Application of powdered activated carbon (PAC) for membrane fouling control in a pilot-scale MBR system
A. I. Zouboulis, P. K. Gkotsis, D. X. Zamboulis and M. G. Mitrakas

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.

Key words | membrane bioreactors, pilot plant, powdered activated carbon, reversible/irreversible fouling

INTRODUCTION

Membrane bioreactors (MBRs) have been widely used during the past few years for municipal or industrial wastewater treatment (Van Dijk & 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. 2013; 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 & Huang 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; Shao et al. 2016; Du et al. 2017).

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 extracellular polymeric substances or soluble microbial products (SMP) which are considered to be primarily responsible for membrane fouling (Cho et al. 2005; Malamis & Andreadakis 2009). 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 & 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 and (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 adsorbed 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, the 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 (Ng et al. 2006; Satyawali & Balakrishnan 2009), 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 MBR. 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. Most research studies also 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 addition, reversible and irreversible fouling are expressed in terms of two novel, easily generated fouling indices, namely ratios TTF_{PAC}/TTF_{no PAC} and SMP_{PAC}/SMP_{no PAC}, respectively.

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 offer excellent retrofit capability for expanding, or upgrading of existing conventional wastewater treatment plants (Hai & 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 (Figure 1(a)). Firstly, the bioreactor (Figure 1(b)) 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, 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. Although the application of chemical additives, such as MPE50 of Nalco and poly-aluminum chloride has demonstrated a remarkable...
performance regarding fouling mitigation according to literature, the addition of adsorbents, such as PAC, in MBRs has not been investigated so extensively, especially in terms of the applied concentration range, and this is why PAC was selected for the specific experiments.

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 the Organisation for Economic Co-operation and Development (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 (×10) 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. The permeate collection unit was the final recipient of the produced permeate.

A flat sheet, microfiltration membrane (Kubota Membranes Inc., Japan) with a pore size of 0.4 μm and an effective area of 0.11 m² (made of chlorinated polyethylene) was operated at a flux of 17 LMH, while one-minute relaxation steps were performed every 10 min. 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. 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.

**Filterability tests with the TTF method (TTF 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. 2022). The TTF method is a well-established method, which can be used as an easy and relatively rapid way to assess sludge filterability (Rosenberger & Kraume 2002; De la Torre et al. 2008). A 90-mm Buchner funnel is used with Whatman #1, #2, or equivalent filter papers (Figure 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 (TTF50). Low TTF50 times indicate high sludge filterability, whereas high TTF50 times indicate low sludge filterability. In our study, except for the TTF50, 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.

**SMP concentration measurements**

The Phenol-Sulfuric Acid method (DuBois et al. 1956) is the most widely used colorimetric method for the determination

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**Table 1 | Composition of synthetic municipal wastewater**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Synthetic wastewater according to OECD guidelines</th>
<th>Synthetic wastewater used in the experiments (respective quantities, ×10)</th>
<th>Physical/chemical parameters of the synthetic wastewater, which was used in the experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peptone</td>
<td>160</td>
<td>1,600</td>
<td>BOD$_5^+$ 1,036 ± 58 mg/L</td>
</tr>
<tr>
<td>Meat extract</td>
<td>110</td>
<td>1,100</td>
<td>COD$_+$ 1,987 ± 73 mg/L</td>
</tr>
<tr>
<td>K$_2$HPO$_4$</td>
<td>28</td>
<td>280</td>
<td>NH$_4$$^-$N 197 ± 18 mg/L</td>
</tr>
<tr>
<td>NaCl</td>
<td>7</td>
<td>70</td>
<td>PO$_4$$^-$P = 67 ± 7.8 mg/L</td>
</tr>
<tr>
<td>CaCl$_2$·2H$_2$O</td>
<td>4</td>
<td>40</td>
<td>TOC$_+$ 735 mg/L</td>
</tr>
<tr>
<td>MgSO$_4$·7H$_2$O</td>
<td>2</td>
<td>20</td>
<td>Turbidity 14.6 NTU</td>
</tr>
</tbody>
</table>

*BOD$_5$: biochemical oxygen demand, COD: chemical oxygen demand, TOC: total organic carbon.
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 (Figures 3 and 4). It is widely accepted that during filtration the dissolved organic matter compounds, mainly comprising of SMP, can be adsorbed onto and/or into the membrane, tending to block membrane pores and form a partly irreversible gel structure on the membrane surface (Patsios & Karabelas 2011) and this is why the irreversible fouling was expressed in terms of SMP concentration in this study. The choice of PAC concentrations was based upon the relevant literature, since the PAC concentrations which are employed in most research studies dealing with fouling mitigation in MBRs fall into this range (0.5–5.0 g/L). By employing an increasing step of 0.5 g/L, it would be more likely to observe significant differences regarding the effect of different concentrations. The green horizontal line in each figure represents the blank ratio value (i.e. TTF\textsubscript{no PAC}/TTF\textsubscript{PAC}, or SMP\textsubscript{no PAC}/SMP\textsubscript{PAC}), which is always equal to 1. As shown in Figures 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 (Iversen et al. 2009; Remy et al. 2009; Ma et al. 2012; Ng et al. 2013).

Figure 5 shows how SMP\textsubscript{PAC}/SMP\textsubscript{no PAC} and TTF\textsubscript{PAC}/TTF\textsubscript{no PAC} ratios change with the increase of PAC concentration, allowing the determination of optimal PAC concentration for mitigating both reversible and irreversible fouling.

As shown in Figure 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 \( \frac{\text{SMP}_{\text{PAC}}}{\text{SMP}_{\text{no PAC}}} \) ratio more, than the \( \frac{\text{TTF}_{\text{PAC}}}{\text{TTF}_{\text{no PAC}}} \) ratio, indicating that it is more beneficial to the confrontation of irreversible, rather than 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 Figure 5 is that above 3 g/L of PAC, both SMPPAC/SMPno PAC and TTFPAC/TTFno 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 TTF50, 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 (TTF10, TTF20, TTF30 and TTF40) (Figure 6(b)). For comparison reasons, the filterability tests after the addition of a low and a high PAC concentration are presented (Figure 6(a) and 6(c), respectively).

This study is part of a research project which aims to develop an integrated technique for membrane fouling control in MBR systems by the use of additives, such as adsorbents, coagulation agents and bio-film carriers. Each additive is added first in batch-mode experiments (Phase I) and then continuous-flow experiments are conducted (Phase II) based on the optimal results obtained from Phase I. Continuous-flow experiments for the case of PAC are currently being conducted and have not been completed yet. For this reason, it was decided not to include them in the present work.

Regarding removal efficiency, although the primary objective of the present study is membrane fouling mitigation in MBRs by the use of PAC, the system’s performance was also assessed in terms of organic content (COD, BOD5) and ammonium (NH4-N) removal in order to estimate the environmental impact of a pilot-scale MBR system treating synthetic municipal wastewater of high strength. Results showed that COD, BOD5 and NH4-N removal were more than 96%, 97% and 94%, respectively.

CONCLUSION

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 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 TTFPAC/TTFno PAC ratios were lower, than the corresponding SMPPAC/SMPno 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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