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Separation of surfactants from water by granular activated carbon/ultrafiltration hybrid process

Muhammad Zahoor[a,b]

[a]*Department of Chemistry, University of Malakand, Chakdara Dir (lower) KPK, Pakistan, email:* mohammadzahoorus@yahoo.com
[b]*Faculty of Chemical Engineering, Department of Chemistry, Avcilar Istanbul University, Istanbul, Turkey*

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ABSTRACT

The aim of the study was to determine the efficiency granular activated carbon (GAC) as foul control in ultrafiltration (UF) membrane process. The adsorptive parameters for triton x-100, sodium dodecylbenzene sulfonate (SDBS), and N-dodecylpyridinium chloride on GAC were determined. The equilibrium data fit well to Langmuir adsorption isotherm rather than Freundlich model. Breakthrough curves were obtained from fixed bed experiments, and column parameter was calculated from it. For UF membrane alone and GAC/UF hybrid process, the percent retentions of the selected surfactants under study were determined and the declines in flux were observed. The percent retention was 4, 10, and 22 % for N-dodecylpyridinium chloride, SDBS, and triton x-100, respectively. In the presence of adsorbent, the improved percent retention was 87, 95, and 98 % for triton x-100, SDBS, and N-dodecylpyridinium chloride, respectively. The problems already reported for powdered activated carbon such as cake formation over membrane surface, long backwash time, and blackening of pipes were not observed for GAC.

Keywords: Surfactants; Granular activated carbon; Adsorption; Ultrafiltration; Foulants; Percent retention; Permeate flux

1. Introduction

In domestic wastewater, the concentration of surfactants is significant as they are used for all types of washing and are responsible for the constantly deteriorating condition of water reserves. The largest amounts of the surfactants are used in laundries and houses for washing, and in addition, they have many useful applications in industries such as textile, oil, metallurgy, foodstuffs, plant protection agents, and agriculture [1]. They cause extensive foaming in natural reservoirs and wastewaters [2]. They increase the solubility of other hazardous contaminants. The increased solubility of substances like pesticides increases their penetration into living organisms and thus increasing their toxicity [2,3]. Although surfactants have a toxic impact on organisms at high concentration but at low concentration they are not toxic to organisms. Usually, the chronic toxicity of anionic and nonionic surfactants occurs at concentrations greater than 0.1 mg dm^{-3} [4,5]. To protect the animals from the hazardous effects, the levels of the surfactants must be reduced to permissible values before the wastewaters are discharged into the sewage systems.

A number of methods such as oxidation [6,7], coagulation or combinations of coagulants and polyelectrolytes [8], adsorption [9,10], ion exchange [11,12], and membrane processes [13–15] are employed to remove surfactants from water, each of these has its merits and limitations. High-pressure membrane processes such as nanofiltration and reverse osmosis are the most successful in removing the surfactants and other organic contaminants from water [14]. However, they have relatively low permeate flux values and high costs. The low-pressure membrane processes such as microfiltration and ultrafiltration (UF) on the other hand are not sufficiently effective for achieving acceptable levels of these contaminants in discharging wastewaters into sewage or surface waters. These contaminants also affect the efficiency of the membrane processes by concentration polarization and fouling, thus shrinking the membrane pores and thereby decreasing the permeate flux. To minimize fouling pretreatments such as coagulation followed by sedimentation [16] and activated carbon adsorptions [17] have been employed. The use of activated carbon adsorption as pretreatment was although considered the most successful but was associated certain secondary problems such as cake formation over membrane, blackening of the pipes and other accessories of the membrane system and long backwash times. To solve these problems, there is need for such adsorbent having comparable surface area as that of powdered activated carbon (PAC) and coarse particle size that could be easily stopped from being entering into membrane system.

In this study, granular activated carbon (GAC) was used as pretreatment to UF membrane process to minimize the fouling caused by the tested cationic, anionic, and nonionic surfactants.

2. Experimental

All the chemicals used in this study were of analytical grade. Triton x-100 (1.07 gcm^{-3}) was obtained from Merck, while sodium dodecylbenzene sulfonate (SDBS) and N-dodecylpyridinium chloride were purchased from Sigma-Aldrich. The physicochemical properties and molecular structures of these surfactants are shown in Table 1. The UF membrane was obtained from IMT Netherland (Table 2), while coconut shell charcoal-based GAC (8 × 30 mesh particle size and BET surface area 500–550 m^2 g^{-1}) was purchased from Activated Carbon Technology UK limited (Table 3).

Stock solutions (50 mg L^{-1} each) of the selected surfactants were prepared in distilled water. A number of dilute solutions (100 mL) were prepared from each 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 surfactant concentrations using UV/Visible spectrophotometer (Thermo Electron corporation Heios) at 275, 223.5, and 213.5 nm for triton x-100, SDBS, and N-dodecylpyridinium chloride, respectively.

The fixed bed column adsorption parameters were determined by passing the solution of selected surfactants from GAC filter containing 140 g adsorbent. The solutions were passed through column at speed of 12 and 16 L h^{-1} through column and at outlet of the column they were collected in 250-mL flasks. The remaining concentration of surfactants after adsorption was determined by UV/Visible spectrophotometer at their particular wavelength.

In order to know the effectiveness of the GAC as foul controlling agent, the GAC was connected with UF membrane pilot plant. The surfactant solutions present in a 12-L container were channelized to UF membrane system. In all the experiments, membrane filtration was performed in a dead-end mode with trans-membrane pressure of 0.8 bar. Samples were collected from outlet of the pilot plant at different time interval in 250-mL flasks, and the difference in feed and permeate concentration was determined by the UV/Visible spectrophotometer. The percent rejection of each surfactant was determined from these differences. The decline in permeate fluxes due to these foulants was determined. The decline in distilled water permeate flux with passage of time was also determined. The diagram of the system is given in Fig. 1.

3. Results and discussion

3.1. Adsorption parameters

The equilibrium adsorption data were analyzed using Langmuir [18] and Freundlich [19] adsorption isotherms. The Langmuir adsorption isotherm has been used by many authors for the adsorption of inorganic and organic substances. The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with 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 adsorbate adsorbed per unit mass of adsorbent, C (mg L^{-1}) is the equilibrium concentration of the adsorbate, Q_0 and b are

Table 1
Characteristic properties of the surfactants used in the study

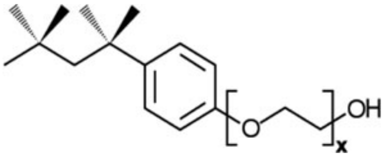
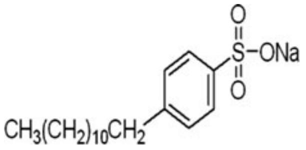
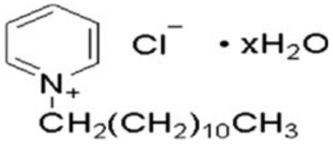
Parameter	Triton x-100	SDBS	N-dodecypyridinium chloride
Molecular structure			
Molar mass (g mol^{-1})	647	348.48	283.88
Appearance	Viscous colorless liquid	Colorless	White
Purity (%)	99.5	99.5	98

Table 2
Characteristic properties of UF membrane

Parameter	Specification
Material	Polyethersulfone
Type	Capillary multibore *7
Diameter bores ID	0.9 mm
Diameter fiber OD	4.2 mm
MWCO	100 kD
Area	50 m^2
Maximum operating temperature	40°C
Trans-membrane pressure operation	0.5–1 bar
Maximum	2.5 bar

Table 3
Physical properties of GAC

Parameter	Properties
Raw material	Coconut shell charcoal
Appearance	Black granular and irregular
Particle size	8×30 mesh
Maximum size	5% max
Minimum size	5% max
Apparent density	0.55 g L^{-1} (min)
Hardness	95% min
Moisture	5% max
Ash	3% max

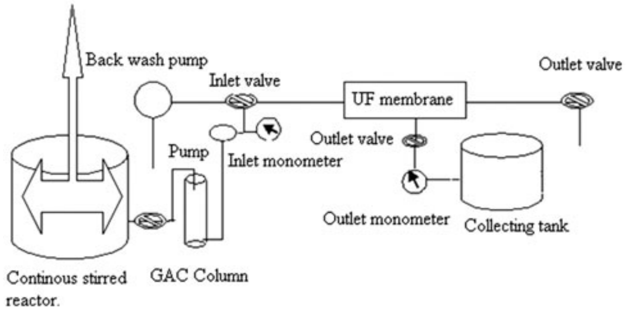


Fig. 1. Diagram of UF system.

Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. C/q was plotted vs. C and straight line with slope $1/Q_0$ was obtained. The values of Q_0 and b for GAC were calculated from the slope, and intercept of the straight line are given in Table 4.

The Freundlich isotherm is a special form of the Langmuir isotherm and is applicable only in the middle ranges of concentrations. The logarithmic form of the Freundlich model can be given as follows:

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

where C is the equilibrium concentration (mg L^{-1}), q is the amount adsorbed (mg g^{-1}). K (mg g^{-1}(L $mg^{-1})^{1/n}$) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. $\ln q$ was plotted against $\ln C$ for the equilibrium data and the values Freundlich constants, K and n for the adsorbents were calculated from intercept and slope of

Table 4
Isotherm parameters for the adsorption of triton x-100, SDBS, and N-dodecylpyridinium chloride on GAC

Isotherm	Triton x-100	SDBS	N-dodecypyridinium chloride
Langmuir			
Q_0 (mg g^{-1})	194.0	205.0	218.5
b (L mg^{-1})	0.015	0.095	0.45
R^2	0.98	0.985	0.989
Freundlich			
K	23.4	43.4	52.7
$1/n$	0.13	0.21	0.34
R^2	0.97	0.95	0.89

the plot and are given in Table 4. The adsorption capacities of these foulants increase in order of N-dodecylbenzene sulfonate > SDBS > triton x-100. The correlation coefficients for the adsorbents in Table 1 for Freundlich adsorption isotherm are too low, and therefore, the values of K and n cannot be compared. The best fit was observed with the Langmuir model.

3.2. GAC fixed bed adsorption parameters

The breakthrough curves of the adsorption in GAC filters are given in Figs. 2–4, while the different parameters determined from the curves are given in Table 5.

From the results, it is evident that with the increase in flow rate, the adsorption capacity of the GAC filters decreases; this can be attributed to less contact time of the contaminants with the adsorbent.

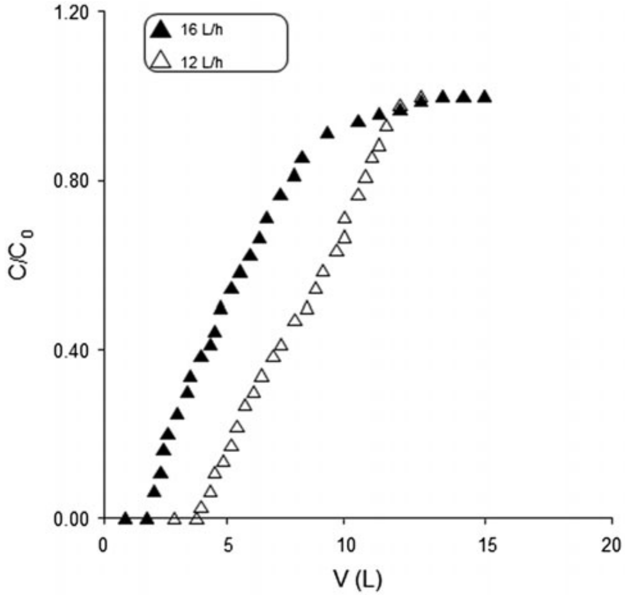


Fig. 2. Breakthrough curve of triton x-100 adsorption on GAC.

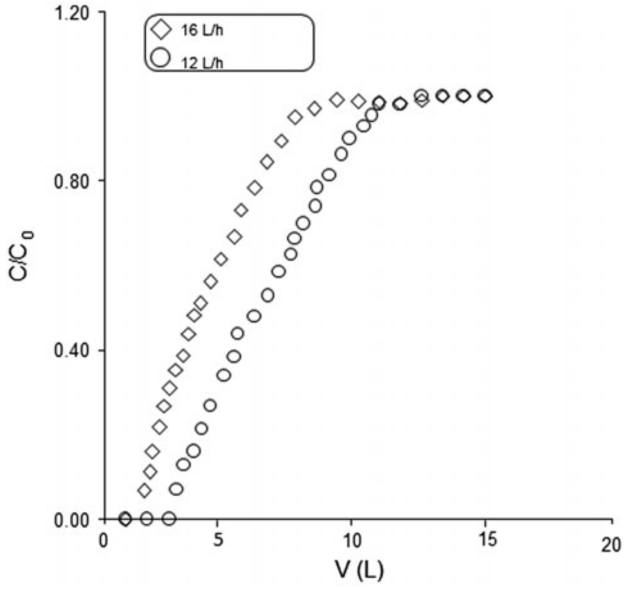


Fig. 3. Breakthrough curve of SDBS adsorption on GAC.

3.3. Hybrid UF membrane/GAC filter adsorption process

The concentration polarization and fouling by organic substances affect the efficiencies of the UF membrane processes. The effects of concentration polarization are usually observed in a very short time at the start of the process, and after this, flux remains constant with the passage of time while a gradual reduction in permeate flux is observed in long-term applications due to fouling. Fouling may be due to cake formation over the membrane surface, pore blocking, and adsorption [20,21].

In order to determine the effects of GAC filter on fouling, the pilot plant was connected with GAC filter in series and membrane parameters such as permeate flux, percent retention of the surfactants under study, and its effect on backwash time were determined.

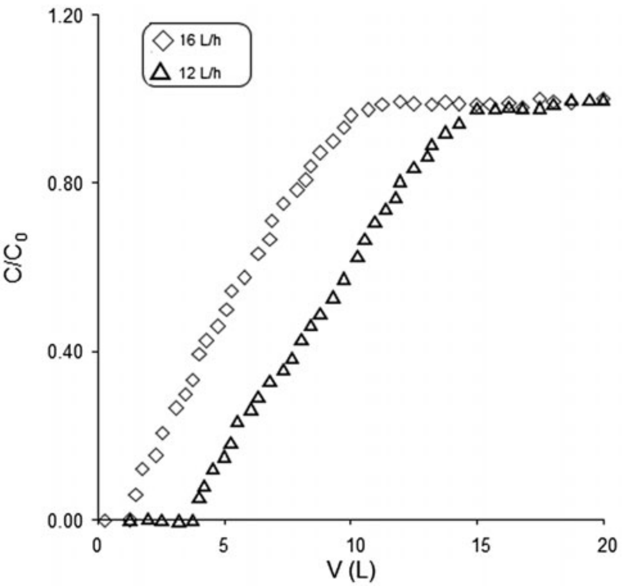


Fig. 4. Breakthrough curve of N-dodecylpyridinium chloride adsorption on GAC.

3.3.1. Retention of surfactants

The retention of organic substances in membrane process is usually expressed in terms of retention coefficient R and is expressed in percent. R is given by the following relation.

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

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

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, such as adsorption, concentration polarization, and fouling, are also important [21,22]. From Figs. 5 and 6, it is clear that the percent retention of the selected surfactants is higher for GAC than that of membrane only. The percent retention by membrane without the aid of adsorbent was higher for triton x-100 and SDBS while lowest for N-dodecylpyridinium chloride. As the membrane used in this study was hydrophobic one, while triton x-100 contains hydrophilic polyethylene oxide group that is why high percent retention was observed for this. In the presence of GAC, the percent retention increases which was due to high adsorptive powers of the adsorbent. PAC has been used by many authors for foul controlling in the membrane processes. However, a decline in flux due to cake formation on membrane surface has been observed by authors [20–22]. The problems associated with the use of PAC were not observed for GAC, as GAC particles are larger than PAC and thus were kept from flowing into membrane system.

3.3.2. Effects of adsorbents on permeate flux

The decline in the permeate flux in the initial stages for water was due to the intrinsic membrane resistance and interaction of the ions present in distilled water with membrane. The flow rate then reached a steady state and was no longer affected within the experimental cycle. The molecular weights of these surfactants under study were smaller than the molecular weight cut-off (MWCO) of the membrane. These substances were expected to pass freely from the membrane and allow the permeate concentration equal to that of the bulk concentration. However, despite low retention, flux reduction was observed for

Table 5
Parameters calculated from breakthrough curves

Parameter	Speed (L h^{-1})	Triton x-100	SDBS	N-dodecypyridinium chloride
V_i (L)[a]	12	4.1	3.0	4.0
	16	2.3	2.0	1.9
X_i (mg g^{-1})[b]	12	18.45	13.5	18.0
	16	10.35	9.0	8.55
V_f (L)[c]	12	12.0	11.0	15.0
	16	9.0	8.0	8.5
X_f (mg g^{-1})[d]	12	57.0	78.25	71.25
	16	42.75	48.0	44.38

[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^{-1}).
[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^{-1}) adsorbed per g of adsorbent at the close point.

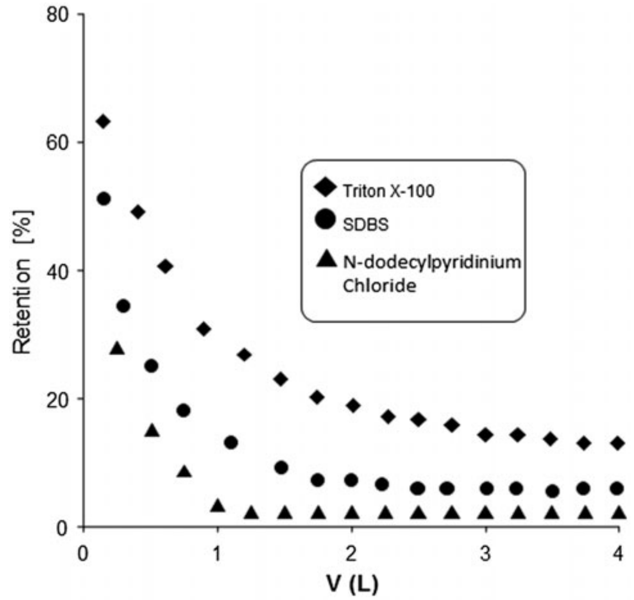


Fig. 5. Percent retention of triton x-100, SDBS, and N-dodecylpyridinium chloride by UF membrane.

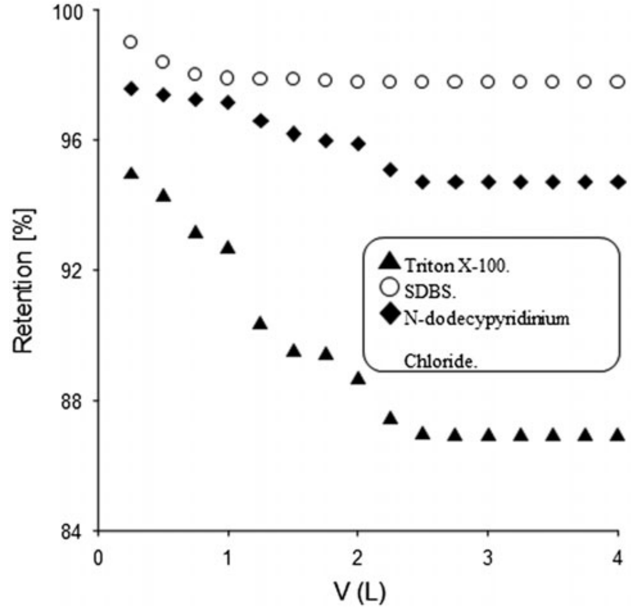


Fig. 6. Percent retention of triton x-100, SDBS, and N-dodecylpyridinium chloride by GAC/UF membrane hybrid system.

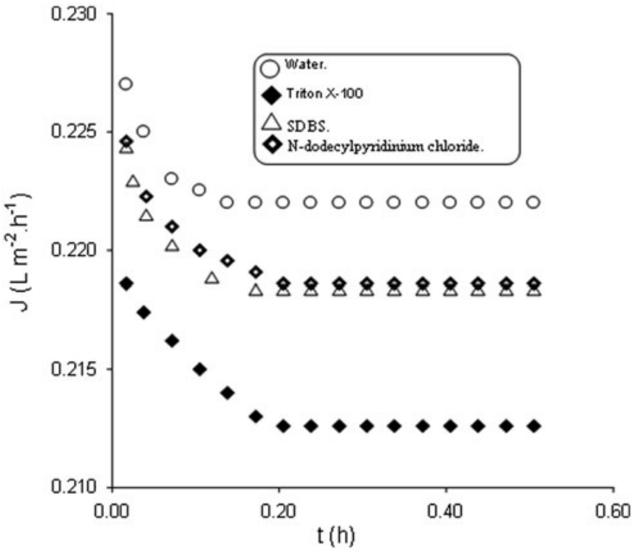


Fig. 7. Effects of triton X-100, SDBS, and N-dodecylpyridinium chloride on UF membrane permeate flux.

these substances. The reduction in permeate flux was high for cationic surfactant, N-dodecylpyridinium chloride as compared to anionic surfactant, SDBS. For nonionic surfactant triton x-100, the reduction in permeate flux was minimum. This was due to high adsorption of N-dodecylpyridinium chloride and SDBS on membrane surface as compared to triton x-100. The adsorption of these substances over membranes partially blocks the pores of membrane resulting in low fluxes.

The influence of GAC on permeate fluxes of triton x-100, SDBS, and N-dodecylpyridinium chloride is shown in Figs. 7 and 8. Improved fluxes were observed for the selected surfactants in the presences of GAC. The differences in permeate fluxes were due to different adsorption capacities of the adsorbents for the foulants.

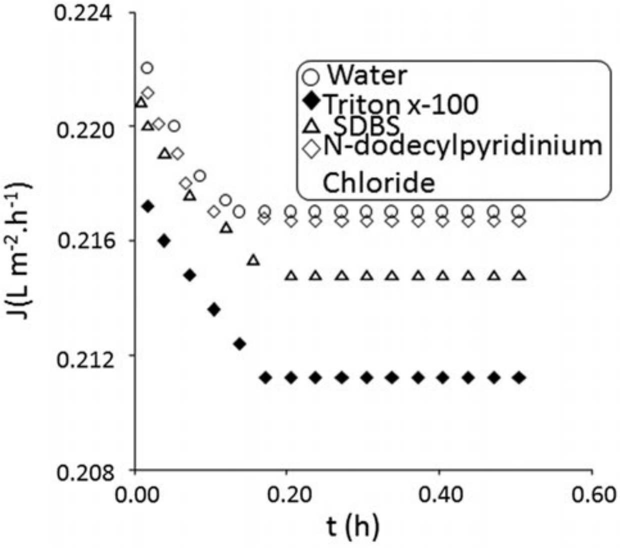


Fig. 8. Effects of triton X-100, SDBS, and N-dodecylpyridinium chloride on GAC/UF membrane hybrid system permeate flux.

3.3.3. Effect of adsorbents on backwash times

After each 30-min cycle, cleaning with deionized distilled water was practiced. For surfactants solutions, the backwash time was high as compared to GAC/UF hybrid process. This was due to the high removal capacity of GAC that kept these foulants from being entering into membrane system. In our previous study for PAC, blackening of the pipes and flow meter of the membrane system have been observed [23]. From an economical point of view, 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.

4. Conclusions

Improved fluxes and percent retention were obtained for GAC. The secondary problems associated with PAC, cake formation, and blackening of pipes were not observed for GAC. Thus, GAC can be used as pretreatment in UF systems since it has high adsorption capacity and can be kept the foulants from flowing with effluents into the membrane system due to its large 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 does not cause blackening of the pipes.

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