Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1137787

57 (2016) 23661–23665
October

Taylor & Francis
Taylor & Francis Group

Effect of granular activated carbon on percent retention of humic acid and permeate flux in GAC/UF membrane process

Muhammad Zahoor[a,b]

[a]*Department of Chemistry, University of Malakand, P.O. Box 18000, Chakdara, Dir (L), KPK, Pakistan, Tel. +92 341 6062388; email: mohammadzahoorus@yahoo.com*
[b]*Engineering Faculty, Department of Chemistry, Istanbul University, Istanbul, Turkey*

Received 27 June 2015; Accepted 28 December 2015

ABSTRACT

In this study, an attempt has been made to produce portable water having low concentrations of natural organic matter. First, the adsorption parameters of granular activated carbon (GAC) were determined by batch experiments. Fixed bed experiments were performed for the determination of GAC column parameters. To evaluate the effect of GAC filter on membrane parameters, the GAC filter was connected with ultrafiltration (UF) membrane pilot plant. Higher percent retentions and permeate fluxes were observed for GAC/UF hybrid process as compared to UF process alone. With GAC about 17.5%, high retention of humic acid was observed. UF membrane system was operated in dead-end mode with transmembrane pressure of 0.8 bar. The back washing duration for GAC/UF hybrid process was lower than that of UF operation alone.

Keywords: Adsorption; GAC; UF; Permeate flux

---

1. Introduction

Natural organic matter (NOM) in water accumulates over membrane surface that causes more membrane fouling and as a result, there is higher demand for disinfection. It not only causes membrane fouling but also produces harmful byproducts [1,2]. Several treatment processes for NOM removal have been used for producing portable water. The selection of treatment processes is based on NOM characteristics in the source water and the required quality of treated water. The conventional methods of removal of NOM from water have a number of drawbacks and time consuming. NOM can be efficiently removed by combining the conventional and modern treatment processes [3].

Humic acids are formed by microbiological degradation of animal and plants decay that enters surface waters reservoirs through rainwater run-off. Its concentration in water depends on climatic conditions. Usually, high concentrations are observed in wet season and lower concentrations in the dry season. The presence of humic acid in water is just a color problem but in conventional water treatment processes like chlorination, carcinogenic byproducts like trihalomethane and haloacetic acid are formed from it [1–3]. It is also considered to be the major foulant that adversely affects 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. Activated carbon has the ability to adsorb efficiently the organic compounds and especially the hydrophobic organic compounds [4–6].

However, Tomaszewska and Mozia [7] have shown that PAC when used in hybrid membrane processes forms a porous cake over membrane that adversely affects the membrane permeability. Also in our previous studies, longer backwash times were observed when PAC was used in combination with UF membrane and some secondary problems like blackening of pipes and other accessories of the membrane system were observed. Thus, economically these drawbacks limit the use of PAC as pretreatment in membrane processes [4,5].

Granular activated carbon (GAC) due to its coarse particles nature that can be stopped from being entering into membrane system, thus can be used as an alternative to PAC and the secondary problems associated with PAC will not be encountered if used in UF hybrid processes. In the present study, granular activated carbon was used in combination with UF membrane for fouling control. The membrane parameters like permeate flux, percent retention of humic acid, backwash time, etc. were determined.

2. Experimental

The chemicals used in this study were of analytical grade. Humic acid was obtained from Sigma Aldrich (catalog no: H1, 675-2). Ultrafiltration membrane was purchased from IMT Netherland. The coconut shell charcoal-based granular activated carbon (8 × 30 Mesh particle size and BET surface area 500–550 $m^2 g^{-1}$) was obtained from Activated Carbon Technology UK limited.

Stock solution (20 $mg L^{-1}$) of humic acid was prepared in distilled water. A number of dilute solutions (100 ml) were prepared and contacted with known amount of adsorbent (0.12 g) at 25˚C in order to determine its adsorption parameters. After 24 shacking at 250 rpm, the adsorbent was removed from solution through centrifuge at a speed of 10,000 rpm and the supernatants were checked for humic acid concentration using UV–vis spectrophotometer (Thermo Electron corporation Heios) at 254 nm.

The fixed bed column adsorption parameters were determined by passing the solution of humic acid from GAC filter containing 140 g adsorbent. The solutions were passed through column at speed of 12–16 L/h through column and collected in 250-ml flasks. The remaining concentration of humic acid after adsorption was determined by UV–vis spectrophotometer at 254 nm.

The GAC filter was then connected with UF membrane pilot plant. First, the humic acid solution was channelized to pass through UF membrane system and the difference in feed and permeate concentrations were determined by the UV–vis spectrophotometer. Then the GAC filter was connected in series with UF membrane system (in between UF membrane and stock solution reservoir) and the concentration differences in the feed and permeate flux were determined. From the data obtained, percent rejection of humic acid by membrane alone and with GAC/UF process was determined. The decline in permeate fluxes for both membrane alone and GAC/UF process was also determined. In all experiments, membrane system was operated in dead-end mode with transmembrane pressure of 0.8 bar. The decline in permeate flux offered to distilled water passage by membrane with time and the effect of GAC on backwash duration were also determined.

3. Results and discussion

3.1. Adsorption isotherms

A number of adsorption isotherms are used to explain the equilibrium adsorption data. In this study, Langmuir [8] and Freundlich [9] adsorption isotherms have been used as these two are more frequently used isotherms in adsorption studies. The Langmuir model assumes monolayer adsorption onto a surface with a finite number of similar sites having no lateral interaction between the sorbed molecules. The linear form of the Langmuir isotherm is given by the following equation:

$$\frac{C}{q} = \frac{C}{Q_0} + \frac{1}{Q_0 b} \tag{1}$$

where q ($mg g^{-1}$) is the amount of humic acid adsorbed per unit mass of adsorbent, C ($mg L^{-1}$) is the equilibrium concentration of humic acid; the Langmuir constants Q_0 and b are related to maximum adsorption capacity and energy of adsorption, respectively. The C/q verses C plot gives a straight line with slope $1/Q_0$. The values of Q_0 and b were calculated from the slope and intercept of the straight line and are given in Table 1.

The Freundlich isotherm is used for adsorption on heterogeneous surfaces and is a special form of the Langmuir isotherm that is applicable only in the middle ranges of concentrations. The logarithmic form of the Freundlich model can be expressed as:

Table 1
Isotherm parameters for the adsorption of humic acid on GAC

Langmuir isotherm			Freundlich isotherm		
Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	K	$1/n$	R^2
108.6	0.103	0.98	13.52	0.543	0.93

$$\ln q = \ln K + \frac{1}{n}\ln C \tag{2}$$

where C is the equilibrium concentration (mg L^{-1}) of adsorbate, q is the amount of humic acid adsorbed (mg g^{-1}). The Freundlich constants; K (mg g^{-1} (L mg^{-1})$^{1/n}$) and n are related to adsorption capacity and adsorption intensity, respectively. When lnq is plotted against ln C, a straight line is obtained. The Freundlich constants; K and n for the adsorbents are calculated from intercept and slope of the plot and are shown in Table 1. The correlation coefficient of GAC in Table 1 for Freundlich adsorption isotherm is too low as compared to that of Langmuir model.

3.2. *GAC fixed bed adsorption parameters*

The breakthrough curve for the adsorption of humic acid in GAC filter is shown in Fig. 1, while the different parameters determined from the curve are shown in Table 2.

From the results in table, it is evident that the adsorption capacity of the filter decreases with the increase in flow rate, which can be attributed to less contact time of the humic acid with GAC.

3.3. *Effect of GAC filter adsorption on membrane efficiency*

The accumulation of foulants on membrane surface causes concentration polarization that affects the efficiencies of the membrane processes. The unwanted effects of concentration polarization are usually observed in a very short time at the start of the process and then the permeate flux remains constant for some time. In long-term uses, a gradual reduction in permeate flux is observed due to fouling which may be due to cake formation over the membrane surface, pore blocking, and adsorption [10,11].

The effects of GAC filter on fouling were observed by connecting the UF pilot plant with GAC filter in series and membrane parameters; permeate flux and percent retention of the humic acid were determined. The effect of GAC on backwashes on membrane efficiency was also determined.

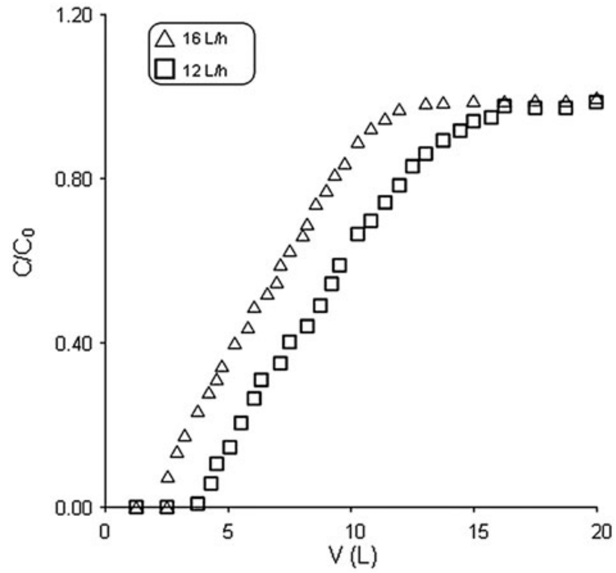

Fig. 1. Breakthrough curve of humic acid adsorption on GAC.

Table 2
Parameters calculated from breakthrough curve

Parameter	Speed (L/h)	Humic acid
V_{i} (L)[a]	12	4.00
	16	2.50
X_{i} (mg/g)[b]	12	7.20
	16	4.50
V_{f} (L)[c]	12	16.00
	16	12.20
X_{f} (mg/g)[d]	12	30.40
	16	23.18

[a] V_{i} is the volume of effluent at the breakthrough point of the column (L).

[b] X_{i} is the amount of phenolic substances adsorbed per g of adsorbent at the breakthrough point (mg/g).

[c] V_{f} is the volume of effluent at the close point of the column (when C/C_0 reaches a plateau).

[d] X_{f} is the amount of phenolic substances (mg/g) adsorbed per g of adsorbent at the close point.

3.3.1. *Retention of humic acid*

Usually, organic molecules having size larger than the molecular weight cut-off of the membrane are retained by the membrane. The retention of a foulant by membrane is expressed in terms of retention coefficient R and is expressed in percent. The retention of the foulants depends on its size and configuration relative to the pore sizes of the membrane. The chemical interactions of the solution with membrane, like adsorption, concentration polarization, and fouling are also important factors that play important role in the retention of foulants [11,12]. R is given by the following relation:

$$R = 100\left(1 - \frac{C_p}{C_b}\right) \tag{3}$$

where C_p is the concentration of solute in permeate and C_b is the solute concentration in bulk.

The percent retention of humic acid by membrane alone is shown in Fig. 2, while GAC/UF process is shown in Fig. 3. From the figures, it is clear that the percent rejection of the humic acid is higher for GAC than that of membrane alone. For GAC/UF process, the percent rejection was high due to high adsorptive powers of the GAC as compared to membrane surface alone. For membrane alone, the retention at equilibrium stage was 60.5%, while for GAC/UF process, it was 78%. In our previous study, powdered activated carbon was used for foul control in the membrane processes. However, the decline in permeate flux was high and the percent retention of humic acid was low; GAC particles are larger than PAC and thus were stopped from flowing into membrane system [4]. Also as pointed out in different studies, the decline in flux due to PAC in PAC/UF processes was due to cake formation on membrane surface [10–12]. Thus, GAC filters can be used as alternative to PAC in hybrid membrane processes.

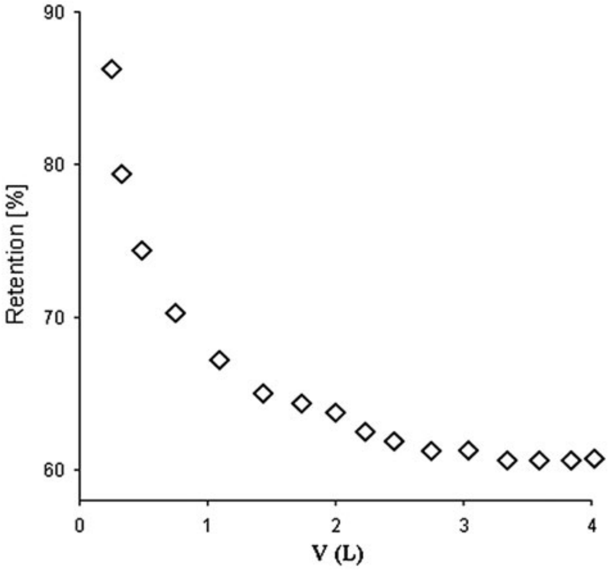

Fig. 2. Percent retention of humic acid by UF membrane.

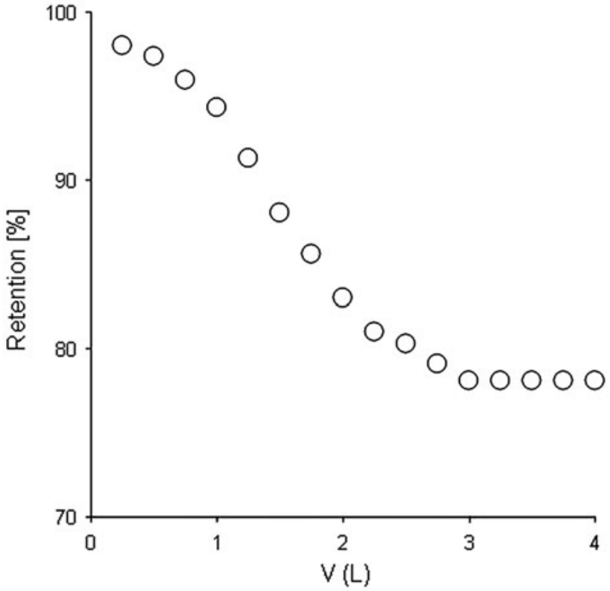

Fig. 3. Percent retention of humic acid by GAC/UF membrane hybrid system.

3.3.2. Effects of GAC on permeate flux

A decline in the permeate flux in the initial stages for water passage through membrane alone in equilibration process was observed which was due to the intrinsic membrane resistance and interaction of the ions present in distilled water with membrane. The flow rate then became steady and was not affected any more within the experimental cycle. The adsorption of the humic acid over membranes partially blocks the pores of membrane resulting in low fluxes.

The influence of GAC on permeate flux of humic acid is shown in Fig. 4. Improved flux was observed in presences of GAC.

3.3.3. Effect of GAC on back wash times

The membrane was cleaned with deionized distilled water after each 30-min cycle. In absence of GAC, the backwash time was high as compared to its presence in GAC/UF hybrid process which can be attributed to high removal capacity of GAC that kept the foulant from being entering into membrane system. For PAC, used in our previous study, blackening of the pipes and flow meter of the membrane system were observed [13]. Thus, economically, the use of PAC in the membrane systems is expensive as compared to GAC as it reduces backwash times, and does not cause blackening of the pipes and other accessories. As there will be need to replace the blackened accessories periodically Fig. 5.

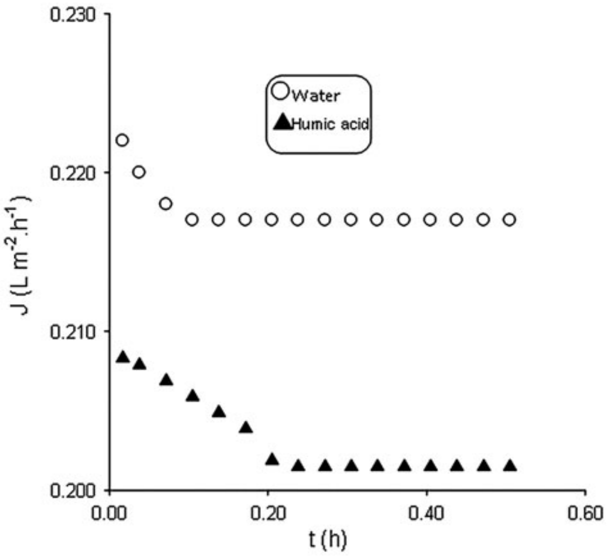

Fig. 4. Effects of humic acid on UF membrane permeate flux.

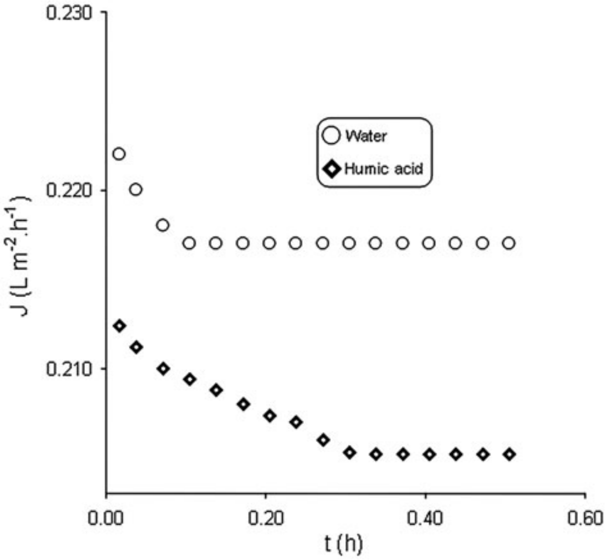

Fig. 5. Effects of humic acid on GAC/UF membrane hybrid system permeate flux.

4. Conclusions

In the present study, improved permeate fluxes and percent retention were obtained with GAC filters as compared to membrane alone. The blackening caused by PAC in our previous work was not observed for GAC due to larger particle size. From economical point of view, the use of PAC in the membrane systems is expensive as compared to GAC as it reduces backwashing time and not causes blackening of the pipes and other accessories of the system. Thus, it is concluded that GAC filters can be used as alternative of PAC in hybrid membrane processes for foul control.

Acknowledgements

This work was supported by the research fund of Istanbul University project number 3822.

References

[1] T.H. Boyer, P.C. Singer, Bench scale testing of a magnetic ion exchange resin for removal of disinfection by product precursors, Water Res. 39(7) (2005) 1265–1276.
[2] D.A. Fearing, J. Banks, S. Guyetand, C. Monfort Eroles, B. Jefferson, D. Wilson, P. Hillis, A.T. Campbell, S.A. Parsons, Combination of ferric and MIEX® for the treatment of a humic rich water, Water Res. 38(10) (2004) 2551–2558.
[3] H.E. Ewerts, A. Swanepoel, H.H. Du Preez, Efficacy of conventional drinking water treatment processes in removing problem causing phytoplankton and associated organic compounds, Water SA 39(5) (2013) 739–750.
[4] M. Zahoor, Removal of humic acid from water through adsorption-ultrafiltration hybrid processes, Desalin. Water Treat. 52(40–42) (2014) 7983–7992.
[5] M. Zahoor, Separation of surfactants from water by granular activated carbon/ultrafiltration hybrid process, Desalin. Water Treat. 57(5) (2016) 1988–1994, doi: 10.1080/19443994.2014.979242.
[6] M. Tomaszewska, S. Mozia, Removal of organic matter from water by PAC/UF system, Water Res. 36(16) (2002) 4137–4143.
[7] S. Jeong, S.J. Kim, C. Min Kim, S. Vigneswaran, T. Vinh Nguyen, H.K. Shon, J. Kandasamy, I.S. Kim, A detailed organic matter characterization of pretreated seawater using low pressure microfiltration hybrid systems, J. Membr. Sci. 428 (2013) 290–300.
[8] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40(9) (1918) 1361–1403.
[9] H. Freundlich, Ueber die Adsorptio in Loesungen (Adsorption in solution), Z. Phys. Chem. 57 (1906) 384–470.
[10] C.F. Lin, Y.J. Huang, O.J. Hao, Ultrafiltration processes for removing humic substances: Effect of molecular weight fractions and PAC treatment, Water Res. 33(5) (1999) 1252–1264.
[11] A.S. Jönsson, J. Lindau, R. Wimmerstedt, J. Brinck, Influence of the concentration of a low-molecular organic solute on the flux reduction of a polyethersulphone ultrafiltration membrane, J. Membr. Sci. 135(1) (1997) 117–128.
[12] M.R. Wiesner, M.M. Clark, J. Mallevialle, Membrane filtration of coagulated suspensions, J. Environ. Eng. 115(1) (1989) 20–40.
[13] M. Zahoor, M. Mahramanlioglu, Removal of phenolic substances from water by adsorption and adsorption-ultrafiltration, Sep. Sci. Technol. 46(9) (2011) 1482–1494.