

The use of natural minerals in a pilot-scale MBR for membrane fouling mitigation

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Abstract

The Membrane Bio-Reactor (MBR) is one of the most successful commercial applications of membrane technology, along with membrane-based desalination and water clarification. However, despite its plentiful advantages, the most significant drawback still remains membrane fouling. Over the last few years, Powered Activated Carbon (PAC) is mainly employed as a sludge additive in several MBR systems in order to mitigate membrane fouling via adsorption and increase permeate flux. Nevertheless, few research studies have been conducted to examine the influence of alternative adsorption agents, such as natural minerals, on membrane fouling. The present work studies the influence of bentonite and zeolite concentration (0.25-5 g/L) on reversible fouling, estimated by sludge filterability measurements, and on irreversible fouling, estimated by the reduction of the carbohydrate fraction of Soluble Microbial Products (SMP_c), which are considered to be the most significant fouling substances (also known as 'foulants') during the MBR operation. Both minerals were added in biomass samples (batch-mode experiments) which were obtained from a fully automated pilot-scale MBR treating high-strength synthetic municipal wastewater. Results showed that the optimal bentonite and zeolite concentrations were 3.5-4 g/L and 2.5-3.5 g/L, respectively. Above these values, the addition of both minerals increased the examined fouling indices, i.e. the SMP_c concentration and the measured filterability times, implying that they might act as 'foulants' at high concentrations. Finally, regarding the system's treating performance, it was found that the pilot-scale MBR can operate successfully with a high-strength synthetic municipal wastewater, since remarkable behaviour was exhibited in terms of organics and ammonium removal.

Keywords: membrane bio-reactor (MBR), fouling, soluble microbial products (SMP), bentonite/zeolite addition

1. Introduction

In recent decades, the Membrane Bio-Reactor (MBR) technology has been widely used for industrial and municipal 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. 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 in recent years [1-2]. Adsorbents provide a large surface area for the adsorption of materials which are present in water and wastewater. In MBRs, adsorbents offer the potential to adsorb dissolved organic substances, notably soluble microbial products (SMP), hence reducing membrane fouling propensity. Powdered activated carbon (PAC) is the most widely applied adsorption agent in MBRs for this purpose [3-4]. Hu et al. [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. [6] studied the way 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. [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.

Nevertheless, few research studies focus on the use of alternative adsorption agents, such as zeolite (clinoptilolite), bentonite or other natural minerals in their powdered form. Damayanti et al. [8] used PAC, zeolite 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. [9] 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. The addition of the adsorbents increased the critical flux and significantly lowered the TMP in long-term operation. In addition, it was found that the addition of both PAC and zeolite resulted in a higher effluent quality in terms of COD removal and residual colour compared to the control MBR without adsorbents. Rezaei and Mehrnia [10] 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. [11] examined the impact of three natural minerals (zeolite, bentonite and perlite), three coagulants (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, with perlite increasing fouling. Results also showed that the use of additives reduced the colloidal substances of sludge, however, their effect on SMP and sludge filterability was not investigated.

In the present study, the effect of two natural minerals, namely bentonite and zeolite, on membrane fouling was examined in a fully automated pilot-scale MBR which treated 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, in terms of sludge filterability improvement and SMP concentration reduction. This paper focuses on the effect of bentonite and zeolite powders on sludge filterability and on the concentration of the carbohydrate fraction of SMP (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.

2. Material and methods

2.1 Pilot-scale MBR operation

The experimental pilot-scale set-up consists of three sub-units: (a) wastewater feed unit (x2), (b) (submerged membrane) bioreactor, and (c) permeate collection unit (**Fig. 1**). Firstly, the bioreactor was inoculated with activated sludge, which was received from the recirculation channel of the urban wastewater treatment plant of Thessaloniki city (located in the area of Sindos, near to Gallikos River), and then, the system was operated

continuously in order to achieve steady-state condition in the bioreactor. In the second stage, bentonite and zeolite powders were added in a series of batch experiments. During these experiments, both minerals were added as a single drop mode in mixed liquor samples, which were obtained from the aeration tank of the pilot plant on a daily basis. The synthetic wastewater, which was fed as the substrate for the activated sludge, was led by a peristaltic pump to the aeration tank (bioreactor), where the concentration of the dissolved oxygen (DO) was controlled by a DO-meter in the range of 2-3 mg/L. The air needed for the biomass aeration (and bio-oxidation of pollutants) and for the cleaning of the applied membrane was supplied by an air compressor, the pressure of which was appropriately reduced to the desired value by means of an air pressure reducer. Gas and liquid flow rates were measured by gas and liquid flow meters, while level sensors were used in order to control the mixed liquor level in the membrane tank. The permeate was withdrawn from the upper-end of the applied membrane by another peristaltic pump, while a high-resolution pressure transmitter was placed in the outlet of the membrane in order to record the Trans-Membrane Pressure (TMP). The permeate collection unit was the final recipient of the produced permeate.



Fig. 1. Pilot-scale MBR system.

The bioreactor was fed with synthetic municipal wastewater (with BOD_5 around 1000 mg/L) under the following operating conditions: Sludge Retention Time (SRT) = 20 d, F/M ratio = 0.21 kg BOD_5 /kg MLVSS·d. In order to maintain an SRT of 20 d, the MLSS concentration was kept constant at 7500 mg/L. The COD: N: P ratio of the synthetic wastewater was 100: 14: 3. The synthetic wastewater composition was based on the standard one proposed by the Organization for Economic Co-operation and Development for performing relevant biological wastewater treatment laboratory experiments [12]. However, the concentrations of the components (peptone water, meat extract etc.) of the applied wastewater were 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**). A flat sheet, microfiltration membrane with a pore size of 0.4 μm and an effective area of 0.11 m^2 was operated at a flux of 15 LMH, while one-minute relaxation steps were regularly performed for mechanical cleaning purposes every 9 min of filtration.

Reversible fouling was assessed in terms of sludge filterability tests, according to the standard Time-to-Filter (TTF) method, while irreversible fouling was assessed in terms of SMP removal, after the appropriate analytical determination of SMP.

Table 1. Composition of synthetic municipal wastewater.

	Synthetic wastewater according to OECD guidelines	Synthetic wastewater used in the experiments	Physical/chemical parameters of the synthetic wastewater, which was used in the experiments (average of 30 replication of measurements)
Substance	Concentration, mg/L		
Peptone	160	1600	BOD ₅ = 1102 ± 28 mg/L
Meat extract	110	1100	COD= 1983 ± 54 mg/L
Urea	30	300	TN= 268 ± 26 mg/L
K ₂ HPO ₄	28	280	NH ₄ ⁺ -N= 189 ± 18 mg/L
NaCl	7	70	NO ₃ ⁻ -N= 1.6 ± 0.1 mg/L
CaCl ₂ ·2H ₂ O	4	40	PO ₄ ³⁻ -P= 49 ± 5.2 mg/L
MgSO ₄ ·7H ₂ O	2	20	

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

The Time-To-Filter (TTF) method is a well-established method [13-14], which can be used as an easy and relatively rapid way to assess sludge filterability (**Fig. 2**). 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 was recorded at the vacuum pressure of 510 mbar (designated as TTF₁₀₀). Low TTF₁₀₀ values indicate high sludge filterability, whereas high TTF₁₀₀ values indicate low sludge filterability. In this study, except for the TTF₁₀₀, the time required to obtain 20, 40, 60 and 80 mL of filtrate was also recorded, in order to plot a full profile of recorded experiments, which can contribute to a better comparison and understanding of obtained results.

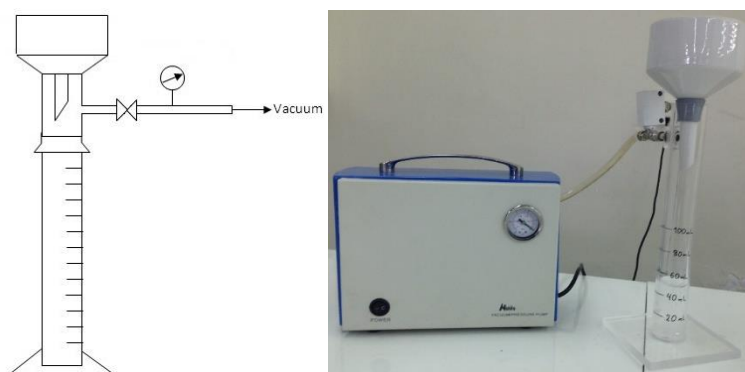


Fig. 2. Test equipment of the Time To Filter (TTF) method.

2.3 SMP_c concentration measurements

SMPs were extracted by the following procedure: mixed liquor samples were daily obtained from the bioreactor and centrifuged in order to separate the solid biomass. Then the Phenol-Sulfuric Acid method [15], which is the most widely used colorimetric method for the determination of carbohydrate concentration in aqueous solutions, was applied in the supernatant for the determination of 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 was mixed with 1 mL of wt. 5% aqueous solution of phenol in a test tube. Subsequently, 5 mL of concentrated H₂SO₄ were added rapidly to the mixture. After allowing the test tubes to stand for 10 min, they were vortexed for 30 s and

placed for 20 min in a water bath at room temperature for color development. Then, light absorption at 490 nm was recorded on a spectrophotometer. Reference solutions were prepared in identical manner as aforementioned, except that the 1 mL of carbohydrate was replaced by glucose. A Hitachi UV/Vis double-beam spectrophotometer was used for these measurements.

3. Results and discussion

3.1 Effect of bentonite and zeolite on membrane fouling

The 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_{100} recorded after the addition of bentonite or zeolite, respectively, in the mixed liquor sample, to the TTF_{100} 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 mineral concentration becomes in terms of SMP_c removal. The effect of bentonite and zeolite on SMP_c removal and sludge filterability was examined at many different concentrations (0.25 to 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 concentrations which fall nearly into this range [4, 9, 11].

Figs. 3-4 shows 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 **Fig. 3**, the addition of bentonite at low concentrations (0.25-2.5 g/L) did not affect the ratio $TTF_{no\ bent}/TTF_{no\ bent}$; nevertheless, sludge filterability was improved at higher concentrations and more specifically at concentrations 3-4 g/L. Regarding the influence of zeolite on sludge filterability (**Fig. 4**), its addition at 3-3.5 g/L slightly decreased the measured TTF_{100} times. However, this decrease was insignificant compared to the respective one caused by bentonite and, thus, it cannot be safely stated that its addition mitigates reversible fouling.

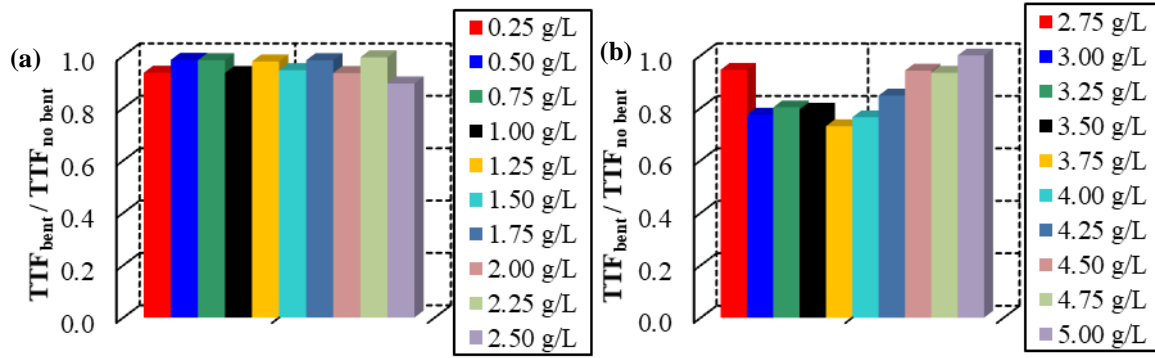


Fig. 3. Effect of: (a) low (0.25-2.50 g/L) and (b) high (2.75-5 g/L) bentonite concentrations on the ratio $TTF_{bent}/TTF_{no\ bent}$ for the estimation of reversible fouling.

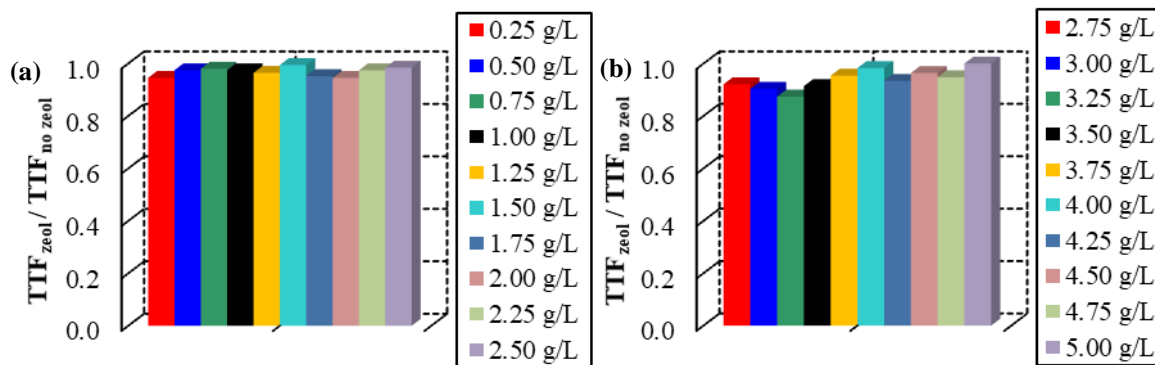


Fig. 4. Effect of: (a) low (0.25-2.50 g/L) and (b) high (2.75-5 g/L) zeolite concentrations on the ratio $TTF_{zeol}/TTF_{no\ zeol}$ for the estimation of reversible fouling.

Figs. 5-6 shows 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 **Fig. 5**, the addition of bentonite at low concentrations (0.25-2.5 g/L) did not affect the ratio $SMP_{no\ bent}/SMP_{no\ bent}$. On the contrary, when bentonite was added at higher concentrations, and more specifically at 3.5-4.5 g/L, SMP_c concentration was significantly reduced. Regarding the influence of zeolite on the reduction of SMP_c , its optimal concentration range is shifted at lower concentrations, namely at 2.5-3.5 g/L (**Fig. 6**).

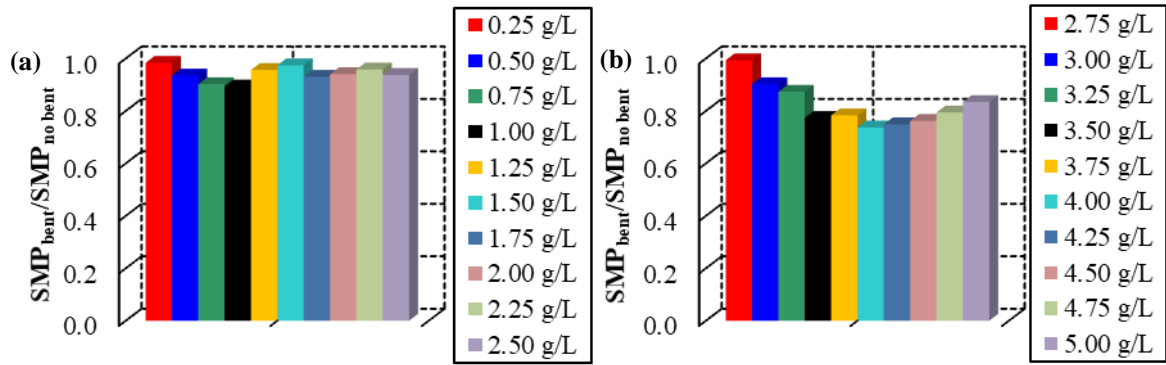


Fig. 5. Effect of: (a) low (0.25-2.50 g/L) and (b) high (2.75-5 g/L) bentonite concentrations on the ratio $SMP_{bent}/SMP_{no\ bent}$ for the estimation of irreversible fouling.

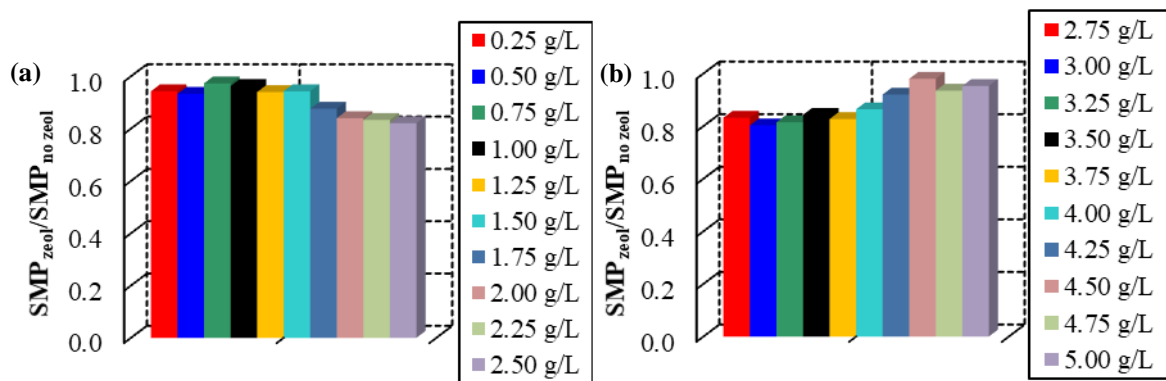


Fig. 6. Effect of: (a) low (0.25-2.50 g/L) and (b) high (2.75-5 g/L) zeolite concentrations on the ratio $SMP_{zeol}/SMP_{no\ zeol}$ for the estimation of irreversible fouling.

Fig. 7 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 easier comparison and determination of optimal concentrations for the mitigation of reversible and irreversible fouling. As shown, the optimal bentonite and zeolite concentrations which reduce the aforementioned ratios and mitigate both reversible and irreversible fouling are 3.5-4 g/L and 2.5-3.5 g/L, respectively. It is interesting to notice that above these concentrations ratios $TTF_{add}/TTF_{no\ add}$ and $SMP_{add}/SMP_{no\ add}$ increase again with the increase of additive concentration, which means that at high concentrations (over the maximum tested concentration of 5 g/L) it is possible that both minerals might act as 'foulants'.

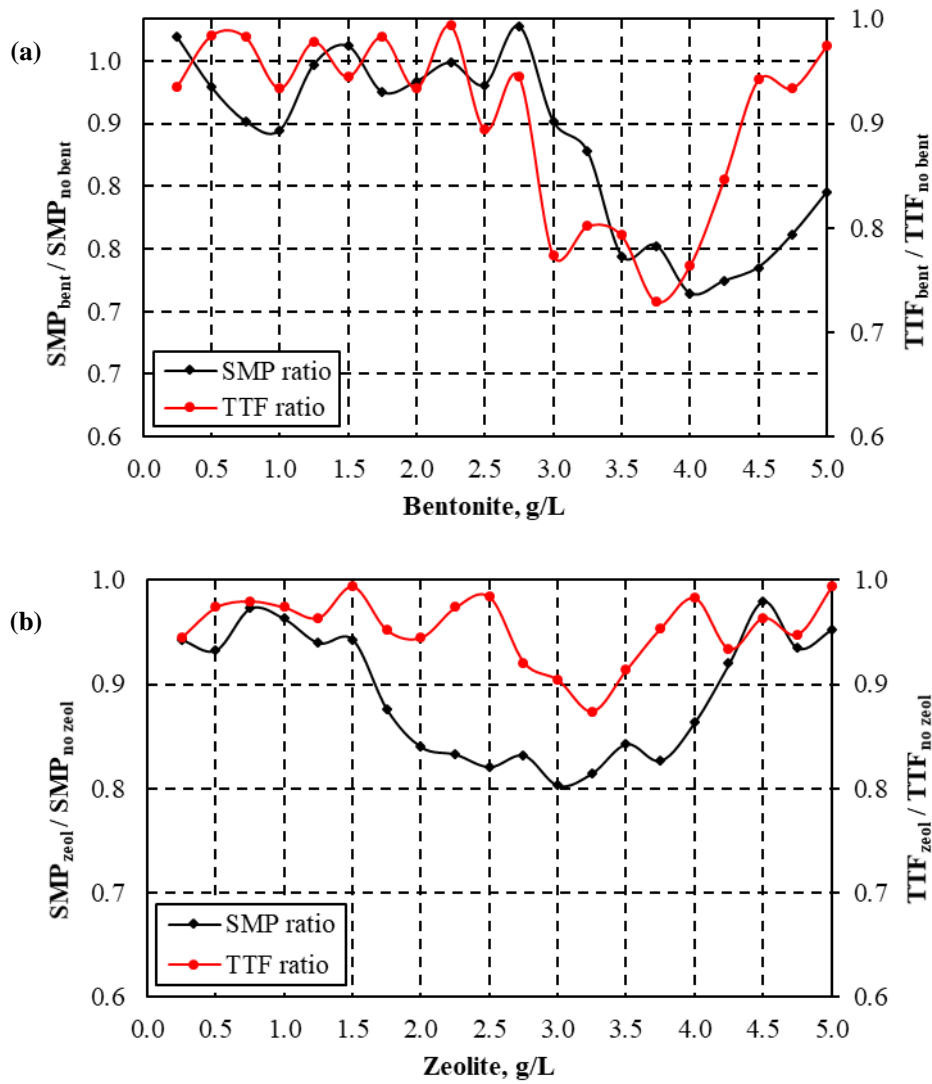


Fig. 7. Effect of: (a) bentonite and (b) zeolite concentration on reversible and irreversible fouling.

3.2 Pilot-scale MBR performance

The primary objective of the present study was membrane fouling mitigation in MBR treatment systems with the addition of bentonite and zeolite powders. However, the effluent quality was also assessed in terms of organics (BOD₅, COD) and ammonium (NH₄⁺-N) removal, in order to estimate the environmental impact of the pilot-scale MBR system, treating synthetic municipal wastewater of high strength. Results showed that the addition of the two minerals did not affect the effluent quality of the pilot-scale MBR since the removals of BOD₅, COD and NH₄⁺-N were more than 98 % in both cases (**Fig. 8**).

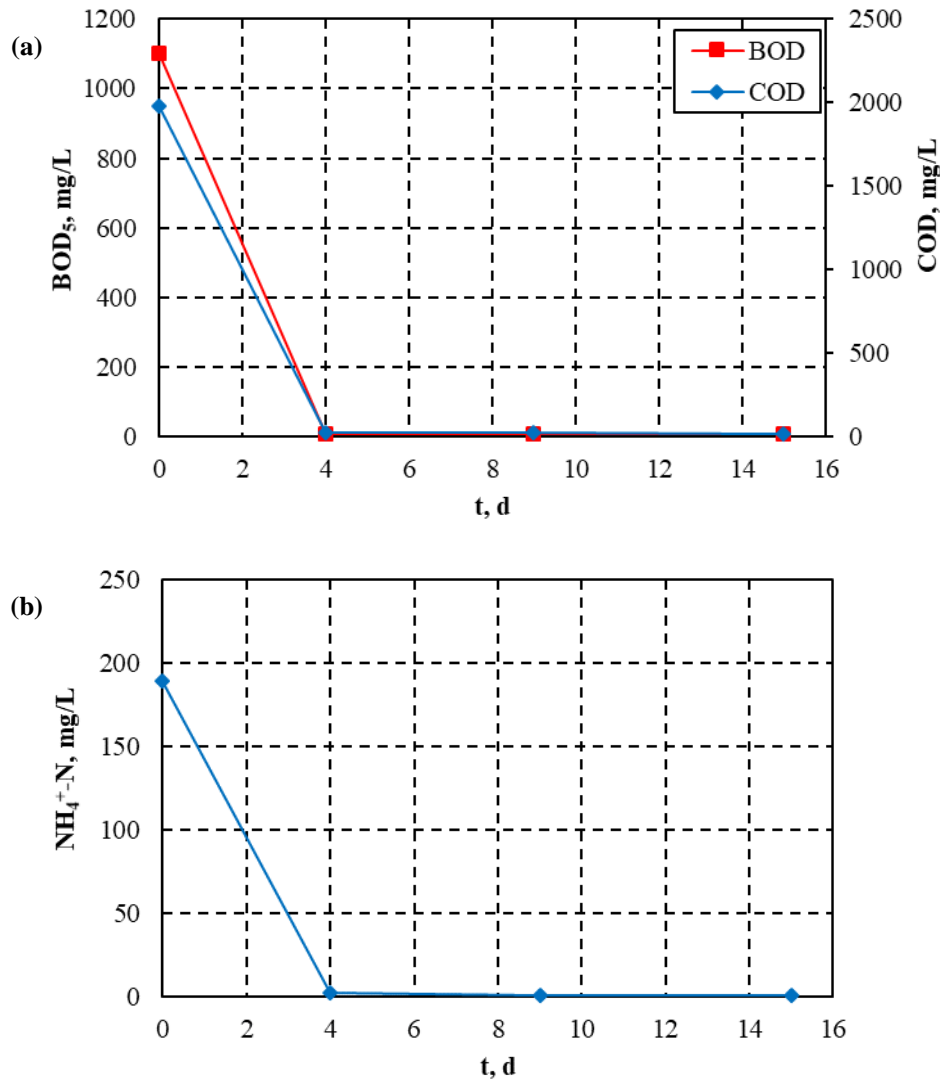


Fig. 8. (a) Organics and (b) ammonium removal in the pilot-scale MBR treatment system.

4. Conclusions

The addition of bentonite and zeolite powders in the mixed liquor samples slightly improved sludge filterability and reduced the SMP at all tested concentrations (0.25-5 g/L). However, 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. In addition, both minerals are likely to act as a 'foulants' at high concentrations, since it was shown that their effect is beneficial only within a short range of concentrations, above which ratios $TTF_{add}/TTF_{no\ add}$ and $SMP_{add}/SMP_{no\ add}$ were not significantly changed. 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 in both cases.

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