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Fouling control in membrane bioreactors with sewage-sludge based adsorbents

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Abstract

The potential application of powdered activated carbon (PAC) to mitigate membrane fouling has been tested in membrane bioreactors (MBRs) fed with cosmetic wastewater. Inexpensive powder activated carbon was prepared from sewage sludge biosolids (B-PAC) by pyrolysis (750 °C; 0.5 h) and air-activation (400 °C; 2 h). Adsorption capacities of 143 and 570 mg g⁻¹ were reached for carbohydrates and proteins, respectively, quite similar to those of a commercial activated carbon (C-PAC). To check the effect of PAC addition on membrane fouling, three MBRs were simultaneously operated without (control-MBR) and with PAC (B-MBR and C-MBR) for 150 days in continuous mode at 8 L m⁻² h⁻¹ flux. Similar COD removal efficiencies were achieved in these three MBR systems. After 100 days of operation, the effect of the PACs on the sludge filterability was studied in the MBRs for 10 days. B-MBR showed stable transmembrane pressure (TMP) after 9 days of operation, unlike of control-MBR and C-

MBR, where the TMP increased after the 2nd and 5th days, respectively. Therefore, operational cost saving can be achieved in the membrane cleaning due to decrease of fouling rate. Operating at stable state condition the addition of PAC gave rise to an increase of the critical flux of 25%. In an extra shear test, carried out at the end of the continuous experiment, a clear reduction in mean size of the flocs from 45 to 28 μm was observed in control-MBR. However, the extra shear led to a slight reduction of the mean size of flocs (less than 5%) in MBRs with PAC, with average sizes of 62 and 71 μm in C-MBR and B-MBR, respectively. The molecular weight fractionation of the MBR demonstrated a higher selectivity of B-PAC toward the adsorption of proteins smaller than 1 μm which prevents the irreversible fouling of the membranes. The membranes lifetime was increased because the B-PAC extended the filtration for a longer period than C-PAC, probably due to its easier in-situ regeneration.

1. Introduction

Membrane bioreactors (MBR) allow improving the quality of effluents by providing high organic matter and nutrient removal. They also greatly reduce the amount of solids discharged and remove pathogens so that disinfection can be milder or even unnecessary. All these advantages combine with a small plant footprint, eliminating the need of tertiary treatment for reclaimed wastewater. However, the widespread application of MBRs is limited by the operational costs and investment associated with membrane fouling (Remy et al., 2010). Different fouling control strategies have been proposed, such as backwash, relaxation, aeration and chemical cleaning (Le-Clech et al., 2006; Meng et al., 2009). Filtration at moderate flux (below the critical) is an extended strategy to avoid the short-term decline in permeability, but fouling usually appears in long-term operations (Aun Ng et al., 2006; Melin et al., 2006). The interactions between

the membranes and microbial substances present in the mixed liquor, such as extracellular polymeric substances (EPS) and soluble microbial products (SMP), decrease the permeability by adsorption, pore blockage and the formation of a gel layer and sludge cake (Bin et al., 2008). Recently, the effect of SMP on MBR fouling has attracted much attention. They are easily accumulated, causing poor filterability of the sludge suspension (Drews et al., 2008; Juang et al., 2013). In general, the fouling rate can be controlled using two approaches: (i) the regulation of operational parameters, such as sludge retention time (SRT), hydraulic retention time (HRT), dissolved oxygen (DO) concentration, temperature, aeration, and (ii) the addition of certain chemicals which modify the characteristics of the mixed liquor upon coagulation (Guo et al., 2010; Koseoglu et al., 2008; Wu et al., 2006; Zhang et al., 2008), flocculation (Collins et al., 2006; Guo et al., 2010; V. Iversen et al., 2009; Ji et al., 2010; Wozniak, 2010) or adsorption (Le-Clech et al., 2006; Meng et al., 2009). These chemical agents include organic polymers (Vera Iversen et al., 2009; Koseoglu et al., 2008) and inorganic flocculants, such as aluminium and ferric chloride (Koseoglu et al., 2008; Wu et al., 2006; Yu et al., 2016), which in general improve the sludge filterability but at the expense of an increase in cost (Huyskens et al., 2012). Alternatively, the use of powdered activated carbon (PAC) to improve the performance of MBRs treating municipal (Bonvin et al., 2016; Chu et al., 2013; Pramanik et al., 2016; Rafiei et al., 2014; Remy et al., 2010; Skouteris et al., 2015; Woo et al., 2016; Ying and Ping, 2006) and industrial wastewaters (Jegatheesan et al., 2016; Kaya et al., 2016; Lesage et al., 2008) has been recently studied. PAC can mitigate fouling by adsorbing the species responsible (Judd, 2006; Lesage et al., 2008). However, frequent repositioning of the PAC is necessary due to its saturation by foulants. Activated carbon also provides a solid support for biomass growth which makes the flocs denser and resistant to breakage

thereby preventing the accumulation of particulate matter on the membranes (Lesage et al., 2008). A low PAC dosage (0.5 g L^{-1}), combined with a long SRT, namely 50 d, reduced fouling significantly in a pilot MBR (Remy et al., 2011). This effect has been ascribed to the deposition of a dynamic and permeable PAC layer on the surface of the membranes, protecting them from deposition by foulants (Pirbazari et al., 1996; Ying and Ping, 2006). Moreover, PAC also adsorbs toxic species, reducing their inhibitory effect on the biomass (Hu et al., 2014; Nguyen et al., 2014; Suárez et al., 2008; Yang et al., 2010).

The cost of PAC has restricted extended implementation for wastewater treatment so far. Therefore, more cost-effective adsorbent, supports are needed. The potential use of more economic alternatives, such as low-cost PAC produced from biomass (Remy et al., 2010) and sewage biosolids (Monsalvo et al. 2011, 2012 ; Mohedano et al. 2014) has been reported for their use in environmental applications. In this sense, the increasing generation of sewage sludge from wastewater treatment demands new ways of valorization. Owing to their low cost, simplicity of preparation, insensitivity to toxic substances, and fair adsorption capacity, sewage sludge-based adsorbents appear to be a versatile and suitable alternative to commercial activated carbons in MBR. Acceptable adsorbents can be obtained from sewage sludge in different ways. Among them, air-activation at moderate temperature has been claimed to be a promising way of valorisation to inexpensive adsorbents for wastewater treatment (Monsalvo et al., 2011). Some studies have been carried out using MBR with PAC for the treatment of industrial wastewaters from distilleries (Satyawali and Balakrishnan, 2009) and tanneries (Munz et al., 2007) as well as landfill leachates (Pirbazari et al., 1996). In this work, wastewater from a cosmetics manufacturer has been treated in a submerged MBR. These wastewater are characterized by relatively high values of chemical oxygen

demand (COD) and suspended solids. In addition, their variable composition and the fluctuations in pollutant concentrations often make their treatment by conventional activated sludge inefficient. However, the biological treatment of those effluents has been scarcely studied. The application of advanced biological systems like upflow anaerobic sludge blanket reactors and sequencing batch reactors has been reported recently (Puyol et al., 2011; Tobajas et al., 2014).

The aim of this work is to investigate the potential use of activated carbon to control membrane fouling in MBR. Therefore, an inexpensive porous carbon, obtained by pyrolysis and air-activation of sewage sludge biosolid, was tested for this purpose and compared with a commercial activated carbon. This material has been previously assayed in 4-chlorophenol adsorption yielding good results in spite of the relative low BET surface area developed compare with conventional activated carbons (Monsalvo et al., 2011). In addition, the SMP adsorption capacity was evaluated and changes in the sludge characteristics, and the development of fouling layers analyzed.

2. Experimental

2.1. Preparation of activated carbon

Aerobic flocculent sludge was collected from a full scale MBR treating cosmetic wastewater. The preparation of activated carbon from biosolids (B-PAC) was carried out by pyrolysis at 750 °C for 0.5 h under N₂ atmosphere (100 mL min⁻¹). Then, the carbonized solid was subjected to air-activation at a flow rate of 100 mL min⁻¹. The working temperature (400 °C) was reached at a 10°C min⁻¹ and then was maintained for 2 h. The resulting material (B-PAC) showed a S_{BET} of 327 m² g⁻¹, and micro- and mesopore volumes of 0.06 and 0.18 cm³ g⁻¹, respectively. The commercial activated carbon (C-PAC) purchased from Merck (Whitehouse Station, NJ, USA) had a S_{BET} of

125 $917 \text{ m}^2 \text{ g}^{-1}$, and micro- and mesopore volumes of 0.33 and $0.04 \text{ cm}^3 \text{ g}^{-1}$, respectively.

126 Both carbons were ground and sieved to a particle size within the range of 0.1 - 0.25 mm .

127 **2.2. Adsorption experiments**

128 Equilibrium adsorption tests were performed with aqueous solutions enriched with
129 proteins and carbohydrates extracted from the MBR bulk sludge. The microorganisms
130 were lysed by osmotic shock with aqueous NaCl (0.9% , w) at 100°C for one hour and
131 then centrifuged at 3200 rpm for 30 min (Wang et al., 2009). The PAC (0.06 g) were
132 dispersed in 60 mL aqueous solutions containing different concentrations of the proteins
133 and carbohydrates extracted (0.1 - 1.0 g L^{-1}). Samples were placed in a thermostated
134 shaker at 25°C working at a 200 rpm equivalent stirring velocity. The contents of the
135 flasks were centrifuged (3200 rpm , 30 min) and the concentration of proteins and
136 carbohydrates were measured. Desorption experiments were also carried out. Samples
137 of PAC were saturated with an extracted solution with a high protein and carbohydrate
138 concentration. Then, the fraction of easily reversible proteins and carbohydrates was
139 extracted from the PAC with 10 mL of miliQ water in shaken flasks (150 rpm
140 equivalent) at 25°C for 10 min . The liquid was analysed for protein and carbohydrate
141 content. This PAC was collected, dried at room temperature, and submitted to a two-
142 steps extraction protocol with 10 mL of methanol (first) and acetone (second) by
143 sonication (200 W , 35 Hz) at 40°C . The proteins and carbohydrates measured in the
144 resulting liquids were ascribed to the hardly reversible fraction. The fraction of proteins
145 and carbohydrates irreversibly adsorbed onto the PAC was calculated by the difference.
146 Control experiments in absence of PAC proved that the removal of these compounds
147 from the liquid phase was almost exclusively due to adsorption. All the experiments
148 were performed in triplicate and the standard deviation was below $\pm 3\%$.

2.3. MBR experiments

Three 15 L MBR systems were simultaneously operated in continuous mode at $8 \text{ L m}^{-2} \text{ h}^{-1}$ flux without PAC (control-MBR) and with the commercial and biosolid-based PACs (C-MBR and B-MBR, respectively). The reactors were inoculated with 8.6 g VSS L^{-1} flocculent sludge sampled from a full scale MBR treating cosmetic wastewater. The bioreactors were acclimatized for 30 days until a steady state was reached and were operated for 150 d at room temperature and neutral pH. C-MBR and B-MBR were supplemented with a PAC concentration of 1 g L^{-1} . PAC was periodically added to replace the loss due to sludge purge in order to maintain a constant SRT and HRT of 30 and 19 h, respectively. The sludge was maintained under aerobic conditions by injecting compressed air through porous glass diffusers. The average diameter of the air bubbles $2.9 \pm 0.1 \text{ mm}$, was determined by the recognition of the size in grayscale using Matlab 7.6 (The Mathworks, INC.) language. The MBRs were equipped with chlorinated polyethylene flat sheet membranes (KUBOTA[®]) with total surface area of 0.1 m^2 and a nominal pore size of $0.4 \mu\text{m}$. A constant specific aeration demand (SAD) of $1.5 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ was used. In order to emulate the fluidodynamic regime in the vicinity of flat sheet membranes in full-scale submerged MBRs, baffles were installed symmetrically at 1 cm on both sides of the membranes. Permeate flux was maintained constant with a peristaltic pump (Gilson Minipuls 3) and the transmembrane pressure (TMP) was measured by a pressure transducer (XA-300, mPm) connected to a data acquisition system. Chemical cleaning of the membranes was carried out when the pressure reached 20 kPa, unless stated otherwise. The cleaning process was carried out by soaking the membranes in 0.4 wt. % hypochlorite sodium at room temperature for 24 h.

The performance of the MBRs was evaluated by measuring the soluble and total chemical oxygen demand (SCOD and TCOD), total and volatile suspended solids (TSS and VSS), total organic carbon (TOC) and total nitrogen (TN).

2.4. Wastewater composition

The MBRs were fed with pretreated wastewater from a cosmetic factory. Due to the low P and N concentration of cosmetic wastewaters, phosphoric acid and ammonium sulphate were added externally to the feed to achieve a COD:N:P ratio of 100:5:1. The following is a representative analyses of the cosmetic wastewater: 9.6 - 10 g L⁻¹ (TCOD), 5.2 - 7.8 g L⁻¹ (SCOD), 2 - 4.2 g L⁻¹ (TOC), 1.6 - 1.8 g L⁻¹ (TSS), 1.4 - 2.0 g L⁻¹ (fats and oils) and 5.5 - 6.5 (pH).

2.5. Membrane fouling analysis

The foulant layers such as the intrinsic, unstable, easily and hardly reversible one were removed sequentially via a three-step procedure, whereby an increasingly stronger method was applied to remove them from the membrane surface and thus assess the preferential deposition of foulants. To remove the unstable layer, the weakly adsorbed fraction, the membranes were submerged in 1.2 L of milliQ water and shaken for 2 min at an equivalent stirring velocity of 100 rpm. The easily reversible layer, the intermediate fraction was removed by backwashing with milliQ water (1.2 L) at 4 L m⁻² h⁻¹ flux. Finally, the hardly reversible layer was removed by submerging the membrane in 1.2 L sodium hypochlorite solution (0.4% wt.) for 24 h at an equivalent stirring velocity of 50 rpm. The aqueous fraction from each cleaning step was analysed for COD, TOC, TN and TSS. This procedure was not primarily aimed at replicating the cleaning strategies applied in the industry, but to obtain three fouling layers in a well-

controlled environment for further characterization. This protocol is not a standardized method but has been previously used to provide further understanding of the fouling layers (Henderson et al., 2011; Metzger et al., 2007; Tran et al., 2013; Wu et al., 2008).

The permeability of the different fouling layers was established by measuring the TMP and permeate flux. At the end of every fouling experiment the overall resistance (R_T) was determined. Then, the fouling resistance (R_F) was calculated by subtracting the intrinsic membrane resistance (R_M) from the overall resistance (R_T). After removing each layer, a clean water permeability test was performed at a permeate flux of $10 \text{ L m}^{-2} \text{ h}^{-1}$ for 20 min to measure the individual fouling resistances. Hence, the hydraulic resistance associated with each fouling layer: rinsed (R_R), backwashed (R_B) and desorbed (R_D), was calculated using the equations [1]-[3]. These experiments were carried out in duplicate. The permeability resistances associated with each fouling layer, namely unstable (R_U), easily reversible (R_{ER}) and hardly reversible (R_{HR}), were calculated as follows:

$$R_U = R_T - R_R \quad [1]$$

$$R_{ER} = R_R - R_B \quad [2]$$

$$R_{HR} = R_B - R_D \quad [3]$$

In all the tests performed, R_D was approximately equal to R_M indicating that irreversible fouling was negligible. Thus, R_T is calculated as:

$$R_T = R_M + R_U + R_{ER} + R_{HR} \quad [4]$$

The flux-step method (Le Clech et al., 2003) was used to determine critical flux. The flux was increased by $2 \text{ L m}^{-2} \text{ h}^{-1}$ every 20 min, working at a constant VSS concentration of 9.3 ± 0.5 , 9.4 ± 0.3 and $9.4 \pm 0.6 \text{ g L}^{-1}$ in the control-MBR, C-MBR

and B-MBR, respectively. The membranes were cleaned before each critical flux test by soaking them in sodium hypochlorite (0.4%wt.) for 2 h, achieving a permeability recovery of 90%. These tests were performed in duplicate.

2.6. Shear experiment

Extra shear was applied to the sludge from the control-MBR, C-MBR and B-MBR. The mixed liquors from the three reactors were stirred with a guarded triple-bladed propeller at a rotation speed of 900 rpm for 10 h. This condition corresponds to 800 s^{-1} shear, which is considered as standard for shear sensitivity determination (Mikkelsen, 2002; Remy et al., 2010). The critical flux was determined to assess the effect of shear on sludge filterability, using the method described above (Le Clech et al., 2003).

2.7. Chemical and physical analyses

SCOD, TCOD, TSS and VSS were measured according to the APHA Standard Methods (APHA, 2012). An automatic analyser was used for TOC and TN (TOC-VCPN and TNM-1, Shimadzu). Serial molecular weight fractionation of the supernatant was carried out in a Amicon 8400 filtration module (Millipore, USA) with 76 mm diameter polyethersulphone UF membranes of nominal molecular weights 10 kDa, 100 kDa, 1 μm and 8 μm (Millipore, USA). SMP fractionations were conducted at a constant shear (under magnetic stirring) and a filtrate/retentate ratio of 0.4. The pressure was regulated at 2 bar using laboratory-grade nitrogen (> 99 %). Proteins and carbohydrates were determined by the respective adapted methods of Lowry et al., 1951 and Dubois et al., 1956. Bovine serum albumin (BSA) and D-glucose were used as standards for the determination of proteins and carbohydrates, respectively. Scanning electron microscopy (SEM) images of the mixed liquor and fouled membranes were obtained

using Hitachi S-3000N apparatus using the samples which had been fixed and sputter-coated with gold. The image processing and analysis procedure comprised image pre-treatment, segmentation and debris elimination (Tian et al., 2011). The image processing and analysis program for flocs and aggregates was developed using Matlab 7.6 (The Mathworks, INC.) language.

Results and discussion

3.1. Adsorption of SMP

Fig. 1 shows the adsorption isotherms of carbohydrates and proteins on C-PAC and B-PAC. The saturation adsorption capacities for carbohydrates (130 and 143 mg g⁻¹) and proteins (634 and 570 mg g⁻¹) were quite similar for both adsorbents despite the much lower surface area of B-PAC.

The size distribution of SMPs was characterized before and after adsorption to learn more about their selective adsorption. Fig. 2 shows the results obtained. No significant differences were observed between the size patterns of carbohydrates adsorbed on both PACs (Fig 2a). However, B-PAC showed a higher adsorption capacity for proteins smaller than 300 kDa (85%), and C-PAC appeared to be more selective for proteins with a molecular size higher than 300 kDa (80%) (Fig 2b). These materials show a high affinity for SMP, which can provide an effective method for fouling mitigation in MBR.

Fig. 3 provides information about the strength of adsorption. Although both PACs showed a lower adsorption capacity for carbohydrates than for proteins, the former were more strongly retained, with the non-desorbable fraction about 65 % of the adsorbed carbohydrates (Fig. 3a and Fig. 3b). A higher adsorption strength was observed for proteins, where the non-desorbable fraction was lower than 45 % (Fig. 3a and Fig. 3b).

In the case of B-PAC the easily desorbable fraction of proteins increased to 33 %. These results are indicative of the easier regeneration of B-PAC when compared to C-PAC.

3.2. MBR performance

Three identical MBRs were simultaneously operated for 150 days at a permeate flux of $8 \text{ L m}^{-2} \text{ h}^{-1}$, a HRT of 19 h and organic loading rate (OLR) of $2.7 \text{ kg COD m}^{-3} \text{ d}^{-1}$. Similar COD (96.0 ± 0.8 , 95.4 ± 0.6 and $96.1 \pm 0.7\%$) and TOC (93.5 ± 0.9 , 94.5 ± 0.9 and $93 \pm 0.7\%$) removal efficiencies were achieved for control-MBR, C-MBR and B-MBR. Furthermore, the addition of PACs did not cause any significant improvement in organic matter removal as the control-MBR gave an excellent performance (data not shown). The average permeate quality was similar for all the MBRs, yielding values of TOC, COD and TN around 45 ± 4.3 , 75 ± 5.3 and $15 \pm 3.3 \text{ mg L}^{-1}$, respectively.

3.3. Effect of PACs on sludge filterability.

The MBRs were continuously filtrated for 10 days at $8 \text{ L m}^{-2} \text{ h}^{-1}$ flux, under steady-state operation, with the aim to evaluate the effect of PACs on sludge filterability. Fig. 4 shows the transmembrane pressure (TMP) profiles along 10 days of operation of MBRs, from the 100th up to 110. Prior to the registration of TMP, a chemical cleaning of the membranes was carried out. At the end of the experiment, the membranes were removed from the MBRs and a cake layer of control-MBR and C-MBR membranes was found while a gel layer attached to the membrane surface was observed in B-MBR, which was previously reported in the literature under sub-critical flux operation (Ognier et al., 2004; Wang and Waite, 2008; Wang and Wu, 2009a). The results in Fig. 4 reveal a very different trend in the B-MBR. B-MBR showed stable TMP after 9 days of operation, unlike of control-MBR and C-MBR, in which the TMP increased after the

2nd and 5th days, respectively. Under constant flux operation, the convection of foulants tends to self-accelerate, which can eventually create a sharp increase in TMP. Although the addition of C-PAC delayed the rise in TMP, similar trends were observed in control-MBR and C-MBR, suggesting that C-PAC did not exert any significant effect on the sludge permeability beyond a certain time. These two fouling profiles followed the typical trend reported for constant flux operation of submerged porous membranes (Le-Clech et al., 2006). Meng and He (2015) found similar TMP trend for synthetic wastewater treatment by a MBR operated at $8 \text{ L m}^{-2} \text{ h}^{-1}$ flux. In that case, TMP increased rapidly, reaching about 35 kPa after 10 days on stream. This fact was attributed to formation and accumulation of SMP and EPS onto membrane. The beneficial effect of B-PAC can be related to the easy regeneration of B-PAC, as describe above, which can maintain the adsorption of SMP for a longer period. These results indicate that the addition of B-PAC, an inexpensive adsorbent obtained from the activated sludge, provides a significant improvement in the MBR operation. Woo et al. (2016) reported the prolonged operation of MBR without chemical cleaning for more than 20 days at $10 \text{ L m}^{-2} \text{ h}^{-1}$ flux, by adding PAC. This effect was attributed to adsorption of dissolved organic matter onto PAC. Similar results were obtained by Du et al. (2016) who reported a slight TMP fluctuation, in the range of 5.2 and 9.6 kPa, along the operation of a PAC-MBR (2 g L^{-1}) at $5 \text{ L m}^{-2} \text{ h}^{-1}$ flux for more than 70 days without chemical cleaning.

Fig 5. shows the SEM images of flocs for control-MBR, B-MBR and C-MBR, respectively. The flocs from control-MBR seem to be formed of filamentous organisms, *Coccus* and *Bacillus* (Fig 5.a and 5.b). Fig 5.c and 5.d reveal that the B- and C-PACs

appeared to be fouled with a dense and rough biomass layer that acts as a support for biofilm growth.

3.4. SMP concentration and composition

The concentration of SMP in the supernatant of the control-MBR, C-MBR and B-MBR was 102 ± 21 , 95 ± 22 , and 86 ± 17 mg L⁻¹ (at steady state conditions) of which the proteins fraction was 62.7, 56.9 and 42.1 %, respectively. The high concentration of SMP in the control-MBR may affect the performance of the membranes as has been shown in previous works by Le-Clech et al., 2006. Fig. 6 shows significant differences in the size distribution of SMP retained by the membranes in the three MBR conditions. Approximately 85 % of the carbohydrates retained in the control-MBR were smaller than 1 μ m, while in the C-MBR and B-MBR that fraction represented less than 70 and 60 % (Fig 6.a), respectively. This effect was even more evident for the proteins, where 94 % (w) of those retained in the control-MBR corresponded to entities smaller than 1 μ m, compared with 80 % and 40 % in the C- and B-MBR, respectively. This might be due to B-PAC adsorption, which was more selective for smaller carbohydrates and proteins, due to microporous texture of that material. Owing to the small size of those biomolecules (below 1 μ m), they can be easily deposited on the membranes by the permeate flow, but they have a lower back transport velocity due to lift forces than the larger entities (e.g., colloids and flocs). It is known that irreversible fouling is predominantly caused by a relative high concentration of linked small SMP (Metzger et al., 2007).

3.5. Role of fouling layers

The control-MBR was operated in continuous mode at $8 \text{ L m}^{-2} \text{ h}^{-1}$ flux, under steady-state with the aim to evaluation the role of fouling layer. The cleaning process was carried out at the beginning of experiment by soaking the membranes (0.4 wt. % hypochlorite). The occurrence of fouling in a long-term experiment with the control-MBR was followed by an SEM examination of the membrane surface (Fig. 7). At the beginning the filtration, internal pore fouling is caused by accumulation of SMPs (Drews, 2010; Gray et al., 2008; Henderson et al., 2011). The fouling deposits grew gradually until a TMP of 9 kPa was reached (Fig. 7b). The consolidation of these deposits has been associated to the deposition of colloids, macromolecules, species from cell lysis, extracellular polymeric substances (EPS) and/or soluble microbial products (SMP) (Wang and Wu, 2009b). In the second step, the deposition of sludge flocs on the membrane surface associated with a significant increase of the TMP was observed. A gel layer was evident appreciate at a TMP of around 20 kPa (Fig. 7c). This seems to be the main fouling below that TMP value. Above 20 kPa the presence of a cake layer was observed (Fig. 7d). This layer was not uniformly distributed over the entire surface of the membranes, which were partially covered by a static sludge cake and a thin sludge film detachable by aeration.

The control-MBR was operated for different time periods until TMP values of 9 (start of fouling), 20 (gel layer formation) and 50 kPa (cake layer formation) were reached. Then, the membranes were cleaned following the three-step protocol described in section 2.5, which resulted in three fouling fractions, i.e. unstable, easily reversible and hardly reversible layers. The membranes from C- and B-MBR were also analysed at the end of the experiments to learn about the distribution of fouling fractions. Fig. 8 shows that, the relative distribution of filtration resistance in the control-MBR changed with

the extension of fouling. Hence, the membrane and the unstable layer represented the major resistances. The deposition of the gel layer, at TMP values above 9 kPa, gave rise to an easily reversible layer which was the main filtration resistance at that stage. Backwashing was efficient at removing this gel layer. Finally, a sharp increase in the filtration resistance was observed associated with the presence of an unstable layer, which seems to be related to the formation of a cake layer at TMP values above 20 kPa. Thus, filtration resistance included membrane (9.3 %), unstable (71.1 %), easily reversible (17.1 %) and hardly reversible (2.5%) layers in the control-MBR. The formation of a cake layer was the main contribution to an overall resistance around $136 \cdot 10^{11} \text{ m}^{-1}$ for the control-MBR and the C-MBR, where the unstable reversible layer was also the main contribution (80 %), but that of the hardly reversible layer decreased to below 1%, which prevented frequent chemical cleaning. Cake layer, with a resistance ranged from $27 \cdot 10^{11}$ to $63 \cdot 10^{11} \text{ m}^{-1}$, was the main mechanism of membrane fouling in the MBR (Hao et al., 2016). The cleaning assay could not be carried out with the membranes of the B-MBR because the formation of fouling layers was not observed after 10 days on stream. This confirms the ability of B-PAC to inhibit the deposition of fouling species.

The easily reversible gel layer removed by backwashing showed the highest solids concentration (67 %) of the overall fouling layer (Table 1). Given the potential oxidation of the organic matter by NaClO in the hardly reversible layer, its composition is not included because it can be seriously affected by the fractionation method. The unstable layer removed by rinsing yielded a higher concentration of soluble organic matter (SCOD and TOC) than the easily reversible layer. Hence, the addition of PAC can potentially control the development of irreversible fouling and reduce the chemical

cleaning required to maintain MBR operation, the frequency of which must be as low as possible to extend the life of the membrane life.

3.6 Critical flux determination

Fig. 9.a shows the time-course of the transmembrane pressure and permeate flux in the control-MBR, C-MBR and B-MBR. The TMP for all MBRs was lower than 2 kPa for fluxes below $10 \text{ L m}^{-2} \text{ h}^{-1}$. In the control-MBR working at fluxes higher than $12 \text{ L m}^{-2} \text{ h}^{-1}$ a fairly rapid increase in the TMP was observed, reaching 16 kPa at $18 \text{ L m}^{-2} \text{ h}^{-1}$. However, C-MBR and B-MBR showed TMP values of 2 and 4 kPa, respectively, at the highest working flux assayed.

Critical flux experiments were carried out in situ after the start-up period to assess the effect of PAC on sludge permeability. Different criteria have been proposed to establish the value of critical flux (J_c). The most common is that of Le Clech et al. (2003), where J_c is defined as the flux above which the TMP increases at a rate higher than 0.6 kPa h^{-1} . Fig 9.b depicts the fouling rate as a function of flux. Fouling did not occur at fluxes lower than $6 \text{ L m}^{-2} \text{ h}^{-1}$ and the TMP always remained below 4 kPa. The control-MBR yielded a critical flux of $8 \text{ L m}^{-2} \text{ h}^{-1}$. The addition of C-PAC and B-PAC improved the sludge permeability, allowing a critical flux of $10 \text{ L m}^{-2} \text{ h}^{-1}$. The positive effect of PAC has been reported in the literature even at low doses (0.5 g L^{-1}) which allow an increase the critical flux by about 10 % working at a SRT of 50 days (Remy et al., 2009). The critical flux increased by 30 % with 1.2 g L^{-1} of PAC in a MBR treating synthetic wastewater (Li et al., 2005). The TMP increased smoothly and fouling rates of 2.1 and 3.6 kPa h^{-1} were observed at the end of the experiment with C-PAC and B-PAC, respectively. It is noteworthy that the so-called TMP jump was not observed in these

PAC-assisted MBRs. The addition of PAC gave rise to a 25 % increase in the critical flux.

The mixed liquors from the three MBRs were subjected to an additional shear for the sake in order to investigate its mechanical consistence and permeability. The sludge from the control-MBR yielded a higher increase in TMP than those from C-MBR and B-MBR.

Fig. 10 shows the size distribution of floc in MBRs before the shear stress test. A clear reduction in mean size of the flocs from 45 to 28 μm was observed in the shear stress experiment. The extra shear did not alter the critical flux observed for the mixed liquor containing PAC. This indicates that the addition of PAC improved the consistency of the flocs, which showed average sizes of 62 and 71 μm in C-MBR and B-MBR, respectively. The extra shear led to a slight reduction of the mean size of less than 5%.

4. Conclusions

The main conclusions of this study are the following:

- The addition of an activated carbon prepared by pyrolysis and air-activation of sewage sludge biosolids resulted in significant reduction in fouling in MBR operation. The beneficial effect of this inexpensive adsorbent was significantly higher than that observed with commercial activated carbon. This enable the membrane to remain on stream for a longer period of time.
- This carbon material also showed a high adsorption of protein and carbohydrates which was similar to commercial activated carbon, despite its lower surface area.

- The improvement caused by PAC on the evolution of TMP in the MBR can be attributed in greater part to the adsorption of small proteins ($< 1 \mu\text{m}$) which cause irreversible fouling, as well as to in-situ regeneration by easy absorption.

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- 627

Table 1. Composition (mg L^{-1}) of the fouling layers extracted.

Cleaning fractions	TCOD	SCOD	TOC	TSS
Unstable	269 ± 23	48 ± 10	13 ± 3	65 ± 0.6
Easily reversible	448 ± 31	21 ± 15	11 ± 6	196 ± 13.1

Figure captions

Fig. 1. Adsorption isotherms (25°C) of carbohydrates (a) and proteins (b) with C-PAC (circles) and B-PAC (triangles).

Fig. 2. Size distribution of the carbohydrates (a) and proteins (b) adsorbed on C-PAC and B-PAC.

Fig. 3. Strength of adsorption of carbohydrates on C-PAC (a) and B-PAC (b), and proteins on C-PAC (c) and B-PAC (d). Fraction (% w) of the total amount adsorbed.

Fig. 4. Time-course of the TMP during the long-term experiments at $8 \text{ L m}^{-2} \text{ h}^{-1}$ flux.

Fig. 5. SEM micrographs of sludge flocs from control-MBR at 200 (a) and 450 X (b), respectively, B-MBR (c) and C-MBR (d) at 300 X.

Fig. 6. Size distribution of carbohydrates (a) and proteins (b) retained by the membranes.

Fig. 7. SEM micrographs (5000 X) along the time-course of the fouling process in the control-MBR: raw membrane (a), start of fouling (b), gel layer formation (c) and cake sludge formation (d).

Fig. 8. Components of the filtration resistance in the control-MBR and C-MBR.

Fig. 9. Time-course of TMP (a) and fouling rates (b) observed in control-MBR (black symbols), C-MBR (grey symbols) and B-MBR (dark grey symbols) at different permeate fluxes.

Fig. 10. Particle size distributions of flocs: control-MBR (a), C-MBR (b) and B-MBR (c).

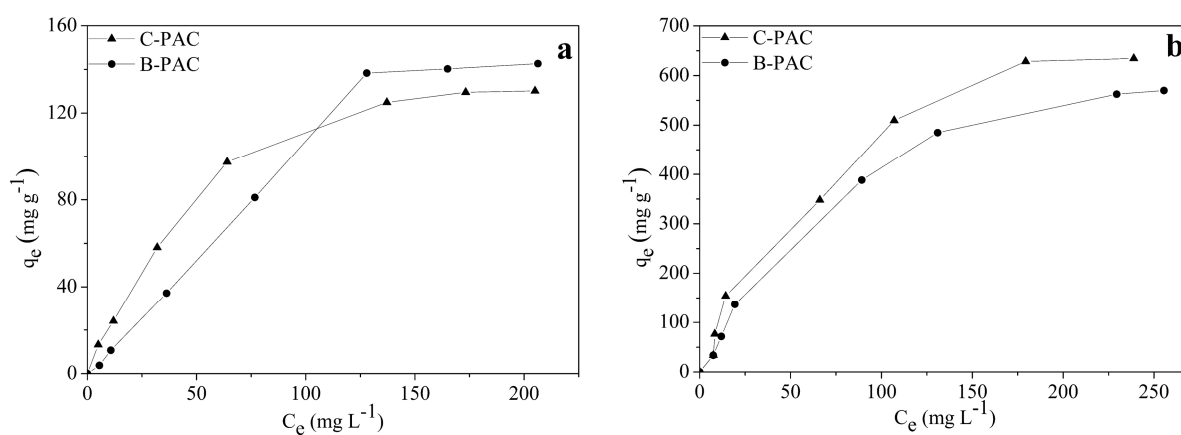
Fig. 1

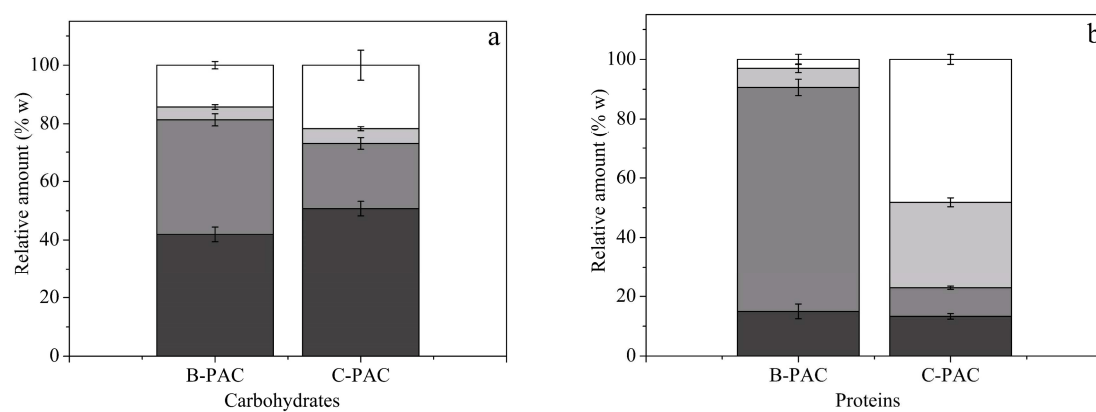
Fig. 2

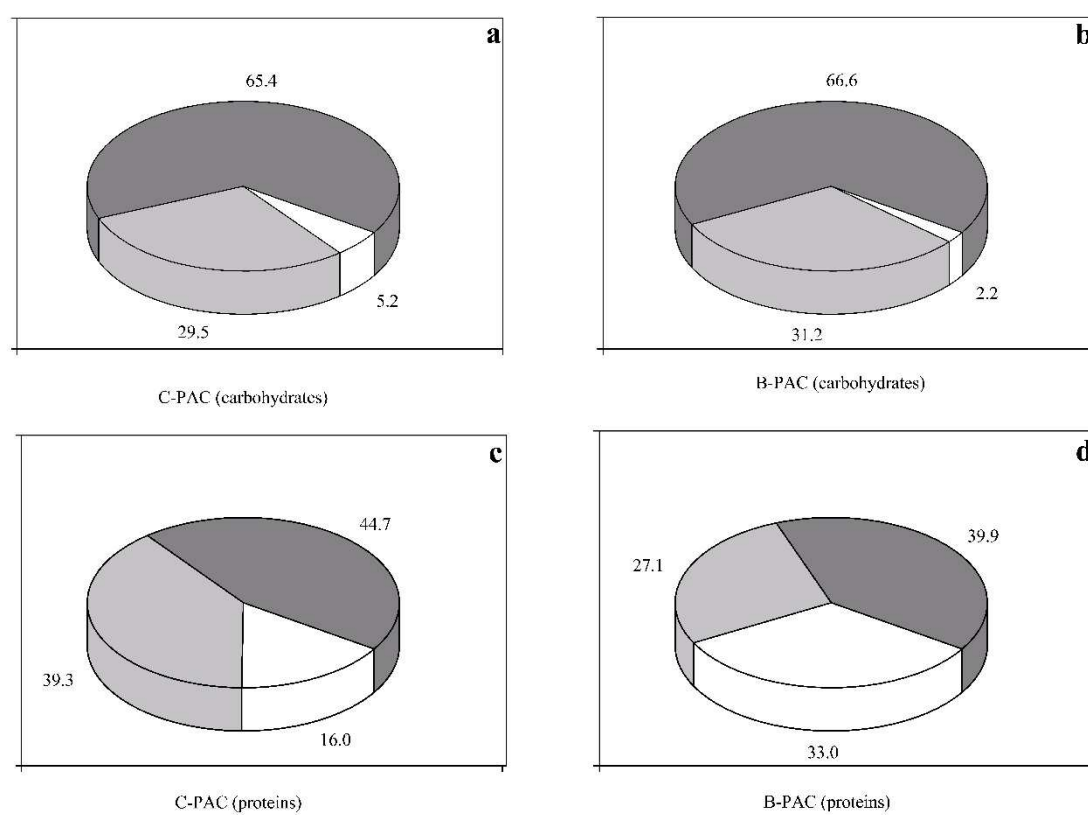
Fig. 3

Fig. 4

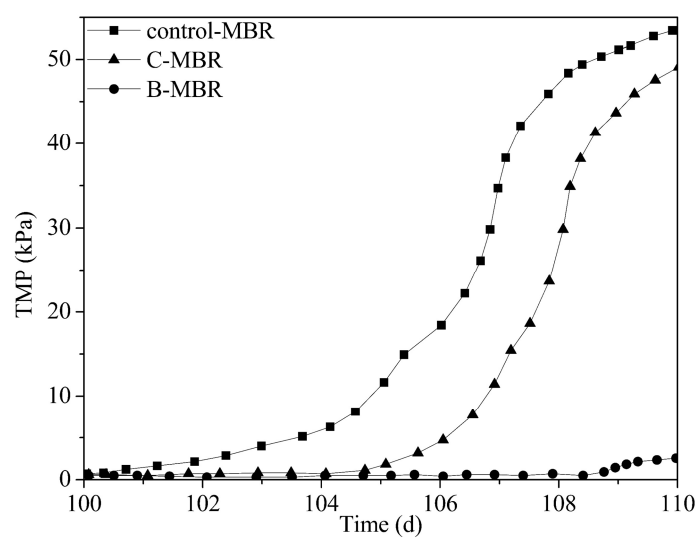
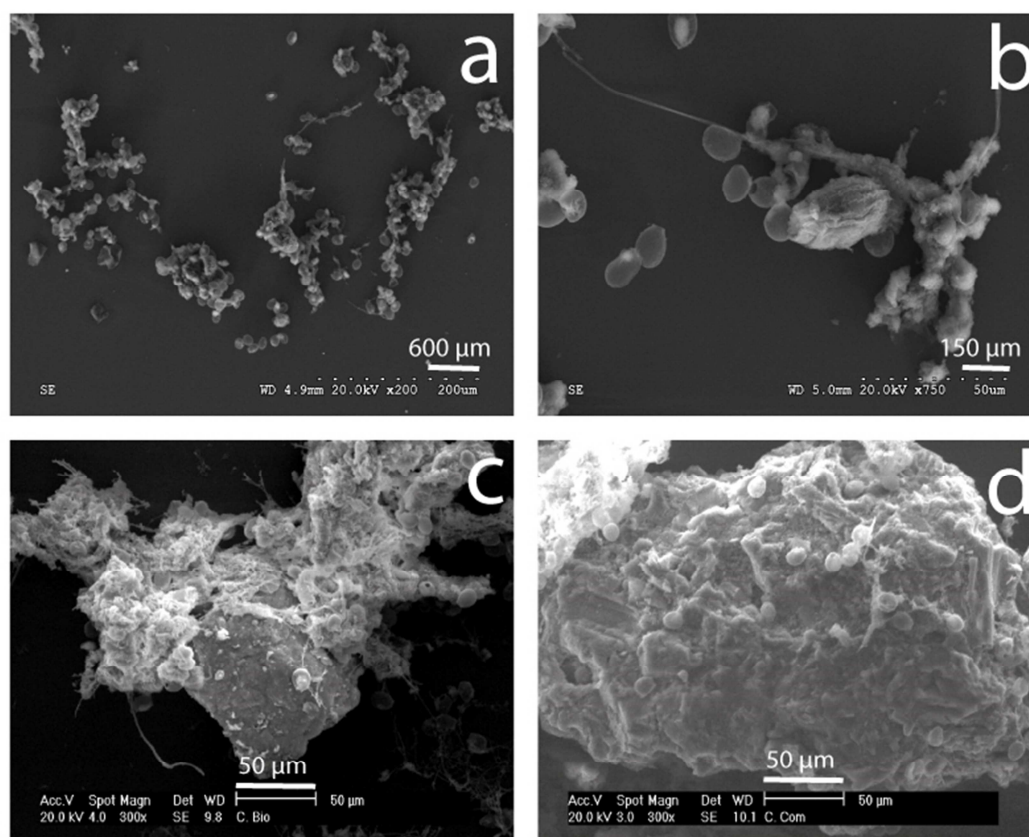
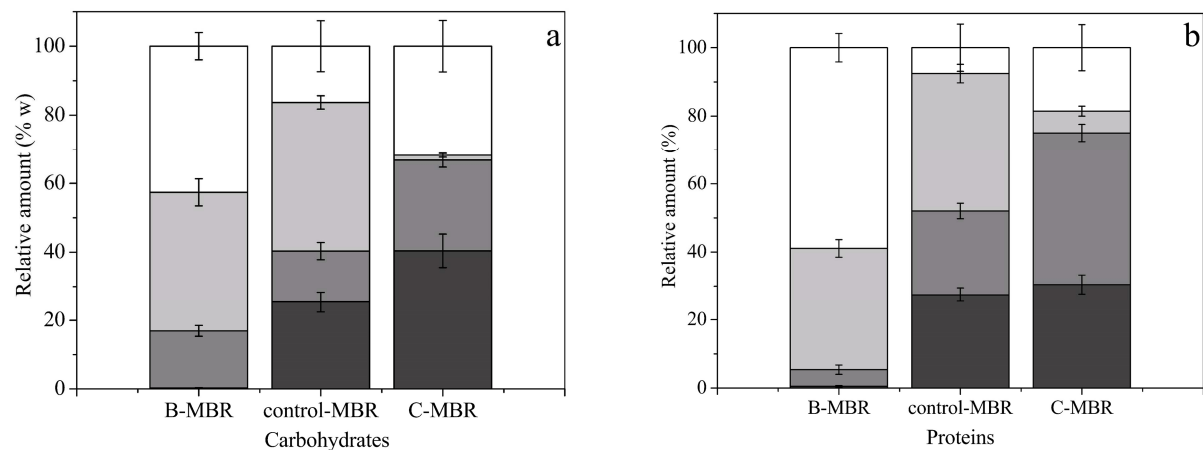


Fig. 5



**Fig. 6**

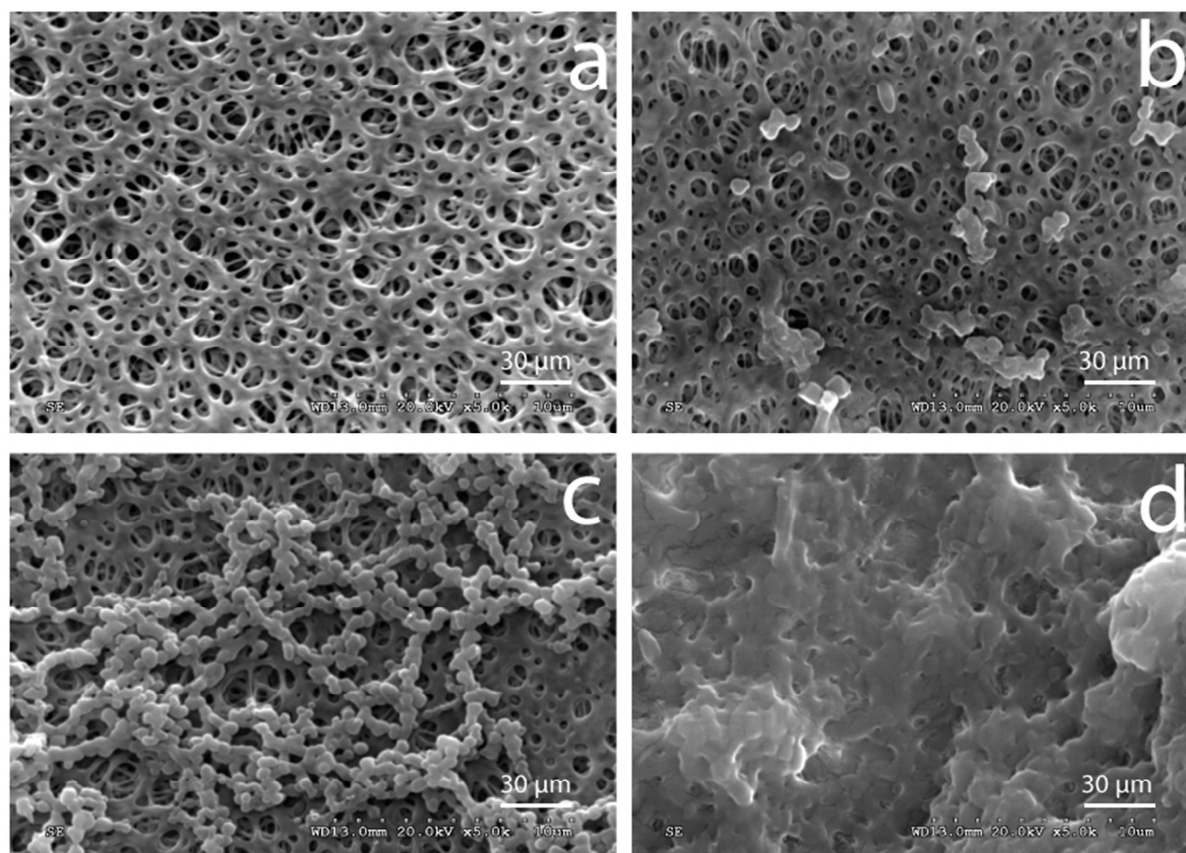


Fig. 7

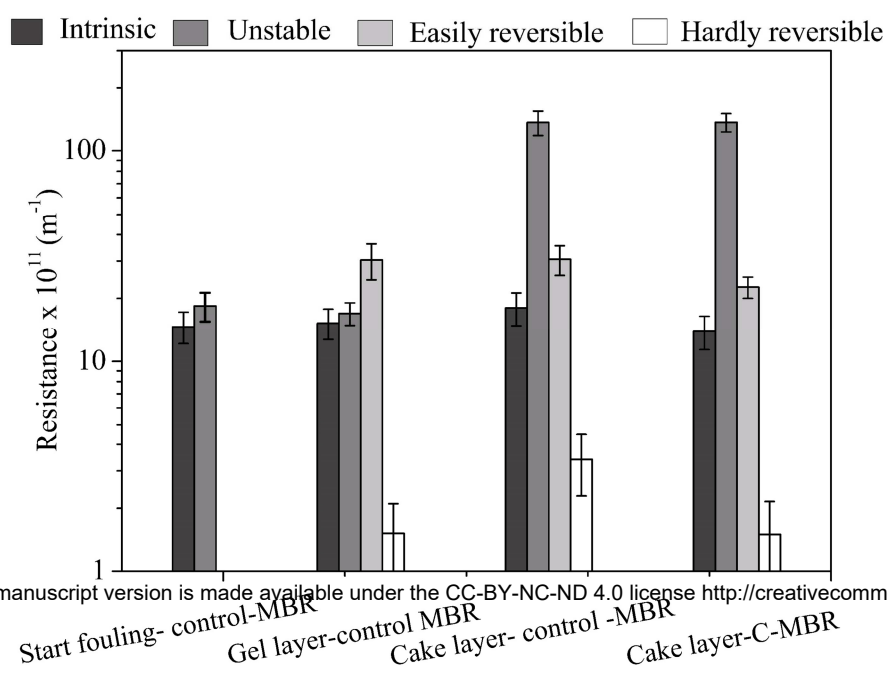
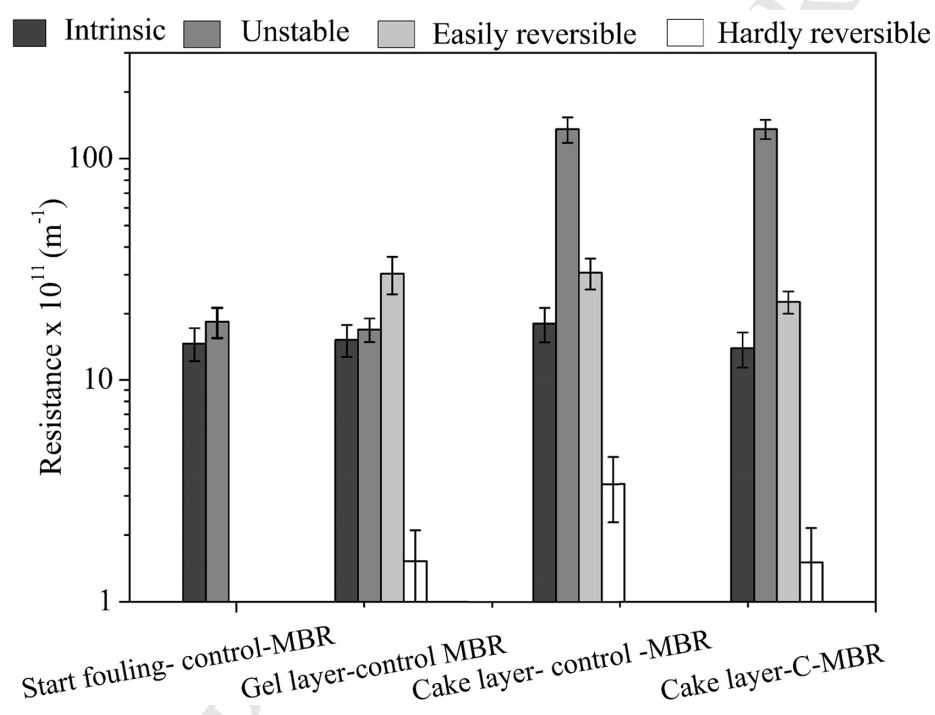


Fig. 8



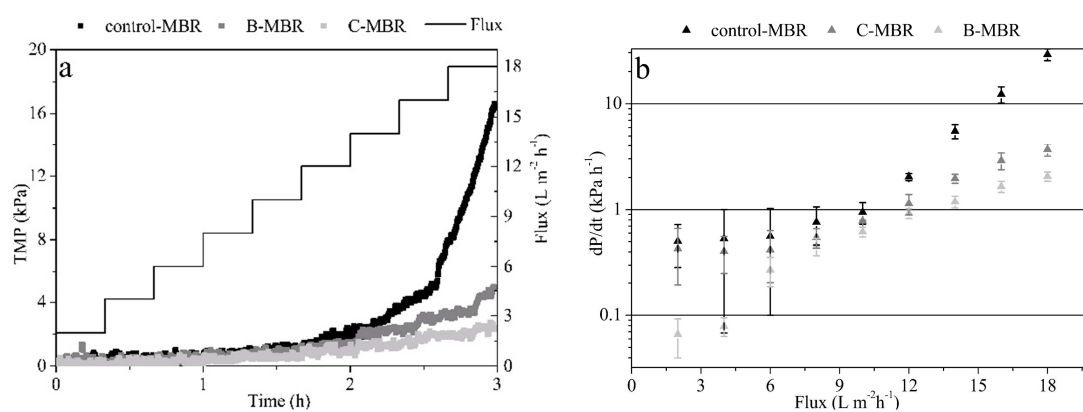
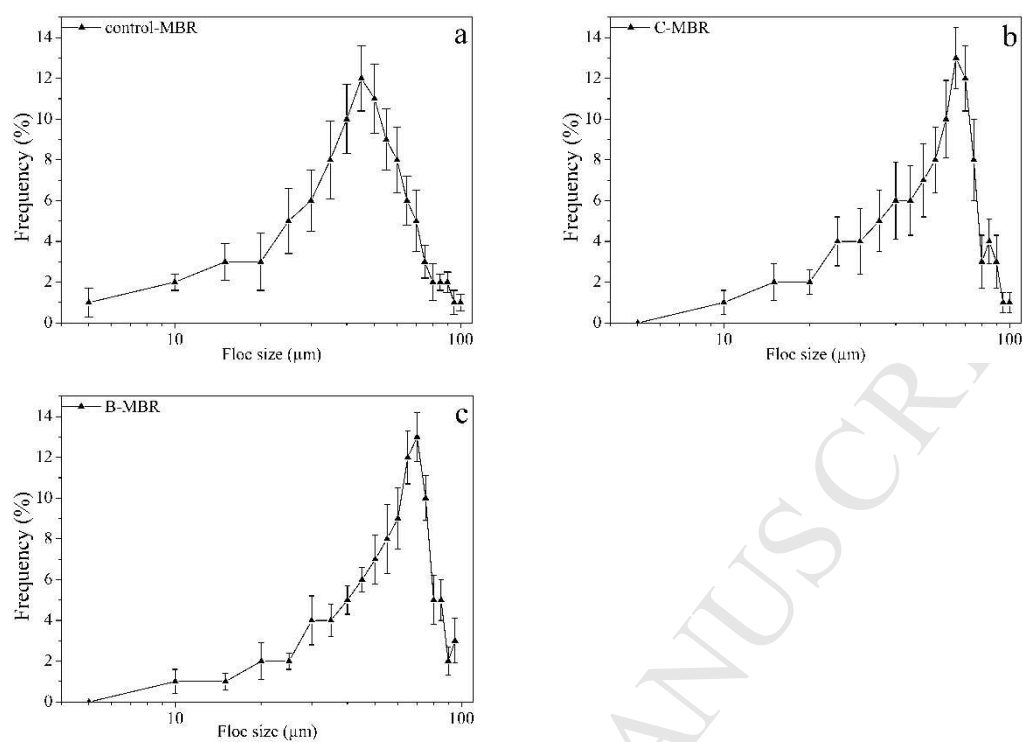


Fig. 9

Fig. 10.

Highlights

- Activated carbon was obtained from sewage sludge biosolids.
- Adsorption of soluble microbial products was verified.
- The activated carbon was easily regenerated.
- PAC addition to mixed liquor decreased fouling rate in MBR.
- Activated carbon preserves membranes against irreversible fouling.