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Application of integrated microfiltration and PAC adsorption for the removal of humic acid as a pretreatment in seawater desalination

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ABSTRACT

This study evaluated the effectiveness of powdered activated carbon (PAC) in removing organic matter under saline condition with the application of microfiltration (MF). Adsorption isotherm test was conducted to compare the adsorptive potential of humic acid (HA) on PAC between reconstituted seawater and aqueous solution. Subsequently, two MF systems were run in parallel to investigate the effect of PAC and filtration process on HA removal. Various parameters such as turbidity, SDI_{15}, UV_{254}, dissolved organic carbon and transmembrane pressure were monitored within one-month operation. The batch experiment results showed that an increase in PAC concentration enhanced the adsorption potential of HA on activated carbon. Same trend was observed in the continuous experiment conducted with microfiltration. Percent removal of organics reached 60% for the control system while 90% for MF-PAC system. Lower SDI_{15} and turbidity values were obtained in the system with PAC. Adsorptive capacity of PAC with organic matter was higher in saline solution due to the ionic strength exhibited by salts present in seawater, and removal of humic acid in seawater was increased by the addition of activated carbon. Consequently, membrane filtration coupled with adsorption enhanced the removal of organic matter in reconstituted seawater producing better quality of effluent water.

Keywords: Adsorption; Desalination pretreatment; Humic acid; Microfiltration; Powdered activated carbon; Seawater

1. Introduction

Reverse osmosis was developed as a water treatment method and first arose as a technique of desalinating seawater. However, when the raw water is not properly treated, reverse osmosis is considered as a very energy intensive process to be used [1]. RO membranes can be deteriorated by natural organic matters present in seawater by accumulating foulants in the membrane surface, thus affecting the performance of RO process resulting to a decreased water flux and reduced ion rejection [2]. It is recommended that a pretreatment for seawater should first be performed through low pressure membrane processes before subjecting it in a water purification process [3]. But these membrane processes, such as microfiltration (MF) and ultrafiltration (UF), are not effective in removing dissolved and synthetic organic compounds [4]. Thus, addition of powdered activated carbon is suggested to enhance the removal of organic matter in seawater [5]. Powdered activated carbon (PAC) is commonly used in removing organic contaminants such as phenolic compounds and widely applied in water purification and wastewater treatment processes [6]. Several studies

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were conducted to further understand the mechanism of adsorption that occurs between activated carbon and organic matter [7–8], and results showed that addition of activated carbon significantly enhanced the organic removal. Combination of membrane filtration and adsorption on activated carbon to reduce organic matter, such as humic acid (HA), was reported to increase the organic removal efficiency [9–10]. However, application of this system is limited for surface water treatment as well as for drinking water production. Therefore, a study on the effect of the integrated membrane filtration and PAC adsorption of organics in seawater is needed to be explored.

This study evaluated the effectiveness of PAC in removing organic matter under saline condition with the application of MF system. The adsorptive potential of humic acid on PAC was also investigated by conducting batch experiments and the data was interpreted using Freundlich isotherm.

2. Materials and methods

2.1. Preparation of humic acid stock solution

The solid humic acid stock solution was prepared by dissolving amount-unit humic acid (Fluka) in deionized water followed by heating at 80°C for 30 min to facilitate dissolution of HA. Then the solution was filtered in a polyphenyl sulfone magnetic filter funnel (Pall) using a microfiber filter (Whatman) with a mean pore size of 0.45 μm. The DOC of the stock solution was measured by Total Organic Carbon Analyzer (Shimadzu TOC–5000). It was reported that the alkaline degradation of HA occurs when the pH is greater than 8 [11], thus pH of the stock solution should be checked regularly.

2.2. Powdered activated carbon

The adsorbent used was Darco® KB-B activated carbon (Norit) purchased from Osung Envitech. The particle size ranges from 100–325 mesh with an approximate effective surface area of approximately 1500 m^2/g. The activate carbon was dried at 105°C for 1 h and cooled down at room temperature inside a dessicator [12].

2.3. Composition of reconstituted seawater

Reconstituted seawater was prepared based on the Standard Method [13]. The composition of the reconstituted seawater as well as the sequence of salt addition is enumerated in Table 1. Dissolution of each salt should be carefully monitored prior to the addition of next salt.

Table 1
Composition of reconstituted seawater

Compound in order of Addition	Final concentration (mg/l)
NaF	3
$SrCl_2 \cdot 6H_2O$	20
H_3BO_3	30
KBr	100
KCl	700
$CaCl_2 \cdot 2H_2O$	1470
Na_2SO_4	4000
$MgCl_2 \cdot 6H_2O$	10780
NaCl	23500
$Na_2SiO_3 \cdot 9H_2O$	20
Na_4EDTA	1
$NaHCO_3$	200

2.4. Experimental set-up

2.4.1. Batch test

Six beakers with a sample volume of 1000 ml each were used in the batch test. Two kinds of samples were analyzed: deionized water and Reconstituted seawater mixed with HA, with an initial HA concentration of 3 mg/l. PAC was added in each beaker at various dosages (0, 50, 100, 200, 500 and 1000 mg/l) and stirred for an hour. Samples were taken at different time intervals (5, 10, 15, 20, 30, 40, 50 and 60 min) and filtered using 0.45 μm PVDF syringe filter to separate the PAC from the sample liquid. These samples were then subejected to UV_{254} and DOC analyses, and the results were used in creating a Freundlich model for both seawater and aqueous samples. Comparison of the adsorptive potential of HA on PAC in seawater and aqueous solutions were assessed using the generated Freundlich isotherms.

2.4.2. Continuous experiment

Two MF systems were run in parallel to investigate the effect of PAC as well as the filtration process on HA removal. PVDF flat-sheet membrane with a mean pore size of 0.08 μm was used in the experiment. The reconstituted seawater was continuously fed to the reactors with an initial HA concentration of 3 mg/l. One reactor was initially dosed with 1 g/l PAC while the other served as a control. Level sensors were installed in both reactors and the aeration rate was set at 2 l/min. The flux was maintained at 0.5 m^3/m^2d with an intermittent suction of 9 min suction and 1 min pause. Summary of the operating conditions, membrane specifications and schematic diagram of the PAC-MF system are presented in Table 2, Table 3 and Fig. 1, respectively.

Table 2
Operating condition of PAC-MF System

Parameter	Target value
Influent flowrate (l/d)	15
Aeration intensity (l/min)	2
Initial PAC dosage (g/l)	1
Influent HA concentration (mg/l)	3
Flux (m/d)	0.5
Intermittent suction time: On/Off (min)	9/1

Table 3
Membrane specifications

Specification	Description
Material	PVDF
Filtration Flux	0.2~1.5 m/d
pH	5~10
Temperature	5~40°C
Scouring air	1~2l/min/element
Membrane Area	0.03 m^2
Dimension (mm)	130 W x 130 H x 7 T

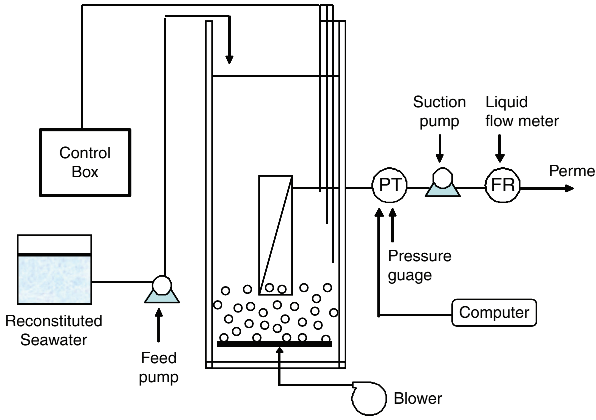

Fig. 1. Schematic diagram of the PAC-MF system.

2.5. Analytical methods

Various parameters such as turbidity, SDI_{15}, UV_{254}, dissolved organic carbon (DOC) and transmembrane pressure (TMP) were monitored within one-month operation. Turbidity was measured by HACH 2100N turbidimeter and SDI15 was analyzed by GE Osmonics auto SDI tester. Shimadzu UV spectrophotometer UV–1800 and TOC–5000 were used to measure UV_{254} and DOC concentration, respectively.

3. Results and discussion

3.1. Adsorption potential of HA on PAC under saline condition in a batch test experiment

The effect of humic acid adsorption was evaluated by conducting a batch experiment for both seawater and aqueous solutions at different PAC concentrations. It was observed that as the concentration of PAC increased, the adsorption potential of humic acid on activated carbon was enhanced, as seen in Figs. 2 and 3. Moreover, the rate of decrease in absorbance was greater in the reconstituted seawater compared to the aqueous solution. Aqueous solution approached an absorbance value of 0.08, while in seawater solution, the final absorbance was found to be negligible.

Removal rates of humic acid in deionized water and reconstituted seawater are plotted in Figs. 4 and 5, respectively. The rate of HA removal increased with the increased PAC concentration, and higher removal rate was observed in the reconstituted seawater. In addition, removal rate of HA in saline condition was found to be faster suggesting that some components of seawater influenced the adsorption mechanism of HA on PAC. Results showed that after 5 min, the percent HA removal in seawater was drastically increased to 78.7%, which is significantly higher as compared to the control with 36.6 %.

The results illustrated in Figs. 2 and 3 are based on the spectrophotometric analysis, while Figs. 4 and 5 are based on DOC analysis. The data gathered from both analyses followed a similar trend, which shows consistency on the results obtained. These graphs prove that either of the two analyses is a reliable method in determining the rate of decrease in humic acid concentration.

To further visualize the effect of water composition to the removal efficiency of HA, the removal rate at 1000 ppm PAC concentration was evaluated. As shown in

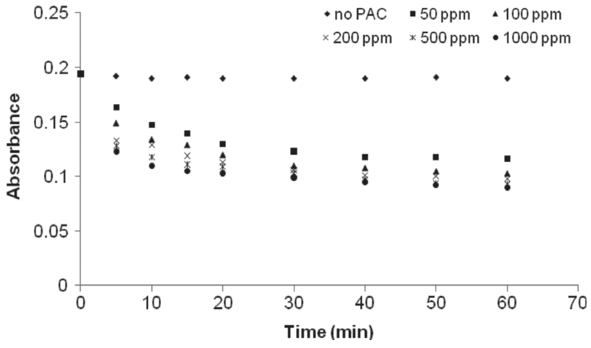

Fig. 2. Adsorption of humic acid at different PAC concentrations in an aqueous solution.

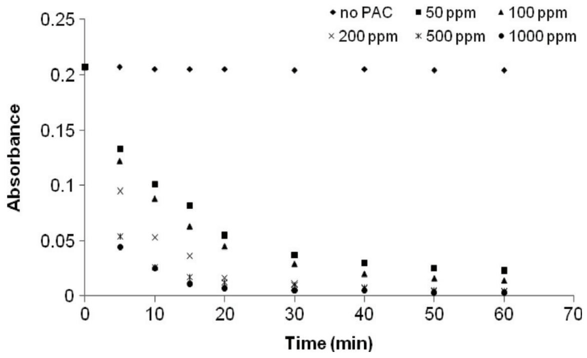

Fig. 3. Adsorption of humic acid at different PAC concentrations in a reconstituted seawater solution.

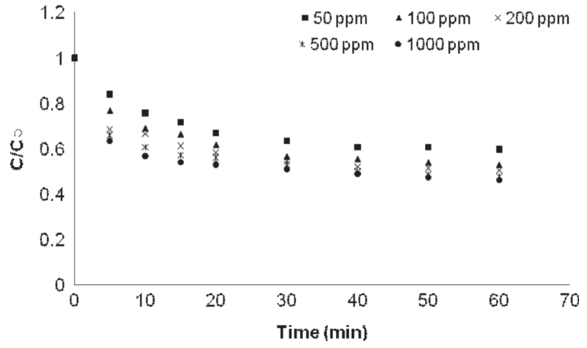

Fig. 4. Removal rate of HA in deionized water (control).

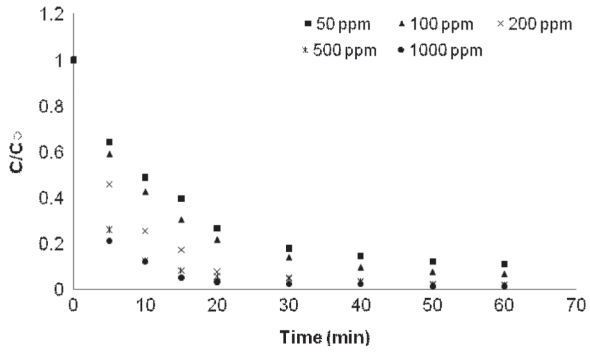

Fig. 5. Removal rate in reconstituted seawater.

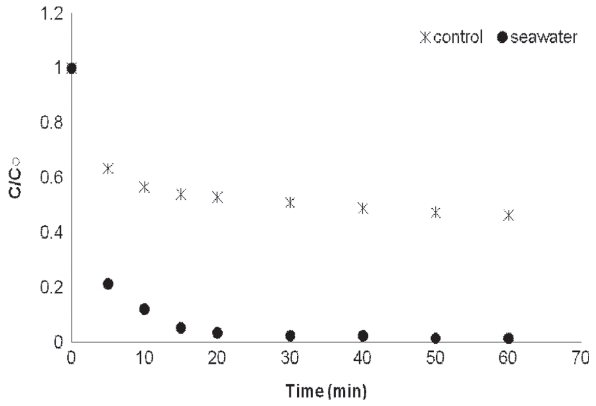

Fig. 6. Removal rate of humic acid at 1000 ppm PAC concentration.

Fig. 6, the rate of decrease in the concentration of HA in seawater is higher than the control, wherein the ratio of the initial and final HA concentrations approaches zero. The main reason is the effect of metal salts such as magnesium and calcium ions present in saline solutions. These salts interact with humic acids to form chelates, which could be explained by the characteristic of humic acid having a polymeric phenolic structure capable of forming complexes with divalent cations. Some of the functional groups that humic acids possess include carboxyl, aliphatic hydroxyl and phenolic hydroxyly [14]. It was reported that most organic ligands present in seawater may form moderately stable complexes through ion-exhange [2]. Hence, high reduction efficiency of humic acid could be obtained in reconstituted seawater solution. The lowest absorbance that could be obtained at different PAC concentrations was illustrated in Fig. 7. Increasing the amount of PAC decreases the final absorbance of the sample solution at equilibrium condition. PAC concentration of 1000 ppm recorded the largest decrease in absorbance as compared to the others. Thus, 1000 ppm PAC concentration was selected as the basis for the evaluation of the removal efficiency of HA.

Electrostatic interaction is also considered as one of the reasons for high removal rate of HA at saline condition. The elctronegativity of the carbon surface

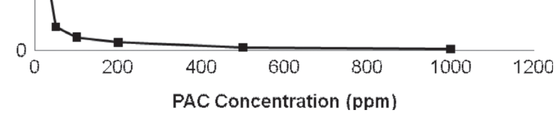

Fig. 7. Comparison of the absorbance between seawater and aqueous solutions at different PAC concentrations.

is considerably weak at high ionic strength solutions favoring the adsorption of humic-cation complex on the surface of PAC [15]. High concentration of ions in the solution decreases the boundaries of the electrical double layer around the carbon surface minimizing the distance between the HA-cation complexes and PAC. Reduction on the effect of electrostatic repulsion favored the van der Waals attractive forces to dominate which increases the tendency of interaction between PAC and organic complexes. In addition, reduced charge effects on humic acid molecules in saline solutions could also allow the molecules to reduce its size increasing the transport and adsorption in the PAC pores.

Fig. 8 shows the Freundlich model generated from the data gathered in the batch test experiments. Two isotherms were plotted to compare the Freundlich model linearity between reconstituted seawater and aqueous solutions. Adsorption by PAC was significantly enhanced by the presence of salt concentration, and a significant difference in HA adsorption between seawater and deionized water was observed. The linearity of the Freundlich model was decreased when salt concentration was present. The linearity of the control (deionized water added with humic acid) with a value of 0.95 was higher compared to the saline solution (R^2 = 0.93). This correlation shows that the salts present in seawater could affect and change the adsorption affinity of humic acid on PAC. Percent removal of humic acid was improved from 53% to 98% with the addition of PAC.

Comparison between reconstituted seawater and aqueous solutions for the amount of absorbance decrease per milligram of activated carbon at different PAC concentrations is presented in Table 4. Higher decrease in absorbance was observed in the reconstituted seawater solution, thus greater adsorptive capacity of activated carbon was obtained. As the concentration of PAC in the solution increased, the adsorptive capacity of activated carbon decreased. This was due to the higher available sites that the humic acid could be adsorbed, hence, aggregation or accumulation on the carbon surface was lesser.

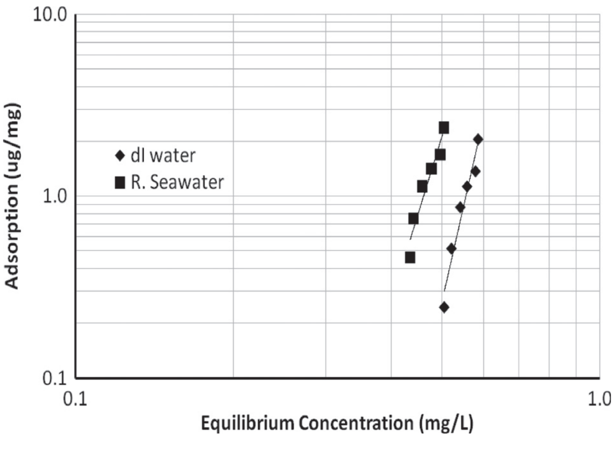

Fig. 8. Freundlich isotherm for the adsorption of HA on PAC in reconstituted seawater and aqueous solutions.

Table 4
Decrease in the absorbance of humic acid per milligram of PAC

PAC concentration (mg/l)	Deionized water	Reconstituted seawater
0	1.74E–01	1.94E–01
10	5.80E–03	1.00E–02
50	1.33E–03	3.50E–03
100	8.05E–04	1.83E–03
200	4.18E–04	9.35E–04
500	1.77E–04	3.82E–04
1000	9.20E–05	1.92E–04

3.2. Effect of PAC addition on HA removal in MF-PAC system

In the batch test experiment, it was found that the adsorption of humic acid on PAC was more efficient under saline condition. However, other organics and nutrients are still incorporated in real seawater sample. To further separate the other unwanted components present in seawater, the well known process of microfiltration was applied. Combining the filtration process with PAC adsorption could increase the effluent quality, and make the permeate more acceptable as a feed in reverse osmosis process for further water purification.

One of the parameters used to predict the extent of fouling that could on the membrane is by conducting an SDI_{15} analysis. Unlike turbidity which is concern to the amount of solids in a given sample, SDI_{15} determines the contaminants that could probably plug the membrane pores. As described in Figs. 9 and 10, lower SDI_{15} values were obtained in the system with PAC, in which the lowest percent plugging factor (PF) of 3% was obtained in MF-PAC system while the highest PF of 71% was attained by the system without PAC addition. Plugging factor was considered as one of the frequently used terms in measuring the amount of suspended solids present in a water sample. Percent PF can be calculated by dividing the measured value of SDI to the maximum value of SDI multiplied by 100, wherein high value of %PF indicates large portion of the membrane surface is plugged with particulates. Thus, MF-PAC system exhibited a more suitable environment for filtration, having a lower %PF values as compared to the system without PAC. Solid contaminants that are still present after filtration was determined by measuring the turbidity of the permeate. Increase in turbidity

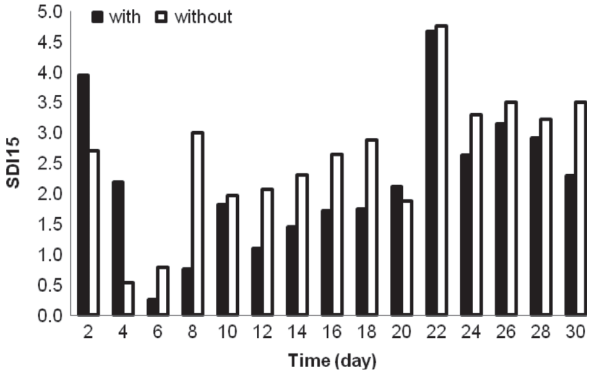

Fig. 9. SDI_{15} of the permeate generated from the system with and without PAC.

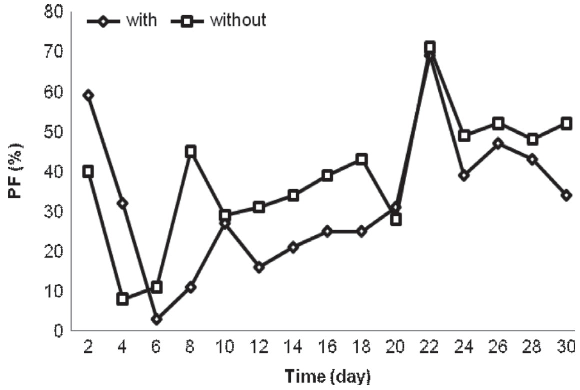

Fig. 10. Percent plugging factor of the permeate samples from the system with and without PAC.

for both systems were observed at the beginning of the operation as depicted in Fig. 11. However, higher peak was recorded in the system without PAC. After 10 d of operation, the difference between the two systems was observed to be almost constant, in which the system added with PAC has lower turbidity values. Contrary to the turbidity result, the difference between the UV_{254} values for both systems was constantly similar throughout the operation as illustrated in Fig. 12. Still, the system with PAC obtained the lower UV_{254} values which resulted to higher HA removal. The average percent removals for the system with and without PAC were 52% and 18%, respectively, on the basis of DOC analysis as described in Fig. 13. The values of DOC concentration at the system with PAC were consistently lower than the control throughout the operation. Percent removal of organics reached as high as 60% for the control system while 93% for MF-PAC system.

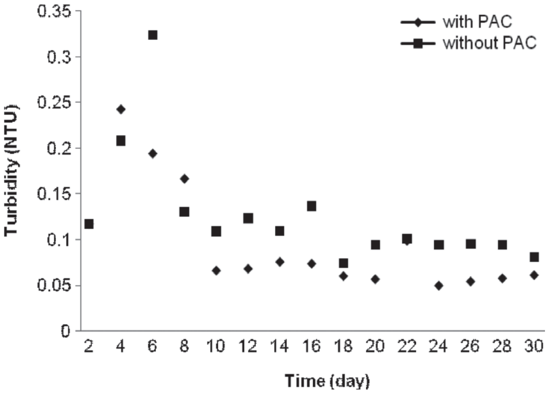

Fig. 11. Difference in the permeate turbidities of the control system and the system with PAC.

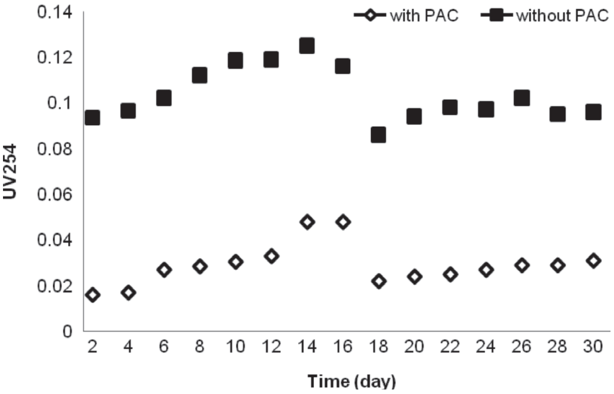

Fig. 12. Comparison between the UV_{254} values obtained from the control system and the system with PAC.

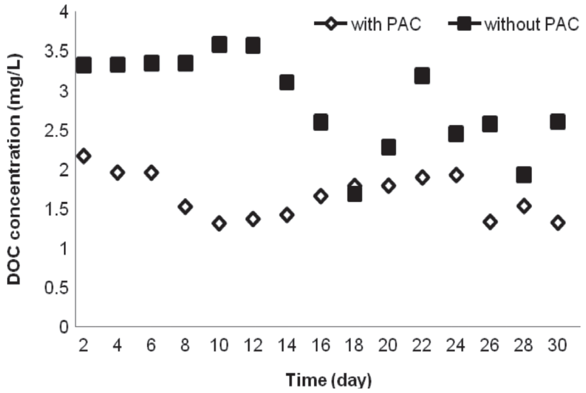

Fig. 13. DOC concentration of the permeate samples from the system with and without PAC.

Adsorption of organics on the membrane surface could result to permeability decline that could result in an irreversible fouling [16]. Therefore, investigation on the extent of contribution of humic acid to membrane fouling was considered. Pictures of the membranes immediately after the experiment and after performing physical washing were shown in Fig. 14. Severe fouling was observed in the membrane submerged in the system with PAC, however, after physical washing,

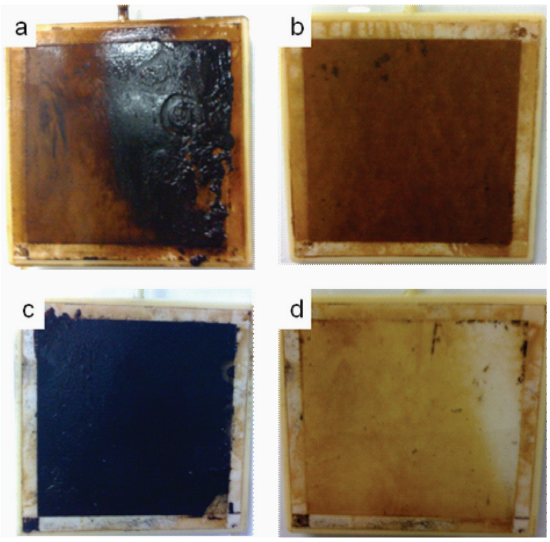

Fig. 14. MF membrane at the end of 30-d operation (a) without PAC – before washing; (b) without PAC – after washing; (c) with PAC – before washing; (d) with PAC – after washing.

it can be seen that the PAC adhered in the membrane was easily removed. This could be attributed to the difficulty in aeration experienced during the operation. Optimization of air supply could alleviate this problem. Also, no significant increase in TMP was observed with final TMP values of 5 and 2 kPa for control and MF-PAC systems, respectively. This could be attributed to the low operating flux used in this study. Experiments has being conducted at higher operating flux to further investigate the extent of membrane fouling caused by humic acid and other organics present in seawater.

4. Conclusions

Adsorptive capacity of PAC with organic matter was higher in saline solution due to the ionic strength exhibited by salts present in seawater. The rate of adsorption of humic acid was observed to be faster in saline solution, and the HA removal was enhanced by the addition of powdered activated carbon. Adsorption effiency of humic acid was significantly enhanced due to the reduced charge effects on humic molecules in high ionic strength solutions, which increased their transport and adsorption within the PAC pores. Membrane filtration coupled with adsorption enhanced the removal of humic acid in reconstituted seawater producing better effluent quality.

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