Application of powdered activated carbon (PAC) for membrane fouling control in a pilot-scale MBR system

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Abstract
Membrane fouling is considered to be the most serious drawback in wastewater treatment, when using Membrane Bioreactors (MBRs), leading to membrane permeability decrease and efficiency deterioration. This work aims to develop an integrated methodology for membrane fouling control, using powdered activated carbon (PAC), which will enhance the adsorption of soluble microbial products (SMP) and improve membrane filterability, by altering the mixed liquor's characteristics. Reversible fouling was assessed in terms of sludge filterability measurements, according to the standard Time-to-Filter (TTF) method, while irreversible fouling was assessed in terms of SMP removal. Results showed that the addition of PAC at the concentration of 3 g/L in the mixed liquor reduced SMP concentration and enhanced substantially the sludge filterability. Furthermore, the $TTF_{PAC}/TTF_{no\ PAC}$ ratios were lower, than the corresponding $SMP_{PAC.}/SMP_{no\ PAC}$ ratios, indicating that the batch-mode, short-term addition of PAC promotes the reversible, rather than the irreversible fouling mitigation.

Keywords
Membrane Bioreactors; powdered activated carbon; reversible/irreversible fouling; pilot plant

INTRODUCTION

Membrane bioreactors (MBRs) have been widely used during the past few years for municipal or industrial wastewater treatment (Van Dijk and Roncken, 1997), as well as for water reclamation (Cicek et al., 1998). However, membrane fouling leads to permeate flux decline, which in turn decreases the time intervals for membrane cleaning and replacement and hence, results in higher operating costs. Therefore, most current MBR studies aim to identify, investigate, control and model the membrane fouling (Akamatsu et al., 2010; Gkotsis et al., 2014). Recent developments in fouling prevention and control strategies include specific membrane surface modifications (Maruf et al., 2014), or the application of ultrasound, electric field, ozone etc. (Wu et al., 2010). A widely used method for fouling control in MBRs involves the use of appropriate additives, such as inorganic or organic coagulants (Yu et al., 2015; Gkotsis et al., 2016), or powdered activated carbon (PAC) (Ng et al., 2013; Remy et al., 2009; Le-Clech et al., 2006).

The simultaneous adsorption and biodegradation, rather than a single biological process, reflect the major advantage of a PAC-MBR system (Hu et al., 2014). In particular, PAC addition increases the removal of low molecular weight organics by adsorption; it also acts as a supporting medium for attached bacterial growth, influences the bacterial population and affects the concentrations of EPS (Extracellular Polymeric Substances) or SMP (Soluble Microbial Products) which are considered to be primarily responsible for membrane fouling (Malamis and Andreadakis, 2009; Cho et al., 2005). Since PAC decreases the compressibility of sludge flocs and increases the porosity of cake layer, membrane flux is also enhanced. Other benefits of PAC addition include the decrease of sludge production and the increase in the resistance to toxic substances (Satyawali and Balakrishnan, 2009). The addition of PAC in the activated sludge can transform the PAC into "biologically activated carbon" (BAC) sludge. The bioactivity of BAC can also improve the removal of pollutants. The reported uses of BAC in wastewater treatment include the removal of (i) inhibitory materials; (ii) colour from wastewater; (iii) micropollutants; (iv) trace organics, as well as the treatment of (i) landfill leachate; (ii) high salinity oil-field brine; (iii) industrial wastewater in general. The enhanced performance of BAC may be due to its similarity with a natural ecosystem equipped with simultaneous processes of adsorption and biodegradation, rather than a single biological process. The simultaneous functional processes may enable microorganisms in the biofilm of BAC to biodegrade the pollutants previously absorbed by the PAC. PAC can act as a support medium and encourage the formation of a biofilm ecosystem, which consists of immobilized, properly acclimatized bacteria. Thus, the formation of a biofilm on the PAC is expected to enhance the partial bio-regeneration of saturated BAC (Ng et al., 2013).

In the relevant literature typical PAC dosages, which have been employed for the mitigation of membrane fouling and the removal of foulants, range between 0.5 g/L (Remy et al., 2009) and up to 5 g/L (Satyawali and Balakrishnan, 2009; Ng et al., 2006), although higher dosages have been tested as well (Whang et al., 2004; Ma et al., 2012). This study is part of a research project, which aims to the development of a systematic and integrated methodology for the fouling mitigation and control, using PAC (for comparison reasons, among other control techniques) as an additive in a pilot-scale membrane bioreactor. To the author's best knowledge, a relationship (expressed in terms of fouling indices) between the short- and the long-term effect of PAC on membrane fouling in MBRs is yet to be determined. In addition, most research studies indicatively employ two or three different PAC concentrations. In our study, the application of PAC for membrane fouling mitigation took place both in batch-mode and in continuous-flow series of experiments, aiming to investigate and compare the short- and long-term effect respectively, of a wide range of PAC concentrations (0.5-5.0 g/L) on sludge filterability and SMP concentration. In this paper, the results of the short-term experiments are particularly presented and discussed.

Even though it is considered to be an expensive solution (Malamis et al., 2013), the MBR technology can also provide decentralized small-scale wastewater treatment for remote or isolated communities, campsites, tourist hotels or industries, which are not connected to municipal treatment plants. In small communities, houses are spread out, the population density is low and hence, the use of an on-site system even for an individual home, or for a small cluster of homes could be a cost-effective option. MBR technology could provide a decentralized, robust and cost-effective treatment for achieving high-quality effluent in such instances. In addition, it can also offer excellent retrofit capability for expanding, or upgrading of existing conventional wastewater treatment plants (Hai and Yamamoto, 2011).

MATERIALS AND METHODS

The experimental pilot-scale set-up consists of three sub-units: (a) wastewater feed unit, (b) (submerged membrane) bioreactor, and (c) permeate collection unit (Fig. 1a). Firstly, the bioreactor (Fig. 1b) was inoculated with activated sludge, which was received from the municipal wastewater treatment plant of Thessaloniki (located in the area of Sindos, near Gallikos river), and then, the system was operated continuously in order to achieve steady-state condition in the bioreactor. In the second stage, powdered activated carbon (PAC) was added in a series of batch experiments. During these experiments, the PAC was added as single drop mode in mixed liquor samples, which were received from the aeration tank of pilot plant on a daily basis.

The synthetic wastewater (Table 1), 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 monitored by a DO-meter in the range of 2-3 mg/L. The synthetic wastewater composition is the "standard" one proposed by OECD for performing relevant biological

wastewater treatment laboratory experiments. However, the concentrations of the synthetic wastewater components (peptone water, meat extract etc.) were selected to be much higher (x10) in this case, than those proposed by the OECD guidelines (OECD 2010), in order to obtain a satisfactory F/M ratio (approximately 0.2).
The air needed for the biomass and for the cleaning of 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 liquid level in the membrane tank. The permeate was withdrawn from the upper end of the 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, a part of which was used for backwashing the membrane filtration unit by another peristaltic pump. Membrane backwashing steps of 1 min were regularly performed every 10 min of filtration operation.
A flat sheet membrane was operated at a flux of 17 LMH, while one-minute relaxation steps were performed every ten minutes. It is noteworthy to highlight the automated operation of the pilot-scale MBR system: the operation of all peristaltic pumps, the DO-meter, the level sensors and the pressure transmitter were controlled by appropriate Programmable Logic Controllers (PLC). The programming allowed also the automatic backwashing of the membrane through pneumatic electro-valves. Reversible fouling was assessed in terms of sludge filterability tests, according to the standard TTF method, while irreversible fouling was assessed in terms of SMP removal.

Figure 1. (a) Pilot-scale MBR system, (b) aeration tank (bioreactor).

Table 1. Composition of synthetic municipal wastewater.

	Synthetic wastewater according to OECD guidelines	Synthetic wastewater used in the experiments (respective quantities, x10)	Physical/chemical parameters of the synthetic wastewater, which was used in the experiments
Substance	Concentration, mg/L		
Peptone	160	1600	BOD 1036 ± 58 mg/L
Meat extract	110	1100	COD 1987 ± 73 mg/L
K_2HPO_4	28	280	NH_4^+-N 197 ± 18 mg/L
NaCl	7	70	PO_4^{3-}-P= 67 ± 7.8 mg/L
$CaCl_2 \cdot 2H_2O$	4	40	TOC 735 mg/L
$MgSO_4 \cdot 7H_2O$	2	20	Turbidity 14.6 NTU

Filterability Tests with the TTF Method (Time-To-Filter Method)

The addition of PAC in order to improve the filtration characteristics of mixed liquor is among the techniques that have been widely used in order to control the membrane fouling mitigation (Khan et al., 2012). The Time-To-Filter (TTF) method is a well-established method, which can be used as an easy and relatively rapid way to assess sludge filterability (De la Torre et al. 2008; Rosenberger and Kraume 2002). A 90-mm Buchner funnel is used with Whatman #1, #2, or equivalent filter papers (Fig. 2). A short description of the procedure is following: after pouring 200 mL of mixed liquor on the Buchner funnel, the time required to obtain 50 mL of filtrate was recorded at the vacuum pressure of 510 mbar (TTF_{50}). Low TTF_{50} times indicate high sludge filterability, whereas high TTF_{50} times indicate low sludge filterability. In our study, except for the TTF_{50}, the time required to obtain 10, 20, 30 and 40 mL of filtrate was also recorded, in order to plot a full profile of the recorded times, which can contribute to a better comparison and understanding of the obtained results.

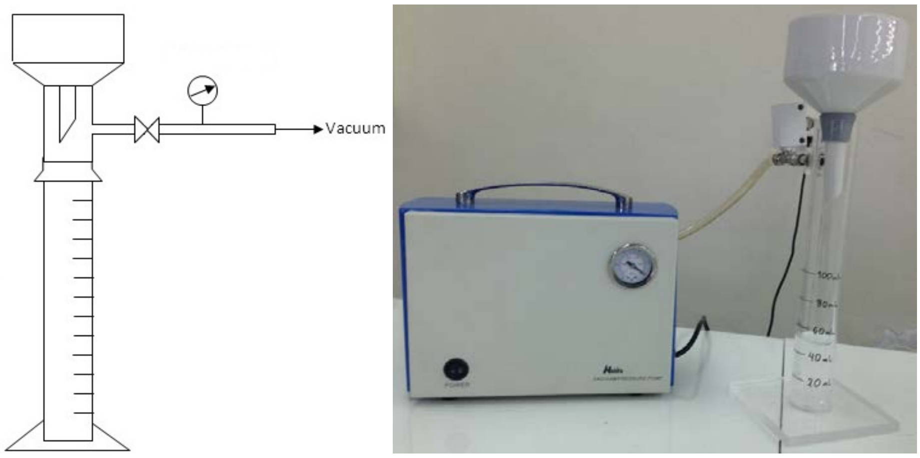

Figure 2. TTF test equipment.

SMP Concentration Measurements

The Phenol-Sulfuric Acid method (DuBois et al. 1956) is the most widely used colorimetric method for the determination of carbohydrate concentration in aqueous solutions. 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 detectible color. A short description of the standard procedure is following: 1 mL aliquot 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 sulfuric acid 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 aliquot of carbohydrate was replaced by glucose. A Hitachi UV/Vis spectrophotometer was used for these measurements. The Phenol-Sulfuric Acid method was applied after the centrifugation of the mixed liquor samples.

RESULTS AND DISCUSSION

The results of the batch-mode (short-term) experiments are presented in terms of the ratios $TTF_{PAC}/TTF_{no\ PAC}$ and $SMP_{PAC.}/SMP_{no\ PAC}$. $TTF_{PAC}/TTF_{no\ PAC}$ is the ratio of the TTF_{50} recorded after the addition of PAC in the mixed liquor sample, to the TTF_{50} 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. $SMP_{PAC}/SMP_{no\ PAC}$ is the ratio of the SMP concentration after the addition of PAC in the mixed liquor sample, to the SMP concentration before this addition (i.e. the respective blank measurement). In the same way, the lower this ratio is the more effective the tested PAC concentration becomes in terms of SMP removal. The effect of PAC on SMP removal and sludge filterability was examined at ten concentrations, i.e. 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 g/L (Fig. 3 and 4). The green horizontal line in each figure represents the blank ratio value (i.e. $TTF_{no\ PAC}/TTF_{no\ PAC}$, or $SMP_{no\ PAC}/SMP_{no\ PAC}$), which is always equal to 1. As shown in Fig. 3 and 4, the addition of PAC for all these concentrations reduced SMP concentration and enhanced sludge filterability in the mixed liquor samples, in agreement with several relevant studies, which suggest the use of PAC for fouling mitigation in MBRs (Ng et al., 2013; Ma et al., 2012; Iversen et al. 2009; Remy et al., 2009).

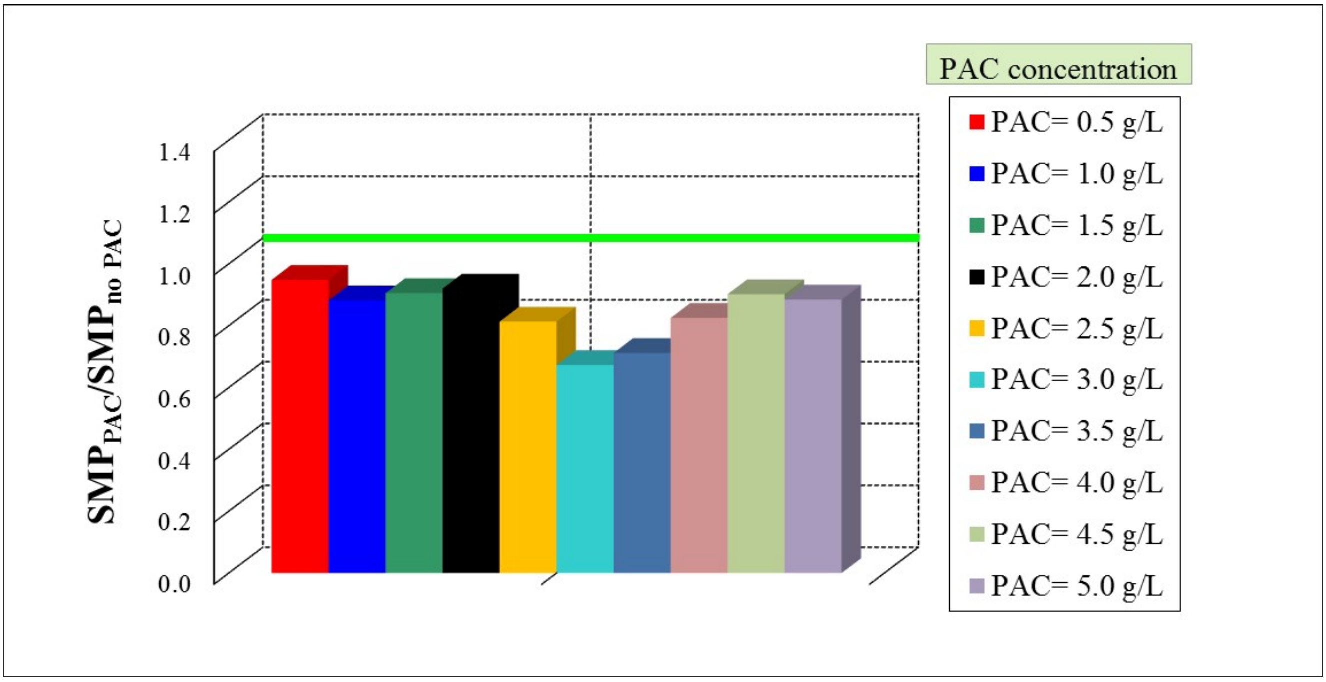

Figure 3. Effect of PAC concentration (0.5-5 g/L) on SMP removal.

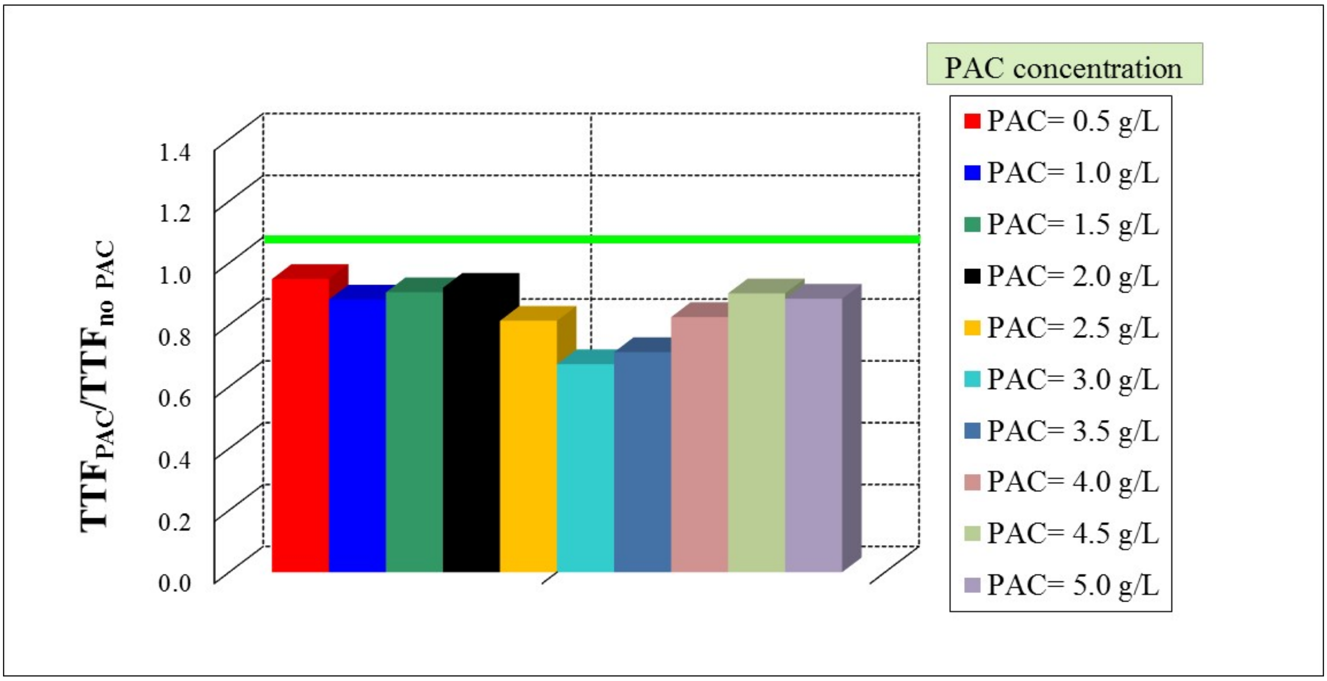

Figure 4. Effect of PAC concentration (0.5-5 g/L) on sludge filterability.

Fig. 5 shows how $SMP_{PAC}/SMP_{no\ PAC}$ and $TTF_{PAC}/TTF_{no\ PAC}$ ratios change with the increase of PAC concentration, allowing the determination of optimal PAC concentration for mitigating both reversible and irreversible fouling.

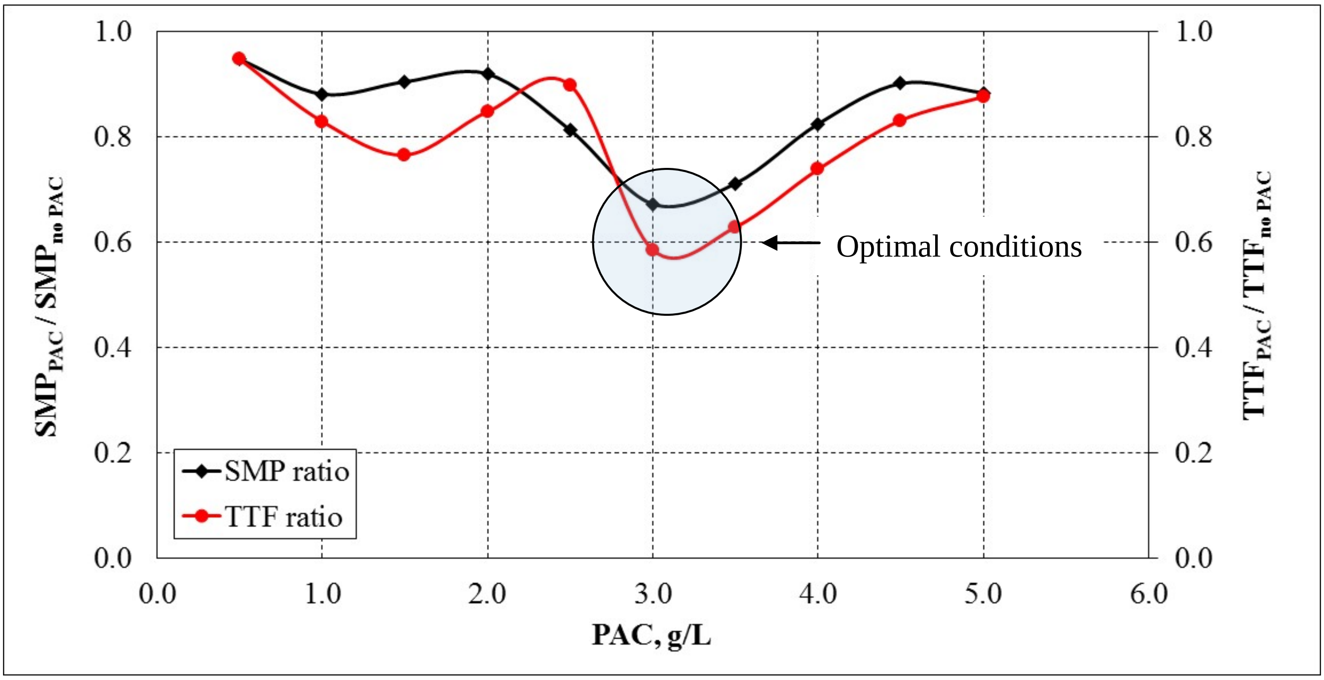

Figure 5. Determination of optimal PAC concentration for mitigating both reversible and irreversible fouling.

As shown in Fig. 5, the concentration of 3 g/L can be considered as the optimal PAC concentration, since its addition in the mixed liquor reduced SMP concentration and enhanced sludge filterability the most. In addition, different PAC concentrations might have different effects on reversible and irreversible fouling. For instance, the addition of PAC at 2.5 g/L was found to lower the $SMP_{PAC.}/SMP_{no\ PAC}$ ratio more, than the $TTF_{PAC}/TTF_{no\ PAC}$ ratio, indicating that it is more beneficial to the confrontation of irreversible, rather than of reversible fouling. However, for most concentrations (i.e. 1.0, 1.5, 2.0, 3.0, 3.5, 4.0, 4.5 g/L) the addition of PAC promoted the reversible, rather than the irreversible fouling mitigation. Another observation that follows directly from Fig. 5 is that above 3 g/L of PAC, both $SMP_{PAC.}/SMP_{no\ PAC}$ and $TTF_{PAC}/TTF_{no\ PAC}$ ratios increased with the increase of PAC concentration, indicating that very high concentrations might have the adverse effect on reversible and irreversible fouling. Overdosing with PAC may fail to reduce membrane fouling, because of its potential to become a foulant itself, either through the formation of a cake layer over the membrane and/or by blocking membrane pores (Skouteris et al., 2015).

As aforementioned, except for the TTF_{50}, the time required to obtain 10, 20, 30 and 40 mL of filtrate was also recorded, in order to plot a full profile of recorded times, which can contribute to a better comparison and understanding of the obtained results. It is interesting to notice that, the addition of PAC at the optimal concentration of 3 g/L caused the decrease of all measured TTF values (TTF_{10}, TTF_{20}, TTF_{30} and TTF_{40}) (Fig. 6b). For comparison reasons, the filterability tests after the addition of a low and a high PAC concentration are presented (Fig. 6a and 6c, respectively).

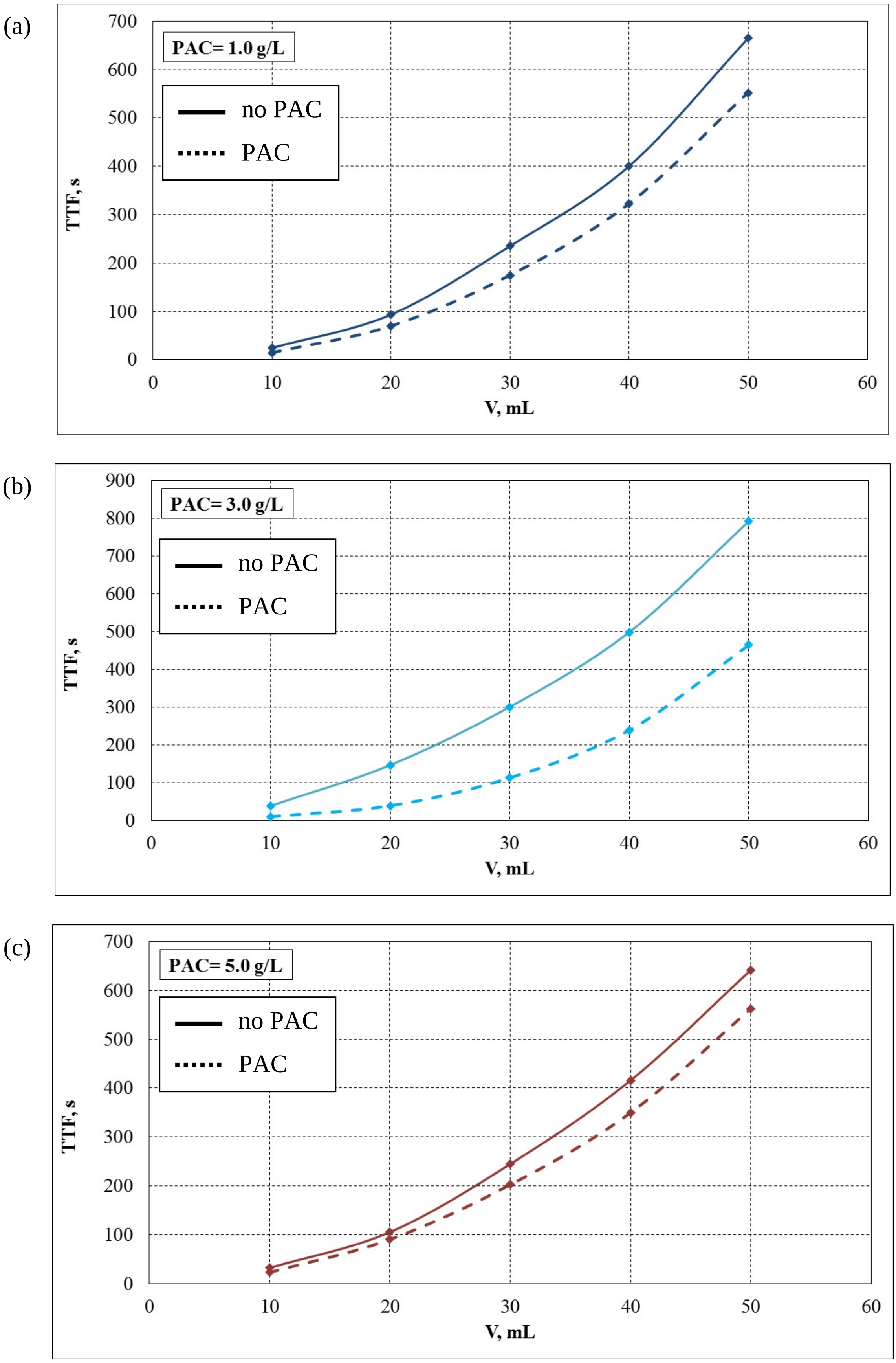

Figure 6. Results of filterability tests for (a) 1.0 g/L PAC, (b) 3.0 g/L PAC and (c) 5.0 g/L PAC.

CONCLUSIONS

The most serious drawback in wastewater treatment using MBR treatment systems is membrane fouling, which gradually leads to membrane permeability decrease and efficiency deterioration, resulting to increased treatment cost, due to higher energy consumption and the need for more frequent membrane cleaning and eventually replacement. In an effort to investigate its effect on membrane fouling, various concentrations (0.5-5.0 g/L) of powdered activated carbon (PAC) were added in mixed liquor samples of a pilot-scale MBR system, which treated high-strength synthetic municipal-type wastewater. The results showed that the addition of PAC at the concentration of 3 g/L in the mixed liquor reduced SMP concentration and enhanced sludge filterability the most. Furthermore, the $TTF_{PAC}/TTF_{no\ PAC}$ ratios were lower, than the corresponding $SMP_{PAC.}/SMP_{no\ PAC}$ ratios, indicating that the batch-mode, short-term addition of PAC promotes the reversible, rather than the irreversible fouling mitigation.

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