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Iron oxide nanoparticle-impregnated powder-activated carbon (IPAC) for NOM removal in MF membrane water treatment system

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ABSTRACT

A novel powder-activated carbon (PAC) by surface modification with iron oxide nanoparticles was applied to microfilter (MF) membrane system for stable operation and removal of natural organic matter (NOM) in water. Two types of PAC (wood-based and coal-based) were used for the preparation of the iron oxide nanoparticle-impregnated PAC (IPAC). The impregnation of the iron oxide nanoparticles played a role to increase the $\mathrm{pH_{PZC}}$ of the PACs which means that the IPAC has higher basicity and larger adsorption capacity than the virgin PAC. From the experimental results of size exclusion chromatography (SEC) and $\mathrm{SUVA_{254}}$, there was no specific selectivity in adsorption of NOM on the IPAC. The saturated magnetization value of the IPAC was in the range of 6.75–8.04 emu/g that was enough to separate the IPAC particle from aqueous solution by magnetic force. An IPAC column followed by MF membrane system was operated to investigate NOM removal and membrane fouling control. A magnetic ring on the column above the IPAC bed surface could effectively hold the overflowing discrete IPAC particles. The system performance was compared with other similar MF membrane systems (PAC column-MF, high concentration PAC-MF (HCPAC-MF),and single MF) in terms of trans-membrane pressure (TMP) increase and NOM removal. For a 30-day operation, TMP of the MF membrane system could be maintained stably at 13 kPa with the IPAC column pretreatment, while the TMP of other membrane systems increased to the operation limit (40 kPa). Dissolved organic compound (DOC) and $\mathrm{UV_{254}}$ removal by the IPAC-MF system were 85.3 and 79.6%, respectively. And the removal efficiency of turbidity was more than 80%. With similar removal efficiency of DOC and $\mathrm{UV_{254}}$, the IPAC-MF process showed much more stable operation for longer periods compared to the other hybrid MF membrane systems (HCPAC-MF and PAC column-MF).

Keywords: Adsorption; Iron oxide nanoparticle; Magnetization; Microfiltration membrane; Natural organic matter (NOM); Powder activated carbon (PAC)

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1. Introduction

Activated carbon adsorption is a common water treatment process for the removal of natural organic matter (NOM). Recently, granular activated carbon (GAC) has been widely used for advanced water treatment for safe drinking water supply. However, the GAC requires ozone pretreatment, because it has low capacities and slow kinetics of NOM adsorption. Powder activated carbon (PAC) is flexible and has excellent adsorption process in removing disinfection by-products (DBPs) precursor and taste/odor. In addition, PAC has faster adsorption rate than GAC. This advantage of PAC has led to the development of a hybrid PAC/MF process for water treatment. A high concentration PAC/MF (HCPAC/MF) process has shown an excellent organic removal from water and/or secondary effluent of wastewater [1]. However, the high concentration PAC resulted in severe filtration resistance and then a rapid increase in trans-membrane pressure (TMP). Seo et al. revealed that the major resistance was caused by bacterial growth on PAC, PAC cake, and gel layer form on the membrane surface [2]. Therefore, some functional characteristics of PAC are required for more stable and enhanced operation of the hybrid process, such as, self aggregation and catalytic reaction of the PAC for easy separation and regeneration. Iron oxide has adsorption ability of humic-like substance in natural water [3,4]. Especially, the iron oxide nanoparticle has extremely large specific surface area and so high reactivity, which is advantageous for various applications. Self-aggregation and catalytic reaction with oxidants are additional characteristics beside the adsorption ability [5]. An idea could be raised that, if PAC particle is combined with the iron oxide nanoparticles, it may have certain properties of self-aggregation and catalytic reaction with oxidants as well as enhanced adsorption. In this study, a laboratory-scale experiment was conducted to synthesize the iron oxide nanoparticles on PAC surface and to evaluate its ability for NOM adsorption. The IPAC contact column was combined to MF membrane system to identify fouling control of the membrane as well as NOM removal.

2. Materials and method

2.1. Preparation of IPAC

Preparation of the IPAC followed the procedure suggested by Seo et al. [6]. Two types of PAC were used in the experiment, SAC (wood-based) and MAC (coal-based). First the PACs were treated by heat at 650 or 900˚C for 1 h under N_2. Heat-treated samples were labeled with codes of SAC650, SAC900, MAC650, and MAC900, respectively. The PAC surface was synthesized with iron oxide nanoparticles by the heat treatment at the same condition. The synthesized PACs were labeled with codes of SAC-M650, SAC-M900, MAC-M650, and MAC-M900.

2.2. Characteristics of the IPAC

Various instrumental analyses were employed to characterize the physical and chemical properties of the virgin and modified activated carbons. Physicochemical properties were determined by scanning electron microscopy–energy dispersive X-ray (SEM–EDX), BET surface area, apparent density, Fe elution, pore size distribution (PSD), magnetic property, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and pH of point of zero charge.

2.3. Adsorption isotherm tests

In order to evaluate the adsorption capacity of the IPAC, isotherm experiments were carried out for NOM purchased from International Humic Substances Society (IHSS). Adsorption kinetic experiments in batch reactors were performed with constant initial NOM concentrations and variable concentrations of the IPACs at the same pH, mixing condition, and temperature. The concentration of the IPACs ranged from 0.1 to 0.5 g/L, while initial NOM concentration was kept at 10 mg/L for all the kinetic experiments. Ionic strength was controlled using 0.01 M of NaCl. All experiments were carried out at 20˚C and 200 rpm in a shaking incubator for 24 h.

2.4. Analysis of NOM

Specific ultraviolet absorbance ($SUVA_{254}$) and size exclusion chromatography (SEC) were used in this study. $SUVA_{254}$ is used as an indicator for the aromatic character of the organic matter. A high $SUVA_{254}$ value (i.e. >4 L/mg-m) indicates hydrophobic nature [7]. The aqueous NOM analysis was carried out using spectrophotometric method (UV–vis spectrophotometer, optizen 2120, Ducksan macasys) and TOC analyzer (TOC-5000A, Shimadzu). Molecular weight (MW) distribution of the samples was measured by high performance size exclusion chromatography (HP-SEC; Shimadzu RF 10A XL) with a silica column (a WATERS Protein Pak 125) and a UV detector set at 254 nm wavelength.

2.5. Experimental apparatus

IPAC (MAC-M900) was applied to MF membrane system for NOM removal and stable operation of the system. Fig. 1 is the experimental apparatus of up flow cylindrical IPAC column (1L, Φ32 mmXH1240 mm) and MF membrane water treatment system. To prevent the overflow of IPAC particles, a magnetic ring was installed on top of the column as shown in Fig. 1(a). IPAC concentration in the column was 20 g/L and the up flow rate was 63 m/d at the rising edge of a layer of PAC, which provided a contact time of 29 min. In order to examine the performance of the IPAC-MF system, various types of PAC-combined MF system (PAC column-MF, HCPAC-MF, single MF as a control) were operated simultaneously as shown in Fig. 1(b). The MF membrane flux was set at 1 m/d without backwash and TMP variation was observed during the operation period at an upper limit of 40 kPa. Poly sulfone hollow fiber MF membrane was used for the experiment. The specification is shown in Table 1.

Raw water was taken from the sedimentation basin effluent of B water treatment plant in Changwon, Korea. Removal of NOM was monitored in terms of dissolved organic compound (DOC) and UV_{254}. Turbidity removal was also observed. Table 2 shows the raw water quality and Fig. 2 shows MW distribution of the raw water analyzed by HPLC-SEC with a UV detector. The NOM in the water is mostly humic acid (MW 1,000–2,000 Da) and fulvic acid (MW 350–1,000 Da) with a fraction of 62 and 33%, respectively.

Table 1
Membrane characteristics

Module type	Material	Area	Pore size
Hollow fiber MF (microfilter)	PS (poly sulfone)	0.04 m^2	0.05 µm

Table 2
Properties of the raw water quality

		Turbidity (NTU)	DOC (mg/L)	UV_{254} (cm^{-1})
Raw water	Max.	1.60	2.541	0.042
	Min.	0.15	0.506	0.017
	Ave.	0.68	1.678	0.029

3. Results and discussion

3.1. Characteristic analysis of IPAC

3.1.1. Surface property

Fig. 3 shows SEM observation of the PAC surface synthesized with the iron oxide nanoparticles, showing that the nano-sized particles are not distributed evenly on the activated carbon surface. Nevertheless, PAC and the nano-sized particles are well coated in FTIR analysis as shown in Fig. 4. The magnetite in the figure is identified by a peak in XRD analysis, which corresponds to standard magnetite (Fe_2O_4) crystal structure data (Joint Committee for Powder Diffraction Standards Cards No. 19-0629).

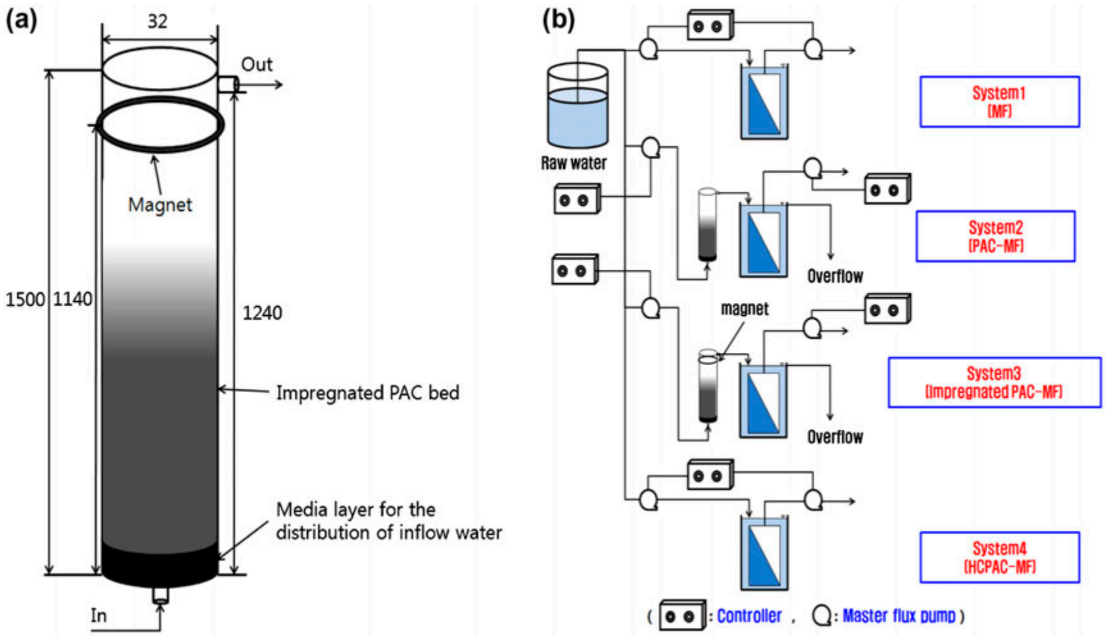


Fig. 1. Experimental apparatus of IPAC column (a) and MF membrane system (b).

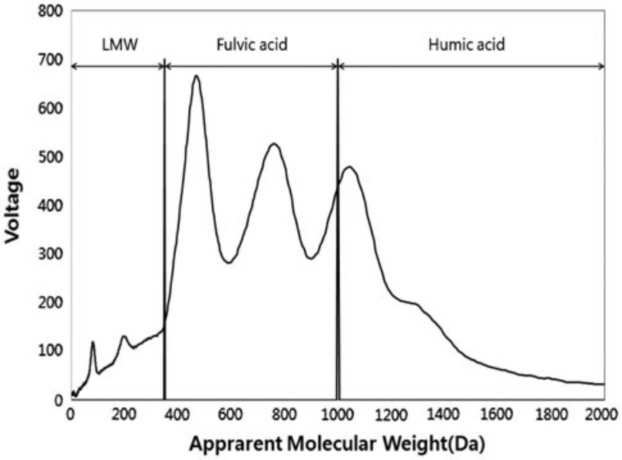


Fig. 2. MW distribution of NOM in the raw water.

It was observed that the impregnation of iron oxide nanoparticle decreases the surface area and pore volume of the PACs as shown in Table 3. Pore volume of the IPAC was higher at 900˚C than at 650˚C. The saturation magnetization of the IPAC was in the range of 6.75–8.04emu/g. It means that, it is possible to separate the IPAC in aqueous solution using magnetic separation technology. The impregnation of the nanoparticle played a role to increase the pH_{PZC} of the PACs. This result implies that the IPAC has higher basicity and adsorption capacity than virgin PAC.

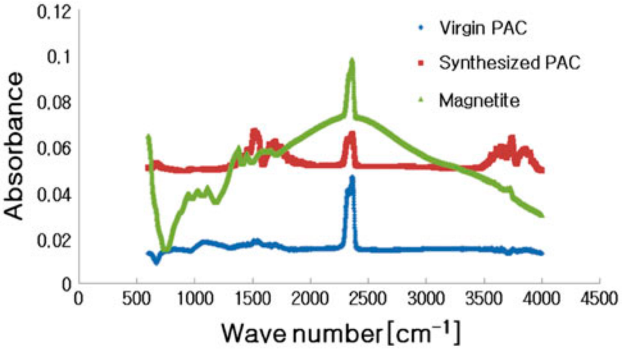
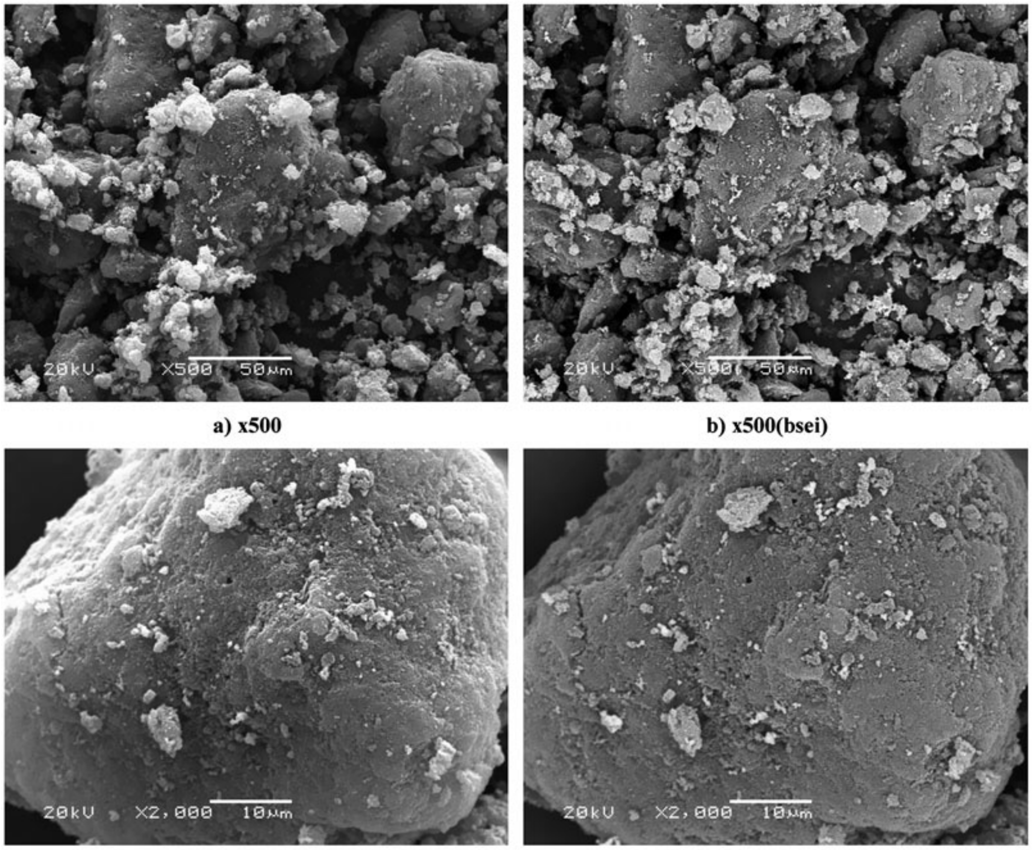


Fig. 4. FT-IR graph of iron oxide (magnetite), virgin PAC and the IPAC (MAC-M900).



a) x500

b) x500(bsei)

c) x2000

d) x2000(bsei)

Fig. 3. SEM image of nano-sized iron oxide-coated PAC (MAC-M900).

Table 3
Physical characteristics of IPAC

	BET surface area (m^2/g)	Micro pore volume (cm^3/g)	pH_{PZC}	Fe elution (mg/L)
SAC	917.19	0.2107	3.9	0.000
SAC900	959.01	0.2203	10.4	–
SAC-M900	744.57	0.1701	8.9	0.000
MAC	1206.89	0.2772	6.2	0.000
MAC900	1238.62	0.2845	7.7	–
MAC-M900	835.40	0.1919	9.3	0.000

3.1.2. Adsorption isotherm test result

Adsorption isotherm curves of NOM are shown in Fig. 5 for virgin and modified PACs. Freundlich model was applied in the analysis. From Fig. 1, the thermal treatment at 900℃ could reduce the adsorption capacity of SAC group (wood-based) by changing SAC structure, such as decrease in surface area, pore volume, and change in pore size distribution [8], whereas there is no significant effect found in MAC group (coal-based).

The iron oxide nanoparticle synthesized PACs (SAC-M650, SAC-M900, MAC-M650 and MAC-M900) have lower adsorption capacity than the only heat-treated ones (SAC650, SAC900, MAC650 and MAC900). Deposition of the nanoparticles on PAC might reduce the surface area of the PAC. Table 4 lists the results of the calculated isotherm constants of Freundlich equation, where K implies adsorption capacity and $1/n$ is the heterogeneity factor [7,9]. It was obvious that the IPACs have higher adsorption affinity and capacity than the virgin PAC from the higher K values. The value of $1/n$ is less than 1 means a favorable adsorbent [7]. The SAC650 was the best at this point in SAC group PACs. In MAC group, heat treatment at 650 and 900℃ enhanced the adsorption characteristics. This was obviously shown in MAC650 and MAC900. For the magnetic nanoparticle-synthetized PACs, only MAC-M900 was suitable for the adsorption of the NOM.

Table 4
Freundlich parameters of the virgin and modified PACs

SAC group	$1/n$	K	MAC group	$1/n$	K
SAC	1.73	1.62	MAC	0.94	13.19
SAC650	0.72	15.16	MAC650	0.45	34.65
SAC900	1.49	3.00	MAC900	0.53	33.38
SAC-M650	2.63	1.57	MAC-M650	1.81	6.60
SAC-M900	3.18	0.49	MAC-M900	0.87	19.36

3.1.3. Specific NOM adsorption analysis

Adsorption characteristics of the PACs were analyzed on the NOM using $SUVA_{254}$ and SEC. Fig. 6 shows time course of DOC (Fig. 6(a)) and UV_{254} (Fig. 6 (b)) adsorption for the virgin and surface-modified PACs. Using those adsorption results, the value of $SUVA_{254}$ could be calculated, which appears a representative aromatic property of the NOM and is delivered from the ratio between UV_{254} and DOC. The calculated $SUVA_{254}$ values are shown in Table 5.

$SUVA_{254}$ above 4L/mg-m is defined as hydrophobic, means that larger MW organics are dominant in NOM substances [10]. In the adsorption test, the value of $SUVA_{254}$ was not changed much for the SAC group PACs even after the surface modification, while the

Table 5
$SUVA_{254}$ of virgin and IPACs

SAC	SAC650	SAC900	SAC-M650	SAC-M900
4.58	5.48	3.86	5.80	3.75
MAC	MAC650	MAC900	MAC-M650	MAC-M900
3.83	12.85	9.97	7.47	8.04

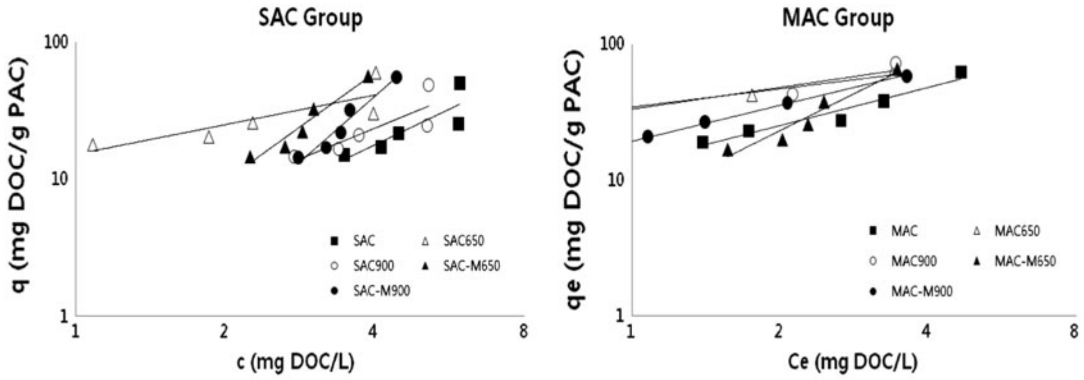


Fig. 5. Adsorption isotherm curves of the virgin and modified PACs.

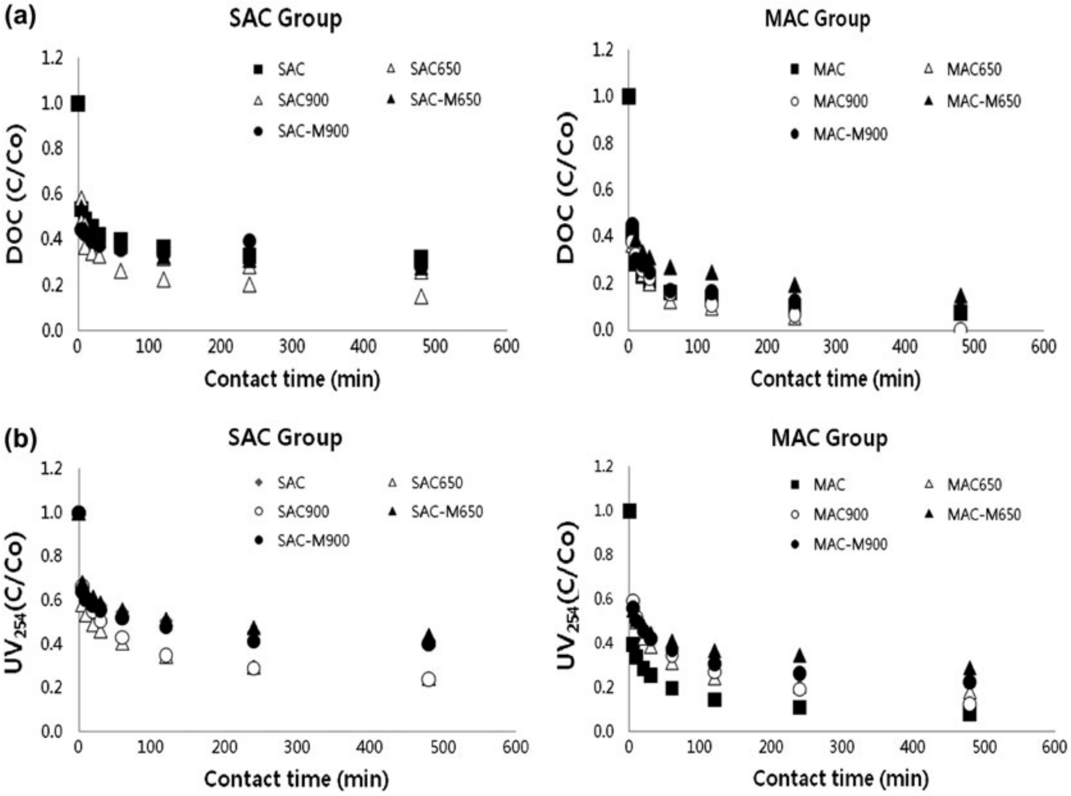


Fig. 6. Adsorption of NOM by PACs: (a) DOC results and (b) UV_{254} results.

value increased significantly for MAC group PACs, of which adsorption of DOC is much higher than UV_{254}. However, it is interesting that the adsorption of DOC remained high by the surface modified MAC (MAC-M650 and MAC-M900).

SEC could reveal the adsorption ability of the PACs as shown in Fig. 7. The SEC was obtained for raw NOM solution at a concentration level of 10 mg DOC/L and then after PAC adsorption. MW distribution of raw NOM solution is in the range 500–6,000 Da and that is removed mostly after PAC adsorption. Especially, it is encouraging that the IPACs could remove most of all MW organics without any specific selectivity, only virgin SAC showed less adsorption at the MW around 2,000 Da.

3.2. Effect of IPAC on MF membrane performance

3.2.1. TMP variation

IPAC column-MF systems were operated to compare with various MF systems (PAC-MF, HCPAC-MF, and single MF system). IPAC of MAC-M900 was selected for the experiment, since it has better adsorption ability than others. TMP variation of the systems is shown in Fig. 8(a) for initial 24hour filtration. The operation of system 4 (HCPAC-MF) resulted in sharp

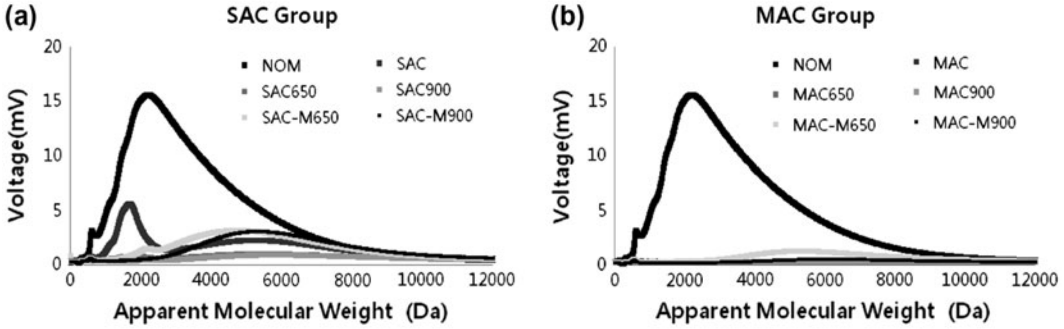


Fig. 7. SEC of the NOM solution (10mgDOC/L) and solution after adsorption by various PACs.

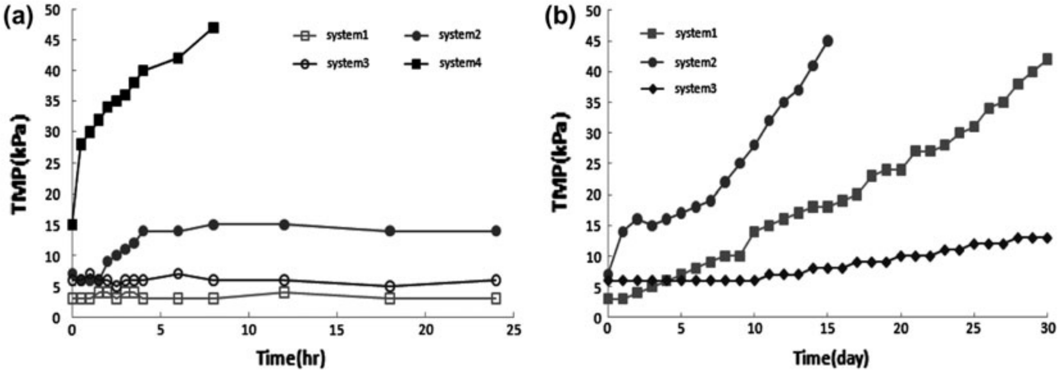


Fig. 8. TMP variation of MF membrane in each system at flux 1 m/day (a: for 24 h, b: for 30 days).

increase of TMP to the limit pressure (40 kPa) in 8 h, while the other systems kept a stable TMP. From the TMP observation for a 30-day, operation as shown in Fig. 8(b), the TMP of system 1 exceeded the operation limit of 40 kPa in 29 days. While, it reached to the limit in 15 days for the system 2, since PAC particles overflowed from the column attached on the membrane surface and caused the cake resistance. However, the TMP of system 3 was maintained at 15 kPa after the operation period. From the results above, it clearly appears that the IPAC column has two effective functions to keep the IPAC contact bed for NOM removal and keeping the particles from over flowing to the MF membrane separation reactor.

3.2.2. Water quality monitoring

Fig. 9 shows variation of filtrate turbidity of the hybrid MF systems. Average turbidity 0.68NTU of the raw water reduced to 0.11NTU in the filtrate of the system 1, 0.12NTU for the system 2, and 0.013NTU for the system 3. The removal efficiency in all the systems was more than 80%. System 3 showed the highest removal among them which means the IPAC contact bed could catch some part of the turbidity too.

Fig. 10 shows daily variation of DOC and UV_{254} removal by the three systems (MF, PAC column-MF, and IPAC column-MF). The DOC was hardly removed by the system 1 showing 7.4% removal. This is obvious that DOC is not rejected by the MF membrane. On the other hand, system 2 and 3 showed the removal efficiency 90.7 and 85.3%, respectively. DOC removal efficiency by the system 3 was comparable to HCPAC-MF (78–97%) and rather higher than the result (80.2 ± 8.6%) of PAC-MF system [11]. The removal of UV_{254} was also similar to the DOC removal.

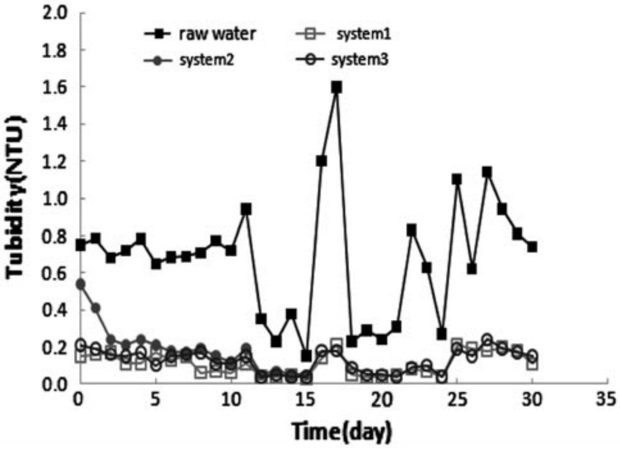


Fig. 9. Daily observation of turbidity removal by the systems.

The removal of DOC and UV_{254} in system 3 is shown in Fig. 11. The DOC was removed in IPAC contact column mostly showing 82.9% in the column and another 2.4% by MF membrane. Most of UV_{254} was also removed in IPAC column showing 75.5% removal and further removal of 4.0% by membrane filtration. Consequently, the IPAC column has a function of excellent pretreatment for the following MF membrane operation. The IPAC adsorbs NOM mostly and the IPAC particles are also trapped in the column, resulting less fouling problems in membrane filtration. If some oxidation process is combined with this column, the IPAC could be regenerated in the column. And, so there is a makeup of new IPAC which is the amount of loss during the oxidation.

4. Conclusions

The iron oxide nanoparticle impregnated PAC (IPAC) showed a high potential to remove NOM by

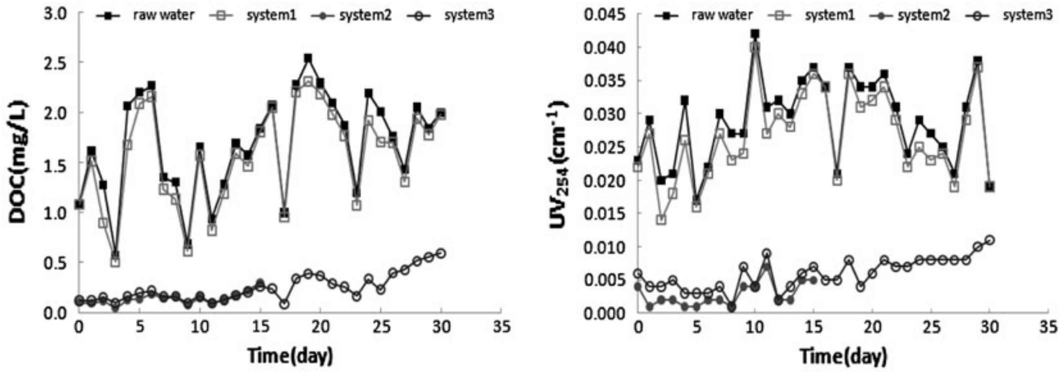


Fig. 10. Daily observation of DOC and UV_{254} removal by the three systems.

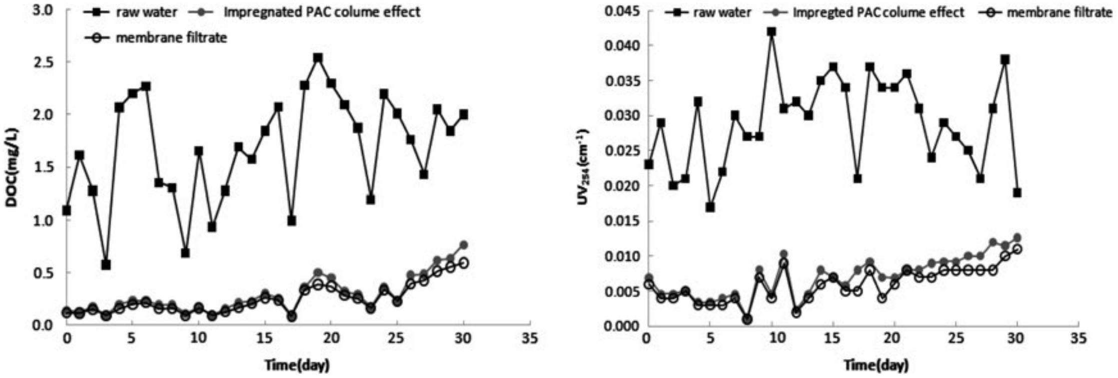


Fig. 11. Daily observation of DOC and UV_{254} removal in the system 3.

hybridizing with MF membrane system. The following results were deduced.

The impregnation of iron oxide nanoparticle on PAC increased pH_{PZC}, which leads to higher basicity and larger adsorption capacity of IPAC than the virgin one. The IPAC has no specific selectivity in adsorption of NOM as well. The saturated magnetization value of the IPAC was in the range of 6.75–8.04 emu/g that was enough to separate the IPAC particle from aqueous solution by magnetic force.

The performance of the IPAC column was excellent in combination with MF membrane. For a 30 day operation, TMP of the MF membrane system was maintained stably at 13 kPa with the IPAC column pretreatment. DOC and UV_{254} removal by the IPAC-MF system were 85.3 and 79.6%, respectively. And the removal efficiency of turbidity was more than 80%. With similar removal efficiency of DOC and UV_{254}, the IPAC-MF process showed much more stable operation for longer periods compared to the other MF membrane systems (HCPAC-MF and PAC-MF).

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