict legislation concerning the reuse and/or discharge of the treated effluent. In addition, the MBR technology is already particularly attractive in cases where advanced treatment is required in order to produce a treated effluent that satisfies strict reuse standards, in cases of discharge to sensitive water bodies and in cases of plant upgrading for improving the treated effluent quality [27].

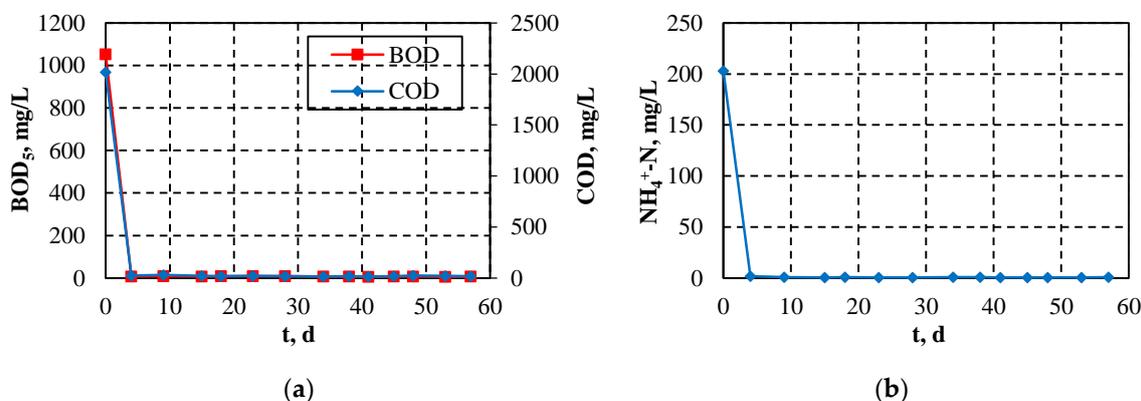


Figure 8. (a) Organics and (b) ammonium removal in the pilot-scale MBR treatment system.

4. Conclusions

Membrane bioreactors have been increasingly employed over the last few years for municipal or industrial wastewater treatment, however membrane fouling still prevents their widespread application. The use of additives, such as adsorption agents, coagulants or biofilm carriers, is included among the novel strategies which are recently used in order to mitigate fouling in MBRs. In this work, two natural minerals, namely bentonite and zeolite, are added in powdered form (at concentrations 0.25–5 g/L) to biomass samples of a pilot-scale MBR treating high-strength synthetic municipal wastewater. The optimal bentonite and zeolite concentrations, in terms of both reversible and irreversible fouling mitigation, were 3.5–4 g/L and 2.5–3.5 g/L, respectively. Comparing bentonite with zeolite, the examined ratios $TTF_{add}/TTF_{no\ add}$ and $SMP_{add}/SMP_{no\ add}$ were more decreased after the addition of bentonite, suggesting its superior performance over zeolite in terms of sludge filterability improvement and reduction of SMP_c concentration, respectively. Based on this assumption, it is more likely that reversible and irreversible fouling are reduced if bentonite is directly added to the bioreactor during continuous-flow experiments. Interestingly, both minerals are likely to act as foulants at high concentrations (>5 g/L), since ratios $TTF_{add}/TTF_{no\ add}$ and $SMP_{add}/SMP_{no\ add}$ started to increase after the additives' concentrations exceeded the optimal values. Optical microscopy images showed that the population of filamentous microorganisms was not affected by the addition of bentonite and zeolite and corresponded to a value of FI~2. Finally, regarding the system's treating performance, the pilot-scale MBR operated successfully with a high-strength synthetic municipal wastewater and remarkable behaviour (improvement) was exhibited in terms of organics and ammonium removal (>98%).

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Nomenclature

ASP	Activated sludge process
BOD ₅	Biochemical oxygen demand
COD	Chemical oxygen demand
DO	Dissolved oxygen
EPS	Extracellular polymeric substances
F/M	Food to microorganisms
FI	Filament index
HRT	Hydraulic retention time
GAC	Granular activated carbon
MBR	Membrane bioreactor
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
OECD	Organization for Economic Co-operation and Development
PAC	Powdered activated carbon
POME	Palm oil mill effluent
SMP	Soluble microbial products
SMP _c	Carbohydrate fraction of soluble microbial products
SRT	Sludge retention time
SS	Suspended solids
TMP	Trans-membrane pressure
TN	Total nitrogen
TTF	Time to filter

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