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Removal of humic acid from water through adsorption–ultrafiltration hybrid processes

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ABSTRACT

Magnetic activated carbon (MAC) was prepared, characterized, and investigated to quantify the effects of pretreatment in a membrane filtration system. The effects of MAC on membrane parameters like percent retention, permeate flux, and backwash times were compared to that of powdered activated carbon (PAC). The prepared adsorbent has magnetization values 10 JT^{-1} kg^{-1} and point of zero charge value of 8.67. The effects of both adsorbents on membrane parameters were almost same. However, the secondary problems like cake formation have been observed for PAC was not observed due to the fact that MAC was removed from slurry through magnet. Also, PAC caused blackening of flow meter and pipes when used in combination with ultrafiltration membrane (UF) in a hybrid manner. The backwash time was shortest for MAC/UF hybrid process as compared to PAC/UF operation.

Keywords: Ultrafiltration; Permeate flux; Percent retention; Adsorption; Foulants

1. Introduction

Ultrafiltration (UF) membrane process has received considerable attention recently in the water utility industry to meet the stringent drinking water standards and to recycle the wastewater for reuse. However, fouling is the major challenge in the use of membrane processes. Fouling can be characterized in general as the reduction of permeate flux through the membrane which leads to permanent loss of system productivity over time. The periodic cleaning of membrane restore the permeate flux, however, eventually it leads to the replacement of membrane resulting in higher operational and maintenance costs [1–4].

Foulants can be classified into four categories: inorganic, organic, colloidal and particulate, and biological growth. Natural organic foulant like humic acid is considered to be the major foulant that adversely affect the membrane parameters like permeate flux, backwash time etc. To overcome this, researchers have used a multifaceted approach like designing new membranes, increasing the efficiency of pretreatment, modifying membrane surface, modifying the system design, altering the hydrodynamics of the solution, and developing an efficient cleaning system [1–4]. Powdered activated carbon (PAC) has the ability to adsorb efficiently the organic compounds and especially the hydrophobic fractions [5]. According to Jacangelo et al. [2], PAC is able to minimize membrane fouling.

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A number of researchers used PAC in a hybrid manner with UF membranes to minimize fouling caused by synthetic and natural organic matter. Combination of Reactors, Including Membrane Separation Treatment and Adsorption in Liquid (CRISTAL) process was one of the successful attempts in this direction [6]. The competence of these hybrid processes depends on reactor size and configuration, backwashing frequency, filtration mode (dead end, cross-flow), and dosing procedure (one time or continuous addition) [6–12]. It was assumed that the PAC when entered into UF membrane form a porous layer on its surface and do not affect the permeate flux. However, a decline in permeate flux due to PAC cake formation has been observed by some researchers [13,14] Cake formed by PAC over the membrane surface prolong the backwash time and also causes blackening of the flow meter, pipes etc.

Magnetic adsorbents have been used by many researchers for the removal of organic and inorganic pollutants from water. They can be separated from the medium by a simple magnetic process. Iron oxide has been used for foul control in the membrane processes [15–17], but due to its low surface area as compared to PAC it cannot be used on commercial scale for water treatment. The impregnated iron oxide over PAC has been used for the removal of phenolic substances from water in hybrid membrane processes [18]. However, the magnetic adsorbents have not been used in hybrid membrane processes for minimizing their fouling effect.

In the present study, magnetic activated carbon (MAC) was used in combination with UF membrane for fouling control and the membrane parameters like permeate flux, percent retention of humic acid, backwash time etc were compared with PAC/UF process.

2. Materials and methods

Humic acid was obtained from Sigma Aldrich catalogue no: H1, 675-2, while UF membrane was purchased from IMT Netherlands. PAC was purchased from Norit and MAC was prepared by standard method described in literature [18,19]. Equal volumes (200 ml) of $FeCl_3$ (28 mmol) and $FeSO_4$ (14 mmol) were mixed with weighed quantities of PAC and the resulting suspension was stirred at 70℃ with dropwise addition of NaOH (5 mmol). The resulting product was washed with distilled water till pH 6.5 and then dried in oven at 100℃ for 6 h. To predict the structural differences between PAC and MAC, pure iron oxide was prepared by the same procedure as mentioned above. The characteristic properties of UF membrane, PAC, MAC, and iron oxide are given in Tables 1 and 2. The PAC and MAC were characterized

Table 1
UF membrane parameters

Parameter	Specification
Matterial	Polyethersulfone
Type	Capillary multibore *7
Diameter bores ID	0.9 mm
Diameter fibre OD	4.2 mm
MWCO	100 kD
Surface area	50 m^2
Maximum temperature	40℃
Maximum pressure	7.5 bar
Membrane back wash pressure	0.5–1 bar
Maximum	2.5 bar
Operation pH range	3–10
Back wash pH range	1–13
Disinfection chemicals	
Hypochlride (NaOCl)	50–200 mg L^{-1}
Hydrogen peroxide (H_2O_2)	100–200 mg L^{-1}

Table 2
Physical properties of PAC, MAC, and iron oxide

Parameter	PAC	MAC	Iron oxide
BET surface area	1,150 m^2/g	868 m^2/g	64 m^2/g
Micropore volume	0.335 (cm^3 g^{-1})	0.212 (cm^3 g^{-1})	0.07 (cm^3 g^{-1})
Mesopore volume	0.085 (cm^3 g^{-1})	0.065 (cm^3 g^{-1})	–
Apparent density	0.51 g/mL	0.63 g/mL	
Particle size			
d10	4 μm	2 μm	–
d50	24 μm	21 μm	–
d90	90 μm	93 μm	–
Ash	12% max	–	–
Chloride (acid extracts)	0.1%	–	–
pH	Alkaline	Alkaline	–

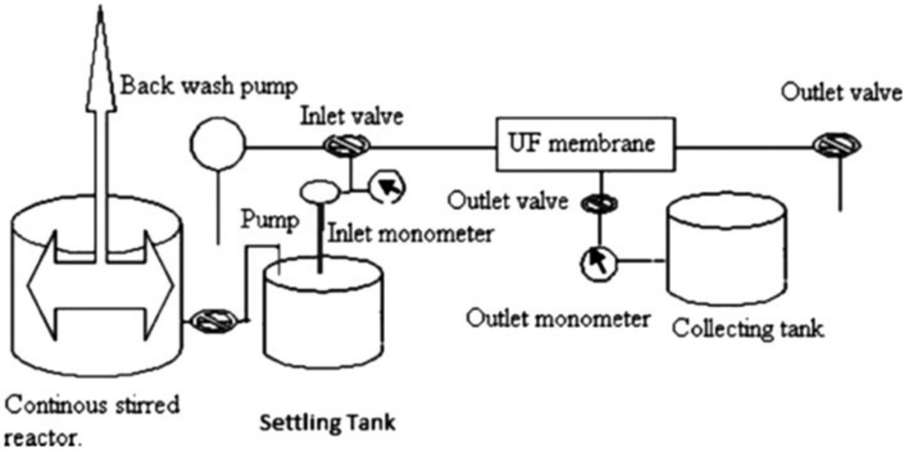

Fig. 1. Diagram of pilot plant.

by XRD, bulk sigma magnetization, Boehm titration [20], and FTIR. The point of zero charge (pzc) for both the adsorbents was determined by method devised by Noh and Schwarz [21].

A pilot plant consisting of parts: a reactor, UF membrane unit, collecting unit, and permeate back washing etc was constructed (Fig. 1). First, the adsorption parameters for PAC and MAC were determined. Both these adsorbent were then used in a hybrid manner in a pilot plant. Membrane parameters like percent retention permeate flux and backwash times were determined for both PAC/UF and MAC/UF processes. For batch adsorption experiments, the initial concentration of humic acid was from 4 to 20 mg/L, while in UF membrane experiments the concentration of humic acid was 20 mg/L. All the experiments were performed at room temperature. The membrane experiments were performed at a pressure of 2 bar.

3. Results and discussion

3.1. Characterization of adsorbents

The characteristic physical properties of both adsorbents and iron oxide are given in Table 2. The surface area of PAC is high as compared to MAC. As MAC is a composite of PAC and iron oxide, the

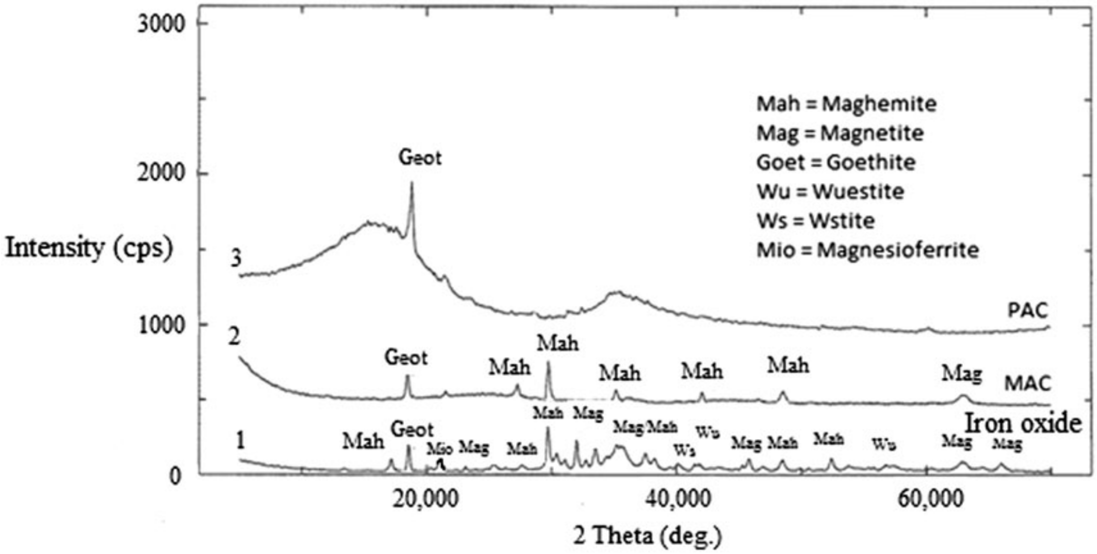

Fig. 2. XRD pattern of PAC, MAC, and iron oxide.

impregnation of iron oxide in micropores of PAC decreases the surface area of MAC. The XRD pattern of MAC, iron oxide, and PAC are shown in Fig. 2. XRD pattern of PAC showed the goethite peak, while iron oxide showed the magnetite, hematite, goethite, and maghemite peaks. Iron oxide/PAC composite showed maghemite and goethite peak. Out of the four iron oxides only magnetite and maghemite are attracted by magnet. The presence of magnetite and maghemite peak in composite shows the possibility that it can be separated from slurry in water treatment processes through magnet. This was further confirmed by bulk sigma magnetization (Figs. 3 and 4). The magnetization values for iron oxide and iron oxide/PAC composite were 62 and 10 JT^{-1} kg^{-1}, respectively.

The isoelectric point (IEP) i.e. the surface is at zero charge of zeta potential of an adsorbent is an important factor which determines the interaction between adsorbent and adsorbate at a given pH. A particular adsorbent may act as cation or anion exchanger depending upon the medium pH which finally acquire a net zero charge. This point is called pzc. If there is no adsorption of ions other than H^+ and OH^- then IEP = pzc. Acid/base titration and pH drift technique are widely used to determine pzc of an adsorbent [22]. Figs. 5 and 6 show the mass titration results for both PAC and MAC. From graph, the pzc of PAC and MAC was found to be 8.98 and 8.67, respectively.

Surface groups of activated carbons are usually determined using “wet” and “dry” methods of analysis. The “wet” techniques involve titrations such as Boehm [20] and potentiometric titrations [22,23]. “Dry” methods include diffuse reflectance FTIR etc. Although FTIR provide qualitative information about the carbon surface, the quantitative insight is not straightforward and requires special mathematical treatment with many approximations used [20]. On the other hand, Boehm and potentiometric titrations provide qualitative and quantitative information on the carbon surface. The FTIR spectrum of PAC and MAC are given in Figs. 7 and 8. Due to black

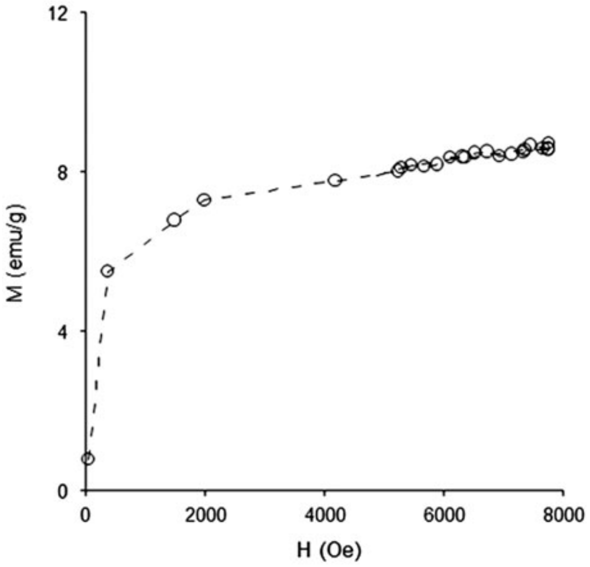

Fig. 4. Bulk sigma magnetization for MAC composite.

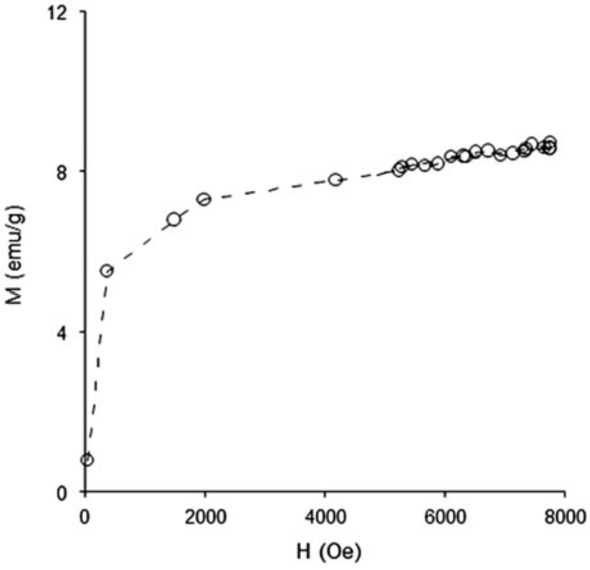

Fig. 3. Bulk sigma magnetization for iron oxide.

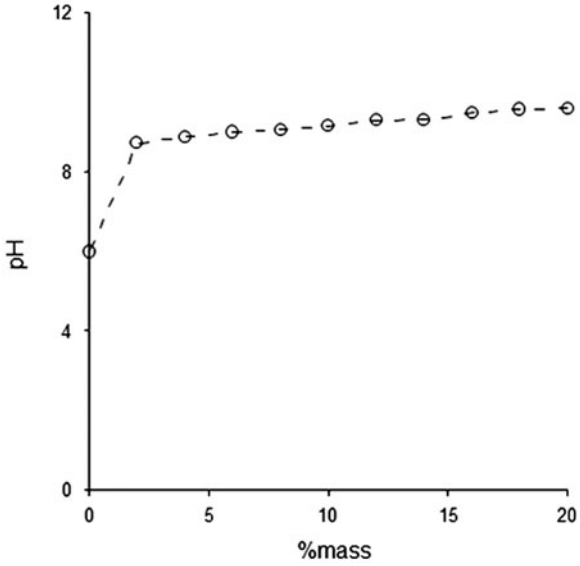

Fig. 5. PAC mass titration graph.

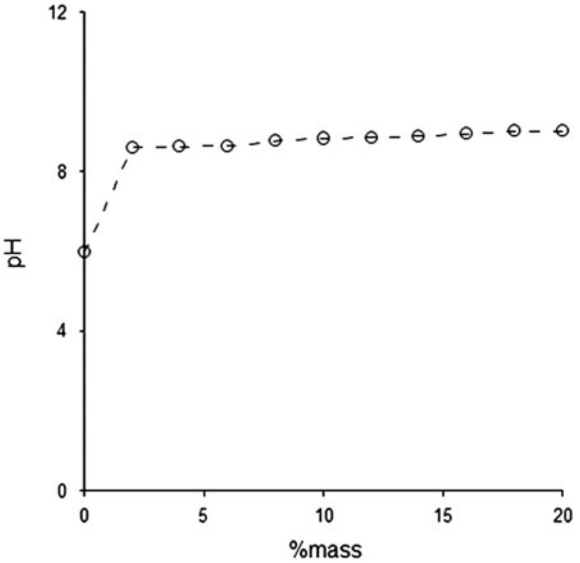

Fig. 6. MAC mass titration graph.

background, it is difficult to get a clear picture of adsorbent from FTIR spectrum. The functional groups determined from FTIR strums of PAC and MAC are shown in Table 3, while Boehm titration results are given in Table 4.

3.2. Adsorption parameters

Langmuir [24] and Freundlich [25] models were used to analyze the adsorption equilibrium data. The Langmuir and Freundlich constants are given in Table 5. The adsorption capacity of PAC was high as compared to MAC (121.2 and 95.7, respectively). This was due to impregnation of iron oxide in micropores which caused a decrease in the surface area of MAC. The values of n for PAC and MAC showed that the adsorption of humic acid on PAC and MAC is favorable (1.57 and 1.01, respectively).

Pseudo-first- and second-order kinetic models were used to determine the kinetics of humic acid adsorption on PAC and MAC. The values of pseudo-first- and second-order kinetic models constants and R^2 are given in Table 6. The R^2 values are high for pseudo-second-order kinetic model from which it is inferred that the adsorption of humic acid on PAC and MAC follow pseudo-second-order kinetic equation rather than pseudo-first-order kinetic model.

3.3. Effect of PAC and MAC on permeate flux

The variations of permeate flux with time for humic acid solution through UF membrane are shown in Fig. 9. The permeate flux dropped from 0.218 to 0.205 Lm^{-2} h^{-1} in 30 min. This drop was

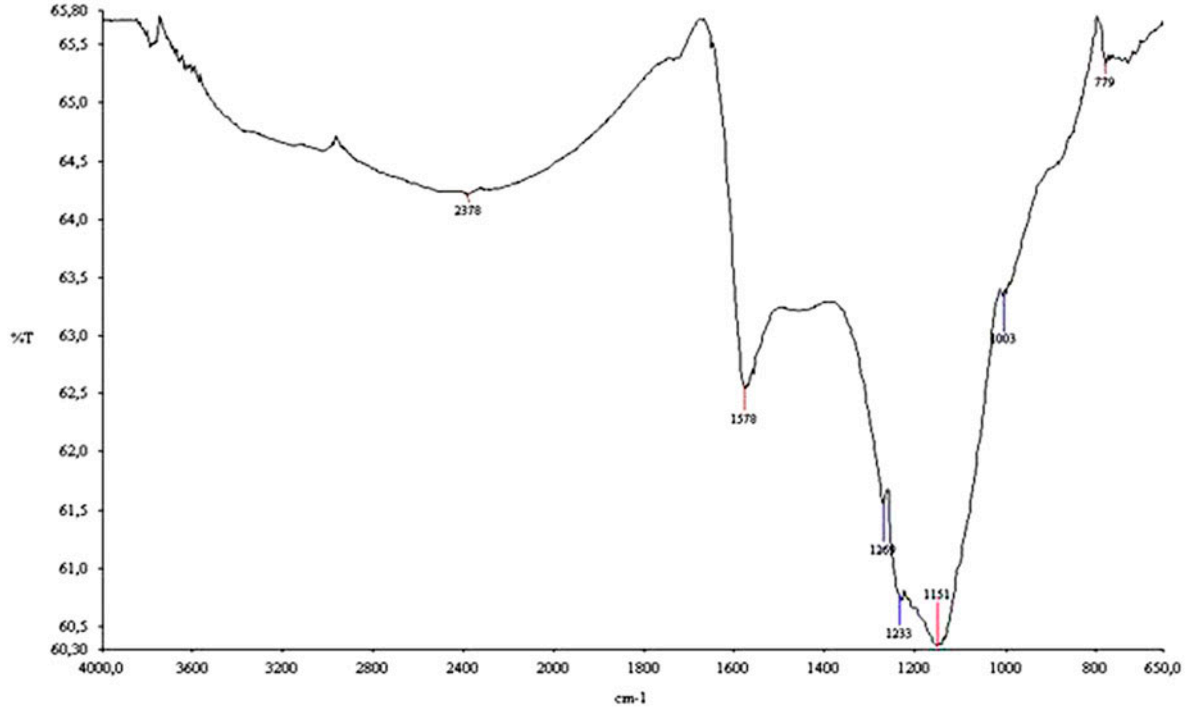

Fig. 7. PAC IR spectrum (ATR method).

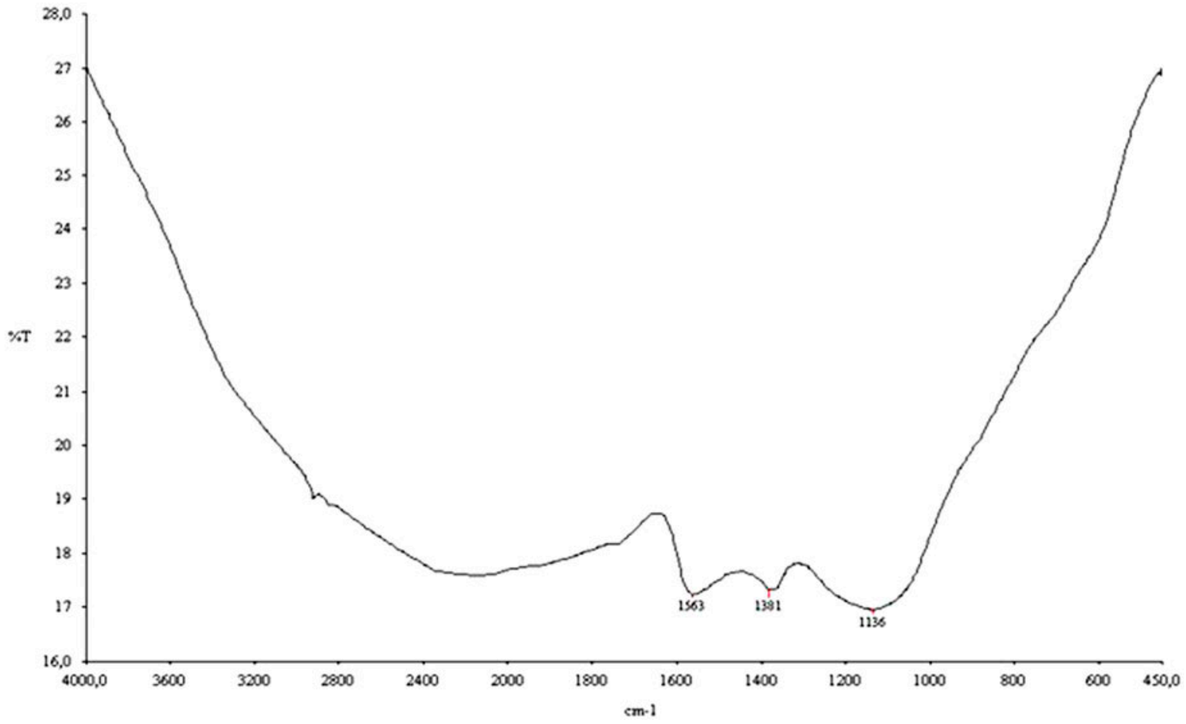

Fig. 8. MAC IR spectrum (ATR method).

Table 3
FTIR analysis of PAC and MAC

Functional groups	Transmission (%)	
	PAC	MAC
N–H (2,400–3,200 cm^{-1}) Amonium ions	64.25	–
C=O (1,550–1,610 cm^{-1}) Carboxylic acid türleri	62.40	17.2
C–O (1,250–1,300 cm^{-1}) Carboxylic acids	61.7	17.4
C–O (1,220–1,260 cm^{-1}) Aromatic ether	60.7	–
C–O (1,050–1,170 cm^{-1}) Acrylic anhydrides	60.36	17
C–X (1,000–1,100 cm^{-1}) Floroalkanes	63.46	–
Ar–H (750–810 cm^{-1}) m-disubstitute	65.5	–

due to blockage of membrane pores by humic acid. Fig. 10 shows the effect of PAC, when used in combination with UF membrane in a hybrid manner. The drop in permeate flux was from 0.218 to 0.207 Lm^{-2} h^{-1} in 30 min. Here, the decrease in permeate flux was low as compared to UF membrane alone which was due the fact that most of the humic acid was adsorbed by PAC and as a result low quantity of humic acid came in contact with membrane, thus the fouling was minimum. Initially, the permeate flux was high but at latter stages PAC formed a cake over membrane that caused a reduction in permeate flux. This was due to the fact that PAC was carried with effluents to membrane system as the settling time of PAC was high and was not completely removed from the slurry in the settling tank. A few secondary problems like blackening of the flow meter and pipes, long backwash times were also observed for PAC/UF operations. Economically, these are unfavorable effects of PAC. To overcome these, MAC was prepared and was used in hybrid manner with UF membrane. The effects of MAC on permeate flux in MAC/UF operation is shown in Fig. 11. Here, the drop in permeate flux was almost equal to that of PAC. If we look at the shape of the three curves we see that in permeate flux for UF process alone and for MAC/UF the drop is initially low, while for PAC/UF the drop is high at latter stages. This shows that PAC particles accumulated over membrane in PAC/UF process cause a decline in flux. Initially, there were lesser number of PAC and humic acid molecules and the decline in permeate flux was lower, but at latter stages the drop due to PAC particles was significant.

Table 4
Boehm titration results

Adsorbent	Acidic groups (meq g)	Carboxylic acid groups (meq g)	Carboxylic + lactonic groups (meq g)	Phenolic groups (meq g)	Lactonic groups (meq g)	Basic groups (meq g)
PAC	21.3525	4.5625	18.98	2.3725	14.4175	1.0
MAC	21.7175	3.1025	18.25	3.4675	15.1475	0.6

Table 5
Equilibrium adsorption parameters for the adsorption of humic acid on PAC and MAC

Isotherm	PAC	MAC
Langmuir		
Q_0 (mg g^{-1})	121.2	95.7
b (L mg^{-1})	0.122	0.113
R^2	0.95	0.935
Freundlich		
K	15.39	6.9
$1/n$	0.636	0.94
R^2	0.98	0.827

Table 6
Kinetics parameters for the adsorption of humic acid on PAC and MAC

Adsorbent	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model	
	K_a (l/min)	R^2	K_2 (g mg^{-1} min^{-1})	R^2
PAC	0.014	0.947	7.5×10^{-4}	0.989
MAC	0.060	0.944	1.3×10^{-2}	0.998

3.4. Removal of humic acid by UF, PAC/UF, and MAC/UF

The removal of humic acid by UF, PAC/UF, and MAC/UF was expressed in terms of percent retention. The percent retention was determined by using following formula:

$$R = 100\left(1 - \frac{C_p}{C_b}\right) \quad (1)$$

where R is percent retention, C_p is concentration of humic acid in permeates, and C_b is concentration of humic acid in bulk. The percent retention of humic acid in UF, PAC/UF, and MAC/UF are shown in Figs. 12–14. An improvement of UF permeated quality in the combination of PAC and MAC was observed. This has also been observed in several studies [26–28]. The membrane provides a physical barrier preventing

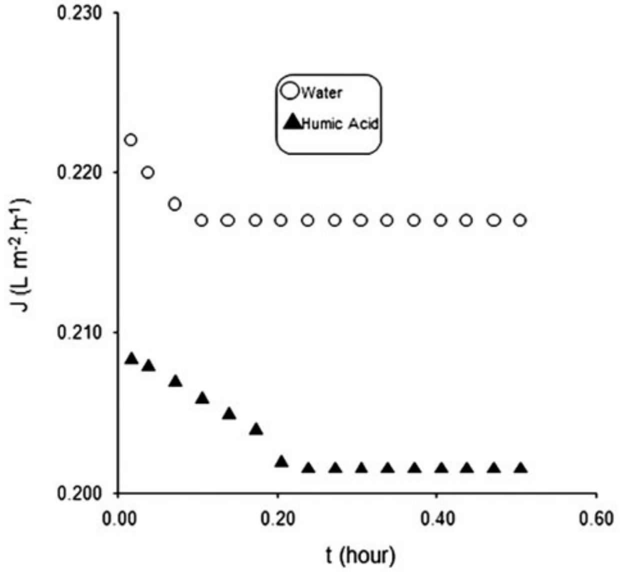

Fig. 9. Effect of humic acid on permeate flux.

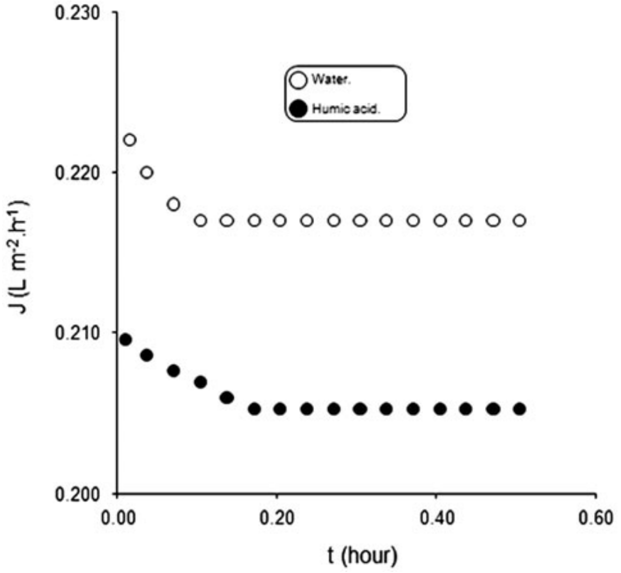

Fig. 10. Effect of humic acid on permeate flux in presence of PAC.

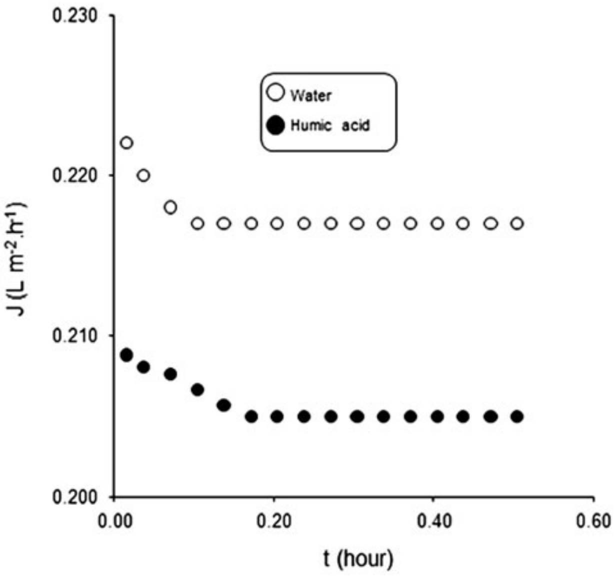

Fig. 11. Effect of humic acid on permeate flux in presence of MAC.

the passage of the PAC, and therefore retaining the humic acid absorbed on it, which otherwise would be trapped by the membrane. The percent retention of humic acid was high in PAC/UF operation as compared to MAC/UF. This was due to high surface area of PAC. However, as mentioned earlier, the use of PAC in membrane processes is associated with certain secondary problems that economically rendered the use PAC in hybrid processes. The percent retention of humic acid in UF process alone was lower than that of PAC/UF and MAC/UF operations.

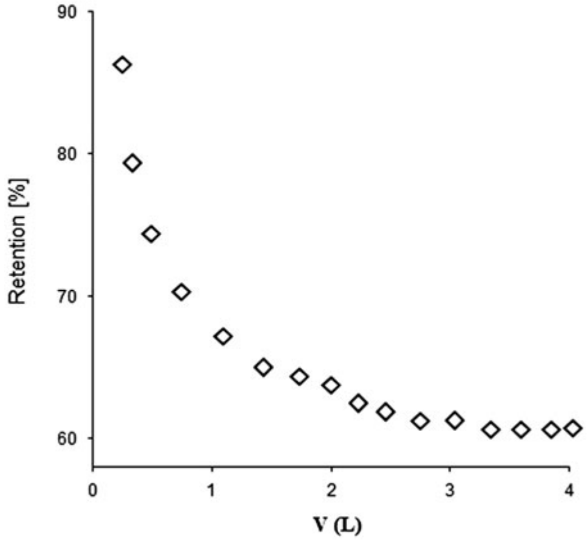

Fig. 12. Percent retention of humic acid by UF membrane.

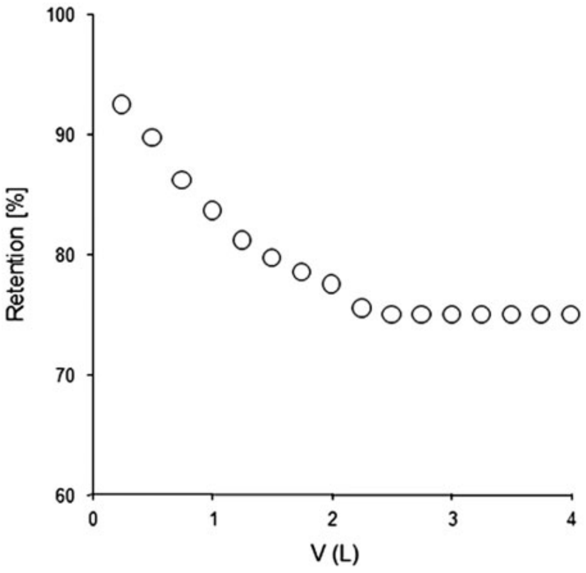

Fig. 13. Percent retention of humic acid by UF membrane in presence of PAC.

3.5. Effect of PAC and MAC on backwash times

Periodic backwashes are widely used in membrane processes to clean the membrane. Using a reverse transmembrane pressure for very short interval of time, the permeate is forced through the membrane in

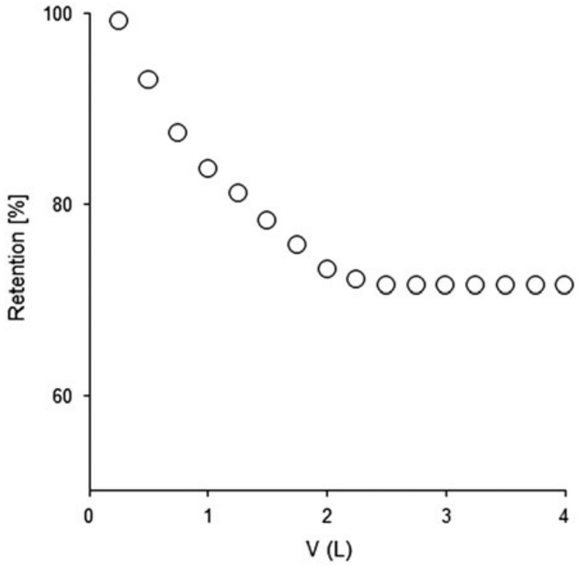

Fig. 14. Percent retention of humic acid by UF membrane in presence of MAC.

the reverse direction and cause the filter cake or gel to expand, de-log, and eventually be carried away. The backwash was applied after each 30 min cycle. The backwash time was longer for PAC/UF (6–8 min) operation as compared to MAC/UF (3–5 min) process. This was due to the fact that MAC was removed from the slurry in the settling tank through magnet, while PAC was not completely removed from the slurry in the settling tank and was carried to membrane. Thus, the backwashes after PAC/UC operation took more time to detach the cake formed over membrane. In case of MAC/UF operation, no such cake was encountered. Thus, MAC/UF operation was more economical as compared to PAC/UF in terms of electric power consumption.

4. Conclusions

PAC/UF processes have already been investigated. Although it is very successful in production of drinking waters in many countries but still suffers a number of problems. The important amongst these problems is the cake formation over membrane that causes a decline in permeates flux. In order to evaluate the possibility of UF membrane for drinking water production and to eliminate the cake formation encountered in PAC/UF processes, a pilot plant was constructed. A magnetic adsorbent MAC was used as an alternative for PAC in UF processes. The percent retention and improvement in permeates flux were almost equal for both PAC/UF and MAC/UC processes. The little differences were due to the difference in surface area of both adsorbents. The secondary problems associated with the use of PAC were not observed for MAC. Thus, it is concluded that the use of MAC in membrane processes will be economical as compared to PAC, if used commercially.

Acknowledgments

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