



## Performance enhancement with powdered activated carbon (PAC) addition in a membrane bioreactor (MBR) treating distillery effluent

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### ABSTRACT

This work investigated the effect of powdered activated carbon (PAC) addition on the operation of a membrane bioreactor (MBR) treating sugarcane molasses based distillery wastewater (spentwash). The 8 L reactor was equipped with a submerged 30  $\mu\text{m}$  nylon mesh filter with 0.05  $\text{m}^2$  filtration area. Detailed characterization of the commercial wood charcoal based PAC was performed before using it in the MBR. The MBR was operated over 200 days at organic loading rates (OLRs) varying from 4.2 to 6.9  $\text{kg m}^{-3} \text{d}^{-1}$ . PAC addition controlled the reactor foaming during start up and enhanced the critical flux by around 23%; it also prolonged the duration between filter cleaning. Operation at higher loading rates was possible and for a given OLR, the chemical oxygen demand (COD) removal was higher with PAC addition. However, biodegradation in the reactor was limited and the high molecular weight compounds were not affected by PAC supplementation. The functional groups on PAC appear to interact with the polysaccharide portion of the sludge, which may reduce its propensity to interact with the nylon mesh.

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### 1. Introduction

The application of membrane bioreactors (MBRs), integrating biological treatment with filtration, is increasing due to both more stringent environmental regulations and growing water reuse initiatives. Further, various innovations such as replacement of microporous membranes by low cost mesh filters [1–3], feed pre-treatment by coagulation/flocculation [4], addition of powdered activated carbon (PAC) in submerged MBRs [5–7], etc. have been attempted to improve the process economics. PAC addition is expected to mitigate membrane fouling as well as enhance the biodegradation of recalcitrants or slowly biodegradable compounds and is thus particularly relevant to MBRs treating industrial wastewater.

Fig. 1 illustrates the effects of PAC addition in an MBR and the underlying reasons for the associated benefits. Munz et al. reported the synergistic effect of PAC addition in an MBR treating tannery wastewater [7]. The negative effects of natural and synthetic tannins that impart toxicity to tannery wastewater are reduced by PAC addition. PAC dosages of 10  $\text{g L}^{-1}$  improved leachate treatment in

a membrane–PAC hybrid system [8]. In a study on biodegradation of trace compounds in an aerobic MBR, it was found that the presence of 0.3% PAC reduced trihalomethane (THM) precursors by over 98% [9]. Addition of up to 5  $\text{g L}^{-1}$  PAC in an anaerobic MBR operated on synthetic wastewater improved effluent quality and provided stability against shock loading [10].

Distillery wastewater generated during alcohol production from sugarcane molasses contains acidic, polymeric and highly dispersed colloidal compounds termed melanoidins. These are formed as one of the final products of Maillard reaction, which is a non-enzymatic browning resulting from the reaction of reducing sugars and amino compounds [11]. Only 6–7% degradation of melanoidins is achieved in the conventional anaerobic–aerobic effluent treatment process [12]. Further, due to their antioxidant properties, melanoidins are toxic to many microorganisms involved in wastewater treatment [13].

In our earlier work [14], we investigated the treatment of distillery spentwash in a bioreactor equipped with 30  $\mu\text{m}$  mesh filter. Up to 41% COD removal was obtained with an acclimatized mixed consortium at an organic loading rate (OLR) of 3.4  $\text{kg COD d}^{-1} \text{m}^{-3}$ ; also, only the low molecular weight component in the melanoidins was degraded. This study examines the effect of PAC supplementation on the operation and performance of this system. To the best of our knowledge, there are no published studies on PAC addition in MBRs using mesh filters and treating high strength industrial wastewaters.

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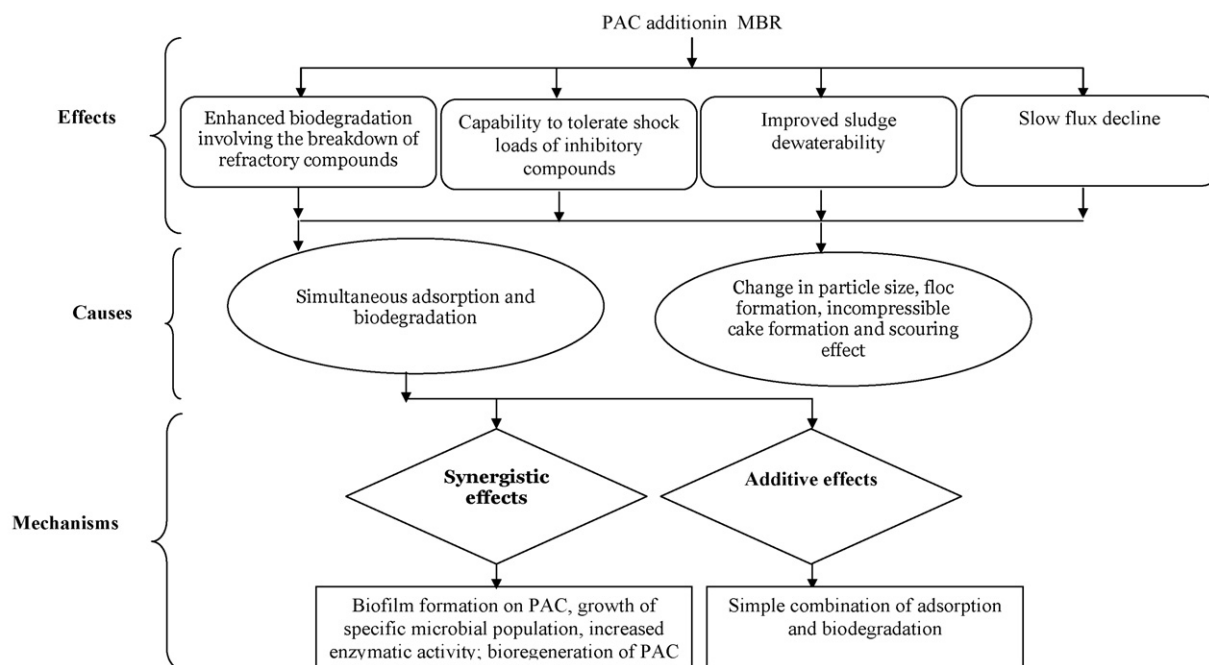


Fig. 1. Schematic illustrating the effects, causes and mechanism occurring in an MBR after PAC addition.

## 2. Materials and methods

### 2.1. PAC, wastewater and sludge

Commercial PAC, manufactured by steam activation of wood charcoal, was obtained from a local manufacturer (Universal Carbons Ltd., Hoshiarpur, India). Activated sludge was obtained from the local municipal sewage treatment plant. It was acclimatized for anaerobically treated distillery wastewater in a fed-batch reactor over a period of 100 days [14] before seeding the continuous reactor. The wastewater was collected from a molasses based alcohol distillery located near Delhi. The COD of this effluent varied between 29,204 and 48,258 mg L<sup>-1</sup>. The typical values for other physico-chemical parameters were as follows: total solids, 165,020 mg L<sup>-1</sup>; total dissolved solids, 13,600 mg L<sup>-1</sup>; ash, 544 mg L<sup>-1</sup>; conductivity 27.2 mS cm<sup>-1</sup>; pH, 7.94–8.12. The effluent was stored at 4 °C and was used as received in all the experiments.

### 2.2. PAC characterization

This involved measurement of ash content, volatile matter, moisture, iodine number and methylene blue number, all as per ASTM standards D 3174, D 5832 and D 2867, D 4607 and D 2330 respectively. The fixed carbon content was determined by subtracting the percentages of moisture, volatile matter and ash [15]. Bulk density and pH was determined using the method described by Ahmedna et al. [16]. Elemental analysis (C, H and N) was carried out using CHNS/O analyzer (PerkinElmer, USA 2400 Series II), particle size was obtained using a particle size analyzer (SYMPATEC, Germany) and surface area was determined by nitrogen adsorption (TriStar 3000, Micromeritics Instrument Corporation, USA).

The adsorption isotherms were obtained using synthetic melanoidins, which was prepared in the laboratory using glucose and glycine [17]. Melanoidin adsorption studies were conducted in shake-flask in batch mode as reported earlier [18]. Adsorption

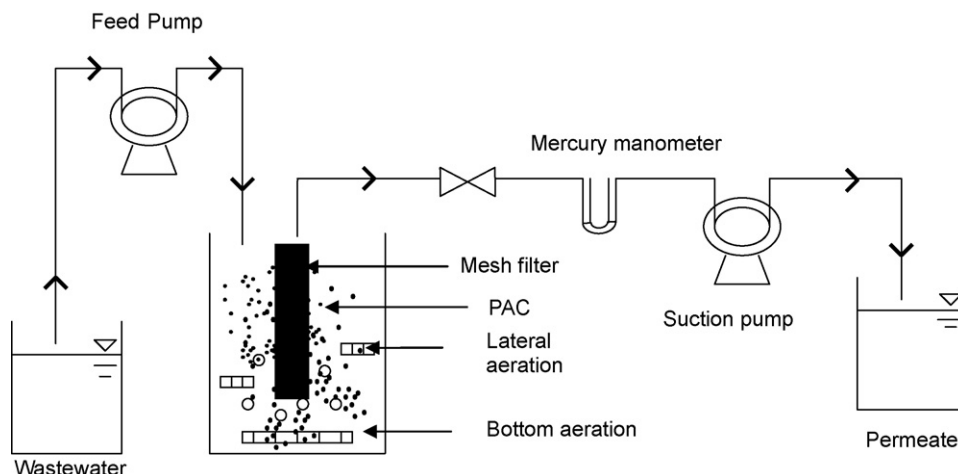


Fig. 2. Schematic diagram of the PAC supplemented MBR equipped with nylon mesh filter.

data was analyzed using Freundlich and Langmuir isotherm models [19,20].

### 2.3. MBR setup, operation and analysis

Fig. 2 shows the schematic of the experimental setup. The reactor, with a working volume of 8 L, employed a submerged 30  $\mu\text{m}$  nylon mesh filter module of 0.05  $\text{m}^2$  surface area. The reactor was equipped with laterally placed aeration units and an air diffuser below the filter module. The total aeration rate was 2.6–4.5  $\text{L min}^{-1}$  and the dissolved oxygen (DO) concentration was between 2 and 4  $\text{mg L}^{-1}$ . Two peristaltic pumps (Enertech ENPD-100 Optima, India), one each for continuously feeding the influent and for withdrawing the permeate from the filter module, were used. The permeate pump was operated in an intermittent suction mode with a cycle of 10 min on and 99 s off. A mercury manometer mounted between the filter and permeate pump measured the transmembrane pressure (TMP). Flux was estimated volumetrically by measuring the permeate collected over a known time. The starting mixed liquor suspended solids (MLSS) concentration was 3.9  $\text{g L}^{-1}$  and a hydraulic retention time (HRT) of 7 days was fixed throughout. The system was operated at ambient temperature (21–26  $^{\circ}\text{C}$ ). The OLR was increased from 4.2 to 6.9  $\text{kg m}^{-3} \text{d}^{-1}$  during the course of this study. PAC at a concentration of 2  $\text{g L}^{-1}$  was added initially at start up and each time the OLR was stepped up. Filter cleaning was done as required by rinsing with tap water.

COD, MLSS and volatile suspended solids (VSS) were determined according to Standard Methods [21]. Dissolved oxygen was measured using DO meter (OXI 330i/SET, Germany). The molecular weight profiles of the feed and permeate was analyzed by gel permeation chromatography (GPC) (Waters 1515 Isocratic HPLC pump, with Waters 717plus autosampler, using Waters 2414 refractive index detector). Two hydroxylated polymethacrylated-based columns viz. Ultrahydrogel 250 (exclusion limit 1–80 kDa) followed by Ultrahydrogel 120 (exclusion limit 0.2–5 kDa) were employed in series. These were preceded by a guard column of the same material. Deionised water, at a flow rate of 0.7  $\text{mL min}^{-1}$ , was used as mobile phase.

## 3. Results and discussion

### 3.1. PAC characteristics

The properties of the PAC used are listed in Table 1. The sample had neutral pH and was characterized by high surface area. Iodine and methylene blue numbers, which are indicators of the adsorption capacity in micropores and mesopores respectively, were also high. Iodine number can be correlated with the ability to adsorb low molecular weight substances, whereas methylene blue num-

**Table 1**  
PAC characteristics.

Characteristics	Values
Moisture content (%)	6.9 $\pm$ 0.6
Ash content (%)	3.66 $\pm$ 0.06
Volatile matter (%)	8.8 $\pm$ 0.98
Fixed carbon (%)	81.4 $\pm$ 2.10
Bulk density ( $\text{g cm}^{-3}$ )	0.25 $\pm$ 0.01
pH	6.9 $\pm$ 0.1
Iodine number ( $\text{mg g}^{-1}$ )	1103
Methylene blue number ( $\text{mg g}^{-1}$ )	386 $\pm$ 2
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	1165
Volume based mean diameter (VMD) ( $\mu\text{m}$ )	31.9
Carbon (%)	83.89
Hydrogen (%)	Nil
Nitrogen (%)	Nil

Values represent mean  $\pm$  standard deviation for three replicates.

**Table 2**  
Langmuir and Freundlich isotherm constants for melanoidins.

	Freundlich isotherm constants			Langmuir isotherm constants		
	$n$	$K$ ( $\text{mg g}^{-1}$ )	$R^2$	$a$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$
Value	4.40	42.9	0.9908	416.7	0.00094	0.9965

ber indicates the ability to adsorb high molecular weight substances and color [22]. The volume based mean particle size was 31.9  $\mu\text{m}$  that is comparable to the mesh filter opening of 30  $\mu\text{m}$ . An analysis of the melanoidins adsorption showed that both Langmuir and Freundlich isotherms fit the adsorption data (Table 2).

### 3.2. PAC-MBR performance

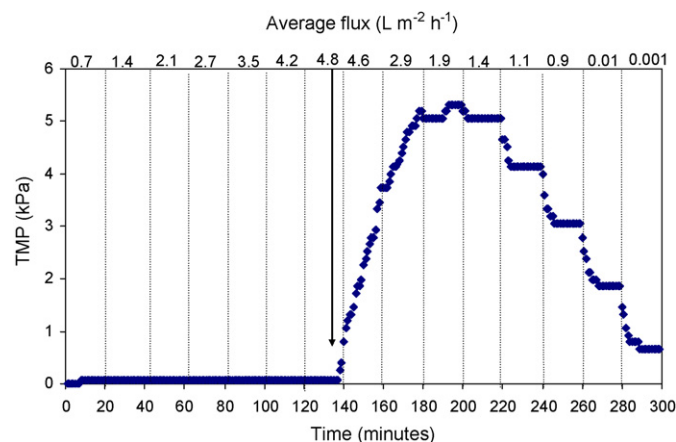
#### 3.2.1. Critical flux

Operating an MBR below the critical flux is one of the many approaches to control membrane fouling. Critical flux, at 11  $\text{g L}^{-1}$  MLSS concentration with a fresh filter module, was determined by the step-change method (step height between 0.65 and 0.72  $\text{L m}^{-2} \text{h}^{-1}$  and step duration of 20 min) [23]. The TMP remained almost constant (0–0.07 kPa) for the first 137 min of operation up to an imposed flux of 4.16  $\text{L m}^{-2} \text{h}^{-1}$  (Fig. 3); thereafter, it rose steeply to 3.72 kPa at an imposed flux of 4.8  $\text{L m}^{-2} \text{h}^{-1}$ . Further increase in imposed flux resulted in a steady increase in TMP. Thus, the imposed flux of 4.8  $\pm$  0.21  $\text{L m}^{-2} \text{h}^{-1}$  was regarded as the critical flux for this system. The same nylon mesh–distillery wastewater combination at 11  $\text{g L}^{-1}$  MLSS without PAC addition displayed a lower critical flux of 3.9  $\text{L m}^{-2} \text{h}^{-1}$  [14]. Therefore PAC addition improved the critical flux by almost 23%.

The observation is in agreement with published reports. For instance, in synthetic wastewater treatment, PAC addition enhanced the critical flux by 5% in an external MBR and 32% in a submerged MBR [24,25]. It was suggested that a more dynamic, looser cake layer with higher porosity is formed on the membrane surface in biological-PAC systems; thus, the cake resistance is less leading to higher flux [24]. Increase in the critical flux value also implies that PAC addition would enhance the filter performance and limit membrane cleaning to some extent. The effect of PAC addition on long-term filtration performance is discussed in the following section.

#### 3.2.2. Flux and TMP profile

The flux and TMP data over a 200-day period is presented in Fig. 4. The reactor was operated under sub-critical flux condi-



**Fig. 3.** Critical flux determination in the MBR.

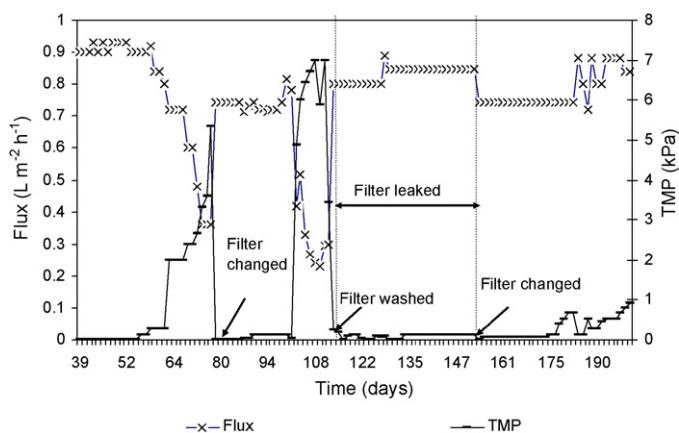


Fig. 4. Flux and TMP profile in the MBR.

tions at an imposed flux between  $0.75$  and  $0.9 \text{ L m}^{-2} \text{ h}^{-1}$ . During the initial stages of reactor operation, the flux decline was negligible. After 39 days, MLSS concentration rose above  $6 \text{ g L}^{-1}$ . At this stage, a new filter was installed and regular monitoring of the flux and TMP was initiated. From the 39th to 59th days i.e. initial 20 days with a new filter, the TMP increased marginally (up to  $0.3 \text{ kPa}$ ) but the flux remained constant. In the subsequent 15 days (60th–74th days of operation), there was a steep TMP increase up to  $5 \text{ kPa}$ , with a corresponding sharp flux decline to  $0.36 \text{ L m}^{-2} \text{ h}^{-1}$ . During this 35-day period (39th–74th days), no filter change or filter washing was performed. Thereafter, the filter was replaced and the operation was continued for the next 34 days cycle (79th–113th days of reactor operation). The flux decline trend was similar to that in the previous 35-day cycle. The filter was washed at this stage and the operation was continued. Over the next 39 days (114th–153rd days of reactor operation) surprisingly no TMP rise was observed; at this stage, the MLSS retention also decreased (Section 3.2.3). It was then discovered that the filter had developed a leak. A new filter module was inserted on the 154th day and the system was operated till 202 days without any further filter wash or change. In these last 48 days of operation, the TMP remained below  $1 \text{ kPa}$ . This was partly attributed to the introduction of additional aerators at this stage to maintain the DO level above  $2 \text{ mg L}^{-1}$  (Section 3.2.3). This in turn provided extra scouring of the filter surface and thus mitigated the fouling [26].

In this investigation, it was observed that PAC addition allowed continuous operation at a constant flux for 20 days without filter change or cleaning. This duration was shorter (8 days) without PAC addition [14]. Thus, for the nylon mesh–distillery spentwash combination, PAC addition resulted in a 2.5-fold enhancement in operation time without filter cleaning. The findings are in agreement with reported studies [24,27]. The positive impact of PAC is attributed to (a) action of PAC as a filter aid that reduces foulants in the bulk solution by adsorption and flocculation of organic compounds; this, in turn, decreases the foulant load to the membrane surface [24]; (b) loose structure and high porosity of the cake deposit and biofloc structure that minimizes surface fouling and concentration polarization; and (c) presence of PAC particles on the membrane surface that reduces the hydrodynamic boundary layer thickness, thereby enhancing permeate transport [27,28].

To estimate the extent and the size of components adsorbed, batch adsorption tests were conducted at different PAC dosages. Figs. 5 and 6 present respectively the molecular weight profiles of the components remaining in solution for distillery effluent and 2% synthetic melanoidins solution. It is evident from Fig. 5 that

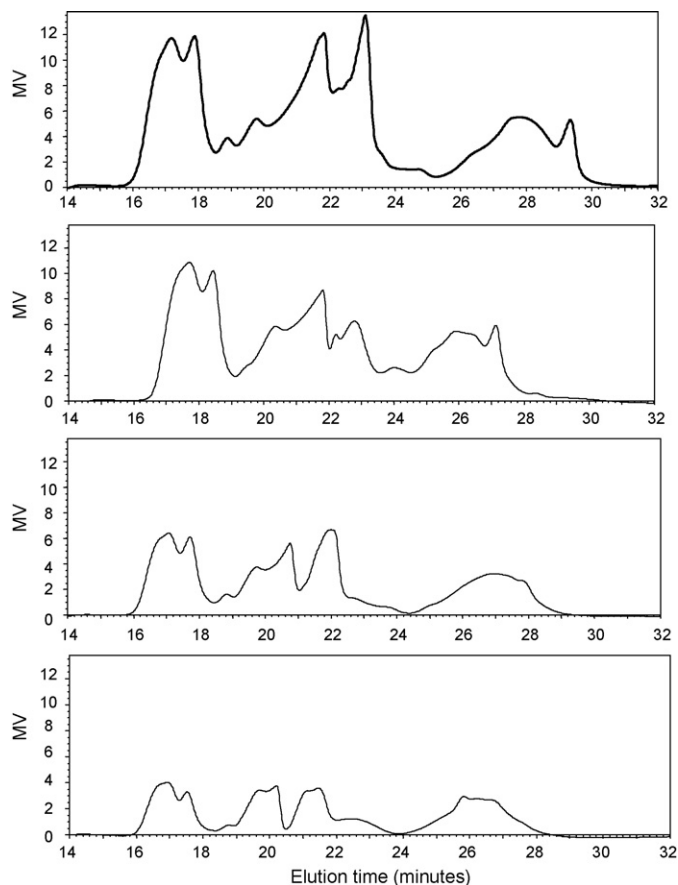


Fig. 5. Molecular weight profile of distillery effluent at different PAC dosages: (a)  $0 \text{ g L}^{-1}$ , (b)  $0.2 \text{ g L}^{-1}$ , (c)  $15 \text{ g L}^{-1}$ , and (d)  $50 \text{ g L}^{-1}$ .

at  $0.2 \text{ g L}^{-1}$  PAC, only compounds below  $6000 \text{ Da}$  (elution time  $18.7 \text{ min}$  and above) were adsorbed to some extent. At higher dosages, adsorption was significant and took place in the entire molecular weight range. This is apparent from the reduced intensity of the peaks in comparison to the control (Fig. 5a). With the melanoidins (Fig. 6), at low PAC dosage, no adsorption was observed in the low molecular weight region. At higher dosage ( $15 \text{ g L}^{-1}$  and  $50 \text{ g L}^{-1}$ ), adsorption of both high and low molecular weight components ( $16$ – $29 \text{ min}$  elution time) occurred. Melanoidins contain components with a wide range of molecular weights ( $>80 \text{ kDa}$  to  $<940 \text{ Da}$ ). It may be possible that larger molecules block the pores through which the smaller size components need to travel to access their final adsorption sites [29,30]. The above results are with a dilute 2% melanoidins solution. With a 100% solution viz. the stock solution obtained after synthesis, no adsorption was detected in the entire molecular weight range even at  $50 \text{ g L}^{-1}$  PAC concentration (data not shown). Thus, adsorption did occur even at low PAC dosages used in this work but the extent of adsorption and the components adsorbed was strongly dependent upon both the PAC concentration and competition between high and low molecular weight components.

### 3.2.3. MLSS buildup and retention

The biomass growth is plotted in Fig. 7a. The MLSS concentration at the start of the reactor operation was  $3.9 \text{ g L}^{-1}$  and the value stabilized at  $8$ – $11 \text{ g L}^{-1}$  between 65 and 143 days. Thereafter, the MLSS concentration increased steeply due to the high solids content in that specific lot of feed. To maintain the MLSS content in the MBR between  $10$  and  $12 \text{ g L}^{-1}$ , around  $32$ – $90 \text{ g}$  sludge was wasted each time on the 147th, 160th and 169th days.

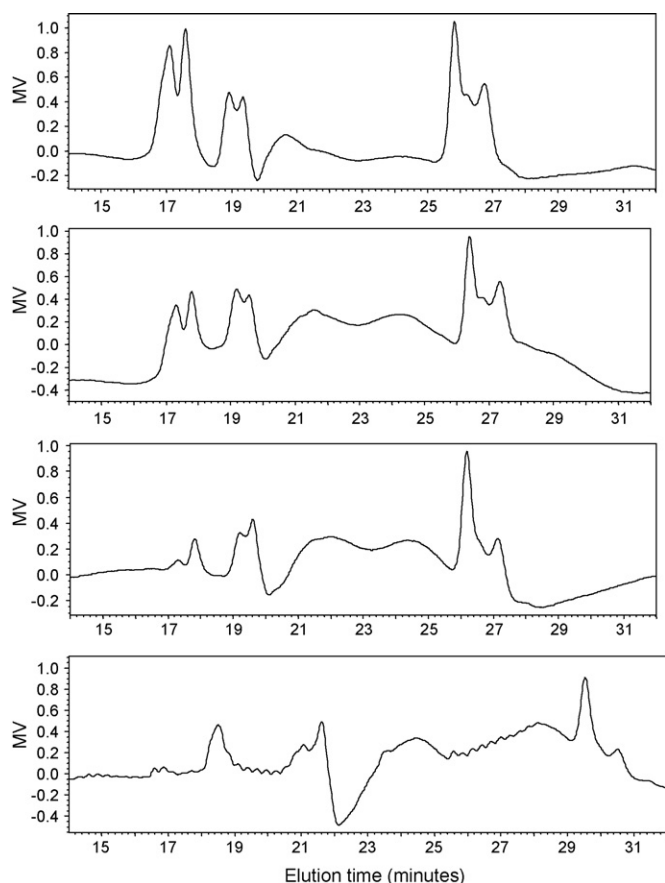


Fig. 6. Molecular weight profile of 2% synthetic melanoidins at different PAC dosages: (a)  $0 \text{ g L}^{-1}$ , (b)  $0.2 \text{ g L}^{-1}$ , (c)  $15 \text{ g L}^{-1}$ , and (d)  $50 \text{ g L}^{-1}$ .

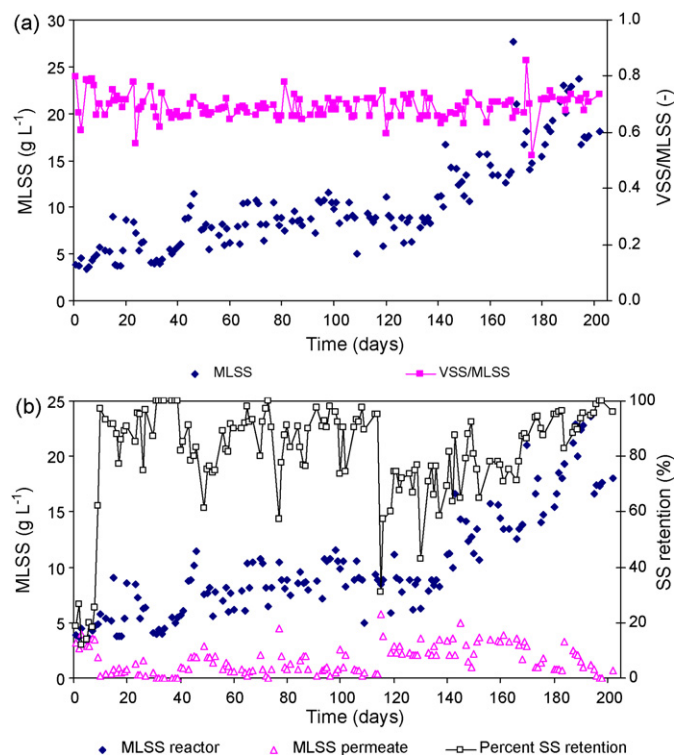


Fig. 7. (a) MLSS profile and VSS/MLSS ratio in the MBR. (b) SS retention by  $30 \mu\text{m}$  nylon mesh in the MBR.

It was observed that the MLSS buildup was faster as compared to operation without PAC supplementation. It took almost 140 days to reach a MLSS concentration of  $8 \text{ g L}^{-1}$  without PAC addition [14]. The same MLSS concentration was achieved in this work in half the time (65 days). Regular PAC addition contributed to the MLSS buildup; also, PAC addition helps in microbial growth due to the increase in available surface area [31].

Over the entire 200-day period of operation, the VSS/MLSS ratio ranged between 0.70 and 0.80. Similar values were observed in the absence of PAC, but the VSS declined after 170 days of reactor operation [14].

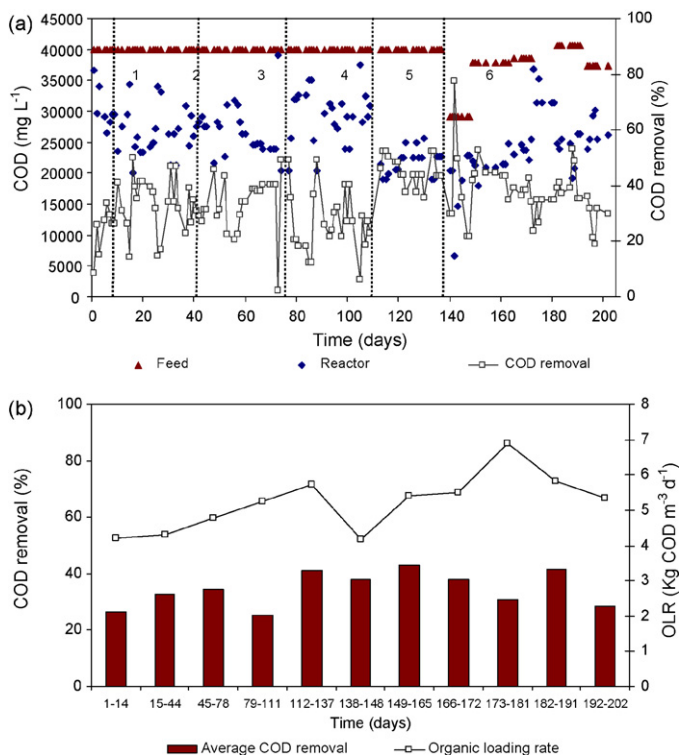
The MLSS retention by the mesh filter is plotted in Fig. 7b. Over the first 10 days, the retention increased from low (18%) to almost complete retention (97%); thereafter, it varied but was mostly above 80%. When the filter was cleaned or was replaced by a fresh unit, the MLSS retention remained low for the initial 2–4 days. This was expected since dynamic layer formation by the rejected particles on the mesh acts as a secondary filter and is responsible for suspended solids (SS) rejection [32]. It is evident from Fig. 7b that there was a drop in the SS retention between the 115th and 153rd days. It was later found that the filter was not properly adhered to the module and there was a continuous leakage. During this period, the SS retention varied widely (31–92%) with maximum number of data points lying between 60% and 75%. Once this problem was rectified on the 154th day by using a fresh module, the SS retention increased. Thereafter, the average MLSS retention was maintained at 80% up to the end of the investigations.

In our previous study on distillery effluent in a mesh equipped MBR without PAC addition [14], we observed that it took around 17 days for the SS rejection to build up to 70%. The retention continued to increase with time and was over 90% on an average between the 18th and 245th days. In the present study with PAC supplemented MBR, a high SS retention of 85–90% was obtained only after 10 days of operation. Despite the rapid increase in SS retention, complete retention was not attained. This was attributed to the fact that the fine PAC particles ( $<30 \mu\text{m}$ , which constituted almost 70% of the sample on a volume basis) could pass through the mesh and escape into the permeate. Further, it appears that the cake layer formed with PAC addition is porous enough to allow the passage of the fine particles. This corroborates well with the results of TMP vs. flux profile that showed low TMP rise (Section 3.2.2).

### 3.2.4. COD removal

The COD removal profile in the MBR is shown in Fig. 8. The reactor was operated at OLR varying from  $4.2$  to  $6.9 \text{ kg COD d}^{-1} \text{ m}^{-3}$ . From beginning of the reactor operation till the 137th day, the organic loading was stepped up from  $4.2$  to  $5.7 \text{ kg COD d}^{-1} \text{ m}^{-3}$  by varying the feed concentration. This was done by mixing a known volume of the treated wastewater with the incoming feed to the reactor. Thereafter, the concentration was not adjusted and the as received anaerobically treated spentwash was fed to the reactor. Hence the variations in OLR after 137 days were due to fluctuations in the composition of the influent batches as received from the sampling site. The sections 1, 2, 3, 4 and 5 in Fig. 8a correspond to five different OLRs viz.  $4.2$ ,  $4.3$ ,  $4.8$ ,  $5.2$  and  $5.7 \text{ kg COD d}^{-1} \text{ m}^{-3}$  respectively that were employed during the reactor operation. In section 6, where loading was not varied intentionally, the values ranged from  $4.2$  to  $6.9 \text{ kg COD d}^{-1} \text{ m}^{-3}$ .

The complete COD profile in Fig. 8a reveals that COD removal varied noticeably (8–53%); also the removal dropped down at each change of loading. Interestingly, the COD removal was relatively higher in section 6 (after 137 days of operation) even though the loading fluctuated between  $4.2$  and  $6.9 \text{ kg COD d}^{-1} \text{ m}^{-3}$ . Fig. 8b shows the average COD removal at various organic loading rates. The values ranged from 25% to 43%, reaching a maximum at a loading of  $5.4 \text{ kg COD d}^{-1} \text{ m}^{-3}$  (attained in section 6, Fig. 8a). Comparing



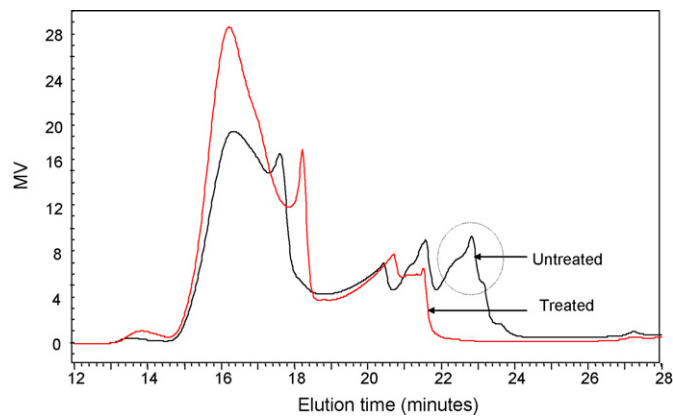
**Fig. 8.** (a) COD removal in the MBR at various organic loading rates. (b) Average COD removal at various organic loading rates.

these findings with the results of our earlier work without PAC [14], we made the following key observations:

- PAC addition helps in foaming control. There was little or no foaming in the PAC MBR; in contrast, severe foaming was encountered during reactor start up without PAC and the reactor had to be dosed regularly with antifoam. For this reason, the latter was started with a lower loading of  $3 \text{ kg COD d}^{-1} \text{ m}^{-3}$  whereas the PAC supplemented reactor could be started at a relatively higher loading of  $4.2 \text{ kg COD d}^{-1} \text{ m}^{-3}$  without any foaming problem.
- For a given OLR, the COD removal is higher with PAC addition. For instance, at an OLR of  $5.7 \text{ kg COD d}^{-1} \text{ m}^{-3}$  (which was the highest loading maintained without PAC), the average COD reduction was 27% whereas with PAC addition, the average COD removal increased 1.5-fold (41%). Thus, the PAC MBR could be operated at relatively higher loading rates. In this study, the maximum OLR in the PAC MBR was  $6.9 \text{ kg COD d}^{-1} \text{ m}^{-3}$  and 31% COD removal was obtained.

MBR performance enhancement upon PAC addition has been reported for other industrial wastewaters as well [7,33]. Two mechanisms have been proposed to explain the effect of PAC in MBRs [34,35]:

- The action of microbial cells and the PAC is mutual and synergistic. The presence of PAC increases the surface available for liquid–solid contact and facilitates the adsorption of microbial cells, enzymes and organics. This, in turn, provides an enriched environment for microbial metabolism. It is also suggested that the microbial cells attached to PAC secrete enzymes into the micropores. This leads to extracellular biodegradation of adsorbed organics and thus results in bioregeneration of the activated carbon. Hence PAC adsorption capacity is enhanced as a



**Fig. 9.** Molecular weight profiles of untreated and treated distillery effluent in MBR.

result of simultaneous adsorption–bioregeneration as compared to adsorption alone.

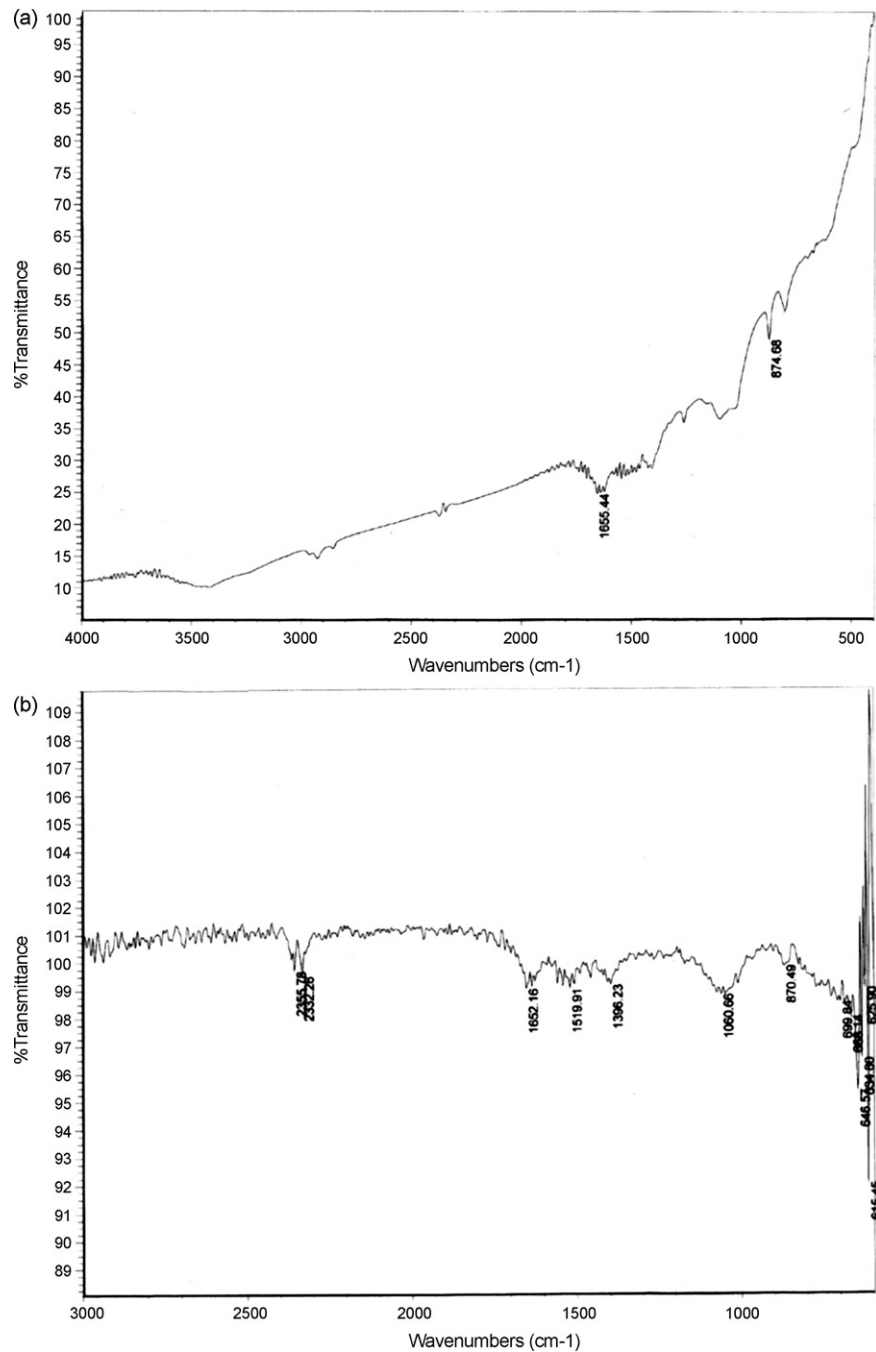
- Combination of biodegradation and adsorption has a simple additive effect. The presence of PAC does not enhance the biodegradation capability of the microbes. Further, since the extracellular enzyme molecules are larger than the PAC micropores size, enzymatic regeneration of the micropores is unlikely.

Studies indicate that both mechanisms exist and their occurrence depends upon the PAC properties and its interaction with the particular pollutant. In the present study, the constant “b” in the Langmuir isotherm (Table 2) was very low with melanoidins (0.00094) indicating low adsorption. Literature reports indicate that PAC is unable to adsorb organics above 17 kDa [36] and high molecular weight fraction of humic substances [37]. Melanoidins are a mixture of high and low molecular weight components ranging from  $>80 \text{ kDa}$  to  $<940 \text{ Da}$  for the synthesized sample. In addition to melanoidins, the anaerobically treated distillery wastewater used in this work contains components like phenols, phenolics, furfurals and caramels ( $<1 \text{ kDa}$ ). Since PAC typically contains  $>80\%$  micropores [28], it is expected that the lower molecular weight organics would be preferentially adsorbed. This was experimentally verified (Fig. 5) wherein at PAC dosage of  $2 \text{ g L}^{-1}$ , only components lower than  $6000 \text{ Da}$  were adsorbed.

A comparison of the molecular weight profiles of the feed and treated effluent did not show degradation of high molecular weight organics (Fig. 9). Only components smaller than  $940 \text{ Da}$  are absent in the treated effluent, but there appears to be no change in the profile of the high molecular weight components. This observation is similar to that in our previous study without PAC addition [14]. The developed microflora, with and without PAC addition, was able to degrade only the low molecular weight compounds. However, PAC addition improved the MBR filtration performance, allowing operation at higher OLRs with marginal improvement in COD removal. It also improved the buffering capacity of the system to handle higher organic loading as well as shock loads. Thus, PAC addition and its adsorption of the low molecular weight components has a positive impact on the biological process thereby pointing to a synergistic effect. To confirm this hypothesis, further investigations on the degradation of single components are required.

### 3.2.5. Functional groups in sludge foulants

Fig. 10a and b shows the FTIR spectra of the sludge foulants scrapped from the filter. The foulants showed two distinct peaks at  $1655 \text{ cm}^{-1}$  (amide I indicating protein) and  $874 \text{ cm}^{-1}$  (calcite). It was observed that the activated sludge foulants in the MBR without



**Fig. 10.** (a) FTIR spectra of sludge foulants in the MBR with PAC addition. (b) FTIR spectra of sludge foulants in the MBR without PAC addition.

PAC addition (Fig. 10b) showed greater number of peaks including  $2355\text{ cm}^{-1}$  and  $2332\text{ cm}^{-1}$  (Si–H group indicating silicate impurities and clay minerals, possibly in complex with humic acids) [38]. This sludge also contained proteins as indicated by the peaks at  $1652\text{ cm}^{-1}$  (stretching vibration of C=O and C–N amide I) and  $1519\text{ cm}^{-1}$  (N–H deformation and C=N stretching amide II) as well as carbohydrate ( $1060\text{ cm}^{-1}$ ). The peak at  $1396\text{ cm}^{-1}$  is typical for phenolic  $\text{OH}^-$ ,  $\text{COO}^-$  and  $\text{CH}_3\text{COO}^-$ . Some bands observed in the “fingerprint” region ( $<1000\text{ cm}^{-1}$ ) could be attributed to the phosphate and sulfate groups arising from nucleic acids [39] as well as the feed (distillery wastewater) itself that is known to contain phosphorus ( $800\text{--}1200\text{ mg L}^{-1}$ ) and sulfur ( $2000\text{--}6000\text{ mg L}^{-1}$ ) [40]. The peak at  $870\text{ cm}^{-1}$  is possibly due to calcite [41]. It appears

that the other functional groups, especially the polysaccharides, are involved in the interaction with PAC.

The FTIR scan for nylon mesh (Fig. 11) reveals standard peaks for nylon. The bands at  $3312\text{ cm}^{-1}$  and  $3074\text{ cm}^{-1}$  can be attributed to hydrogen-bonded N–H stretch and overtone of N–H in-plane bends respectively. The band at  $2933\text{ cm}^{-1}$  corresponds to asymmetric C–H<sub>2</sub> stretch. The band at  $588\text{ cm}^{-1}$  is due to amide VI, C=O out-of-plane bend. One possible interaction of mesh with the sludge could be the proton of N–H bond with hydroxyl groups (frequent in polysaccharide). This suggests that masking of the hydroxyl groups in the sludge polysaccharides by the added PAC would avoid the sludge–mesh interaction and thereby reduce the fouling.

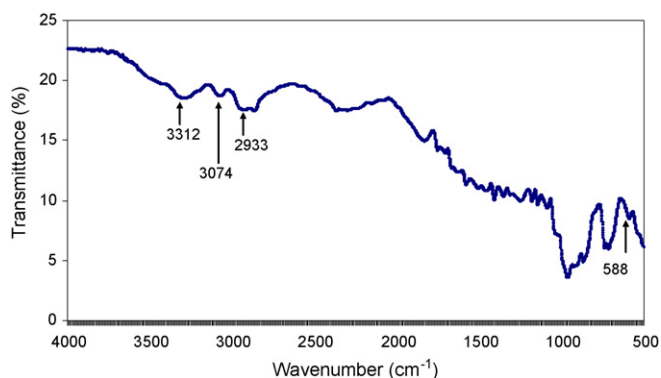


Fig. 11. FTIR spectra of nylon mesh filter.

#### 4. Conclusions

This study investigated the effect of PAC addition on a MBR operated on high strength molasses distillery wastewater. The wood charcoal based commercial PAC sample was characterized and subsequently used in a submerged mesh equipped MBR. The performance of this PAC assisted MBR was assessed over a duration of 200 days. The main conclusions are as follows:

- PAC enhances filtration performance in terms of increasing the critical flux and extending the operation period without mesh cleaning. Operation at higher loading rates is also possible.
- For a given OLR, the COD removal is higher with PAC addition. However, the developed microflora was unable to degrade the high molecular weight compounds. PAC supplementation results in adsorption of low molecular weight components (<6000 Da) but PAC dosage has a major impact on the extent of adsorption. Further, an appropriate combination of micropores, mesopores and macropores in the PAC would be more effective in adsorbing multiple contaminants.
- The changes after PAC addition in MBR performance point to a synergistic effect due to the combined biodegradation-adsorption process. This aspect needs further investigation.
- Complete suspended solids retention may not be attained in mesh equipped MBRs. Thus, continuous sludge and PAC wastage should be considered in the operation.
- The functional groups on PAC appear to interact with the polysaccharide portion of the sludge; this may reduce its propensity to interact with and deposit on the nylon mesh.

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