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Further treatment of coking wastewater treated in A_2O-MBR by the nanofiltration-powder activated carbon hybrid system

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ABSTRACT

In this study, further treatment of coking wastewater treated in anoxic-oxic-membrane bioreactor (A_2O-MBR) was investigated to meet the standards of the ministry by means of nanofiltration (NF) (with two different membranes and different pressures), microfiltration -powder activated carbon (MF-PAC) hybrid system and NF-PAC (with two different membranes and five different PAC concentrations) hybrid system. In addition to the parameters determined by the ministry, other parameters such as ammonium, thiocyanate (SCN^-), hydrogen cyanide (HCN), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), color were also examined to evaluate the flux performance and treatment efficiency of the hybrid processes. According to the results, chemical oxygen demand (COD) in the NF process, COD and total cyanide (T-CN) in the MF-PAC process could not meet the discharge standards. As for the NF-PAC hybrid system, XN45 membrane met the discharge standards in all parameters (COD = 96 ± 1.88 mg/L, T-CN =<0,02 mg/L, phenol =<0.05 mg/L), with a recovery rate of 78% at 0.5 g/L PAC concentration.

Key words: coking wastewater, further treatment, microfiltration, NF-PAC hybrid system, nanofiltration, powder activated carbon

HIGHLIGHTS

- The effluent coking wastewater of the A_2O-MBR system was treated by a membrane process.
- NF, MF-PAC, and NF-PAC hybrid systems were used.
- The flux performances of hybrid systems were investigated.
- The removal efficiencies of pollutants, such as ammonium and HCN, were determined.
- The hybrid system of XN45 with 0.5 g/L PAC achieved standards for all discharge parameters.

1. INTRODUCTION

The correlation between the increasing production in the iron and steel sector and its environmental footprint is unquestionable, particularly regarding the generation of coking wastewater. Coking wastewater occurs during the production of high-energy coal in coke production facilities in the iron and steel industries. The wastewater consists of water formed during heating the coal in an oxygen-free-inert environment, stripping the resulting ammonia, cooling, and washing the gases of the coke oven or processing and treating the coke by-products (Kwiecińska *et al.* 2017; Rai *et al.* 2021). As a result, coking wastewater contains toxic pollutants, such as thiocyanate, cyanide, oil-grease, phenol, etc., characterization of which also varies depending on the coal type used and operating conditions of coke ovens (Staib & Lant 2007). In addition, some substances in this wastewater have added value; crude tar, crude benzol, light oil, carbolic oil, tar dye, pressed naphthalene and ammonium sulfate, etc. (Pal & Kumar 2014; Bargiel *et al.* 2022).

For the treatment of this wastewater, physical treatment methods, such as adsorption (Gao *et al.* 2021), steam stripping (Minhalma & Norberta de Pinho 2004), coagulation and precipitation (Chen *et al.* 2009), membrane processes (Yin *et al.* 2011), biological processes such as sequencing batch reactor (Staib & Lant 2007), biofilm systems (Yuan *et al.* 2020), and, hybrid processes, such as anaerobic-anoxic–oxic-MBRs (Zhao *et al.* 2009) can be used. However, in view of effluent quality, cost, and applicability, a sustainable solution has not been found for all constitutes of the wastewater. Among these treatment methods although anoxic–oxic membrane bioreactor (A_2O-MBR) systems improve the effluent quality and energy consumption (Daigger *et al.* 2005), they cannot sufficiently meet the heavy and toxic pollutant load of coking wastewater (Tamang &

Paul 2021). For these wastewaters, discharge standards are limited in the Water Pollution Control Regulation published by the Ministry of Environment, Urbanization and Climate Change of the Republic of Türkiye, are shown in Table 1. T-CN, one of the important pollutants specified in these standards, refers to the sum of cyanide types such as free cyanide, decomposable weakly acidic cyanides, cyanide metal complexes, etc., found in water. Exposure to cyanide can occur directly through the skin or inhalation of dust and gas. Acute cyanide poisoning results in asphyxia and death due to blockage of oxygen transfer to the blood (EPA 2010). Also, phenol, another pollutant specified in the standards, poses serious health hazards. Phenol, being lipophilic, can enter the human and animal body through inhalation, digestion, and skin contact. It is also known that phenol affects the central nervous system and damages various organs such as the kidneys, liver, spleen, heart, and lungs (Mohammadi *et al.* 2015).

Nanofiltration (NF) membranes, which produce high-quality effluent than ultrafiltration (UF) membranes, provide some advantages such as higher flux and lower energy costs than reverse osmosis (RO) membranes (Acarer 2023). While neutral species are rejected according to their size, ions are rejected by the effects between ions, solution, and NF membrane, namely Donnan exclusion (ion type) and/or dielectric exclusion (ion presence). Also, a complex adsorption mechanism stemming from the membrane materials, pollutant species, and operating conditions can affect the flux and rejection efficiency of both neutral and ionic pollutants.

Although high solid–liquid separation efficiencies can be achieved by the use of MF and UF membranes in water treatment, dissolved organic and inorganic pollutants cannot be treated effectively. This deficiency can be eliminated using microfiltration-granular/powdered activated carbon (MF-G/PAC) hybrid systems. Additionally, compared to RO and NF having the ability to reject dissolved pollutants, MF-PAC requires less energy consumption and can offer similar organic removal efficiencies. In the MF/UF-PAC, there are two factors that affect concentration polarization resulting in flux reduction and membrane fouling (Ince *et al.* 2010) are the effective fluid dynamics and the PAC concentration. However, these hybrid systems may not provide the desired discharge values for some wastewater. In such cases, NF-PAC hybrid systems can be a solution, providing better water quality values. The effect of the PAC to be used in the hybrid system on the flux and rejection characterizing the membrane process by several types. PAC has a mechanical effect on the membrane surface as well as the adsorption of pollutants (Meier 2010; Echevarría *et al.* 2020). The efficiencies of flux and rejection of the hybrid system increase due to the rejected pollutants being transported back by a secondary flow resulting from particles moving from the membrane surface (boundary layer) to the bulk flow (Noordman *et al.* 2002). However, an increase in permeate flow with the decrease in rejection may be due to mechanical damage such as abrasion to the active layer of the membrane by PAC (Ziegmann *et al.* 2010). Furthermore, the formation of an additional particle layer on the membrane surface rejects pollutants as a second membrane, resulting in a decrease in flux and an increase in rejection (Meier 2010).

The main aim of this study is to investigate further treatability effluent of the A_2O-MBR treating coking wastewater to meet the 'Coking wastewater discharge limit values' enacted by the Ministry of Environment, Urbanization and Climate Change of the Republic of Türkiye. For this purpose, the wastewater treatment and flux performances of NF, MF-PAC, and NF-PAC hybrid systems were determined. In the literature, to the best of our knowledge, there is not any study investigating the performance of MF-PAC and NF-PAC hybrid systems for the treatability of effluent A_2O-MBR treating coking wastewater.

2. MATERIALS AND METHODS

Coking wastewater treated using an A_2O-MBR was further treated using three different systems, namely the NF unit, MF-PAC and NF-PAC hybrid system. The characterization of effluent from A_2O-MBR treating wastewater used in this study is given in Table 2.

Table 1 | Coking wastewater discharge standards in Türkiye (The Ministry of Environment Urbanization and Climate Change 2022)

Parameter	Unit	Composite sample (24 h)
Chemical oxygen demand (COD)	(mg/L)	100
Oil and grease (O&G)	(mg/L)	10
Total cyanide (T-CN)	(mg/L)	0.5
Phenol	(mg/L)	0.5
pH	–	6–9

Table 2 | Characterization of coking wastewater treated in A_2O-MBR

Parameter	Unit	Composite sample (24 h)
Chemical oxygen demand (COD)	(mg/L)	371.20 ($\pm$6)
Oil and grease	(mg/L)	10 < N.D.
Total cyanide (T-CN)	(mg/L)	1.20 ($\pm$0.03)
Phenol	(mg/L)	0.64 ($\pm$0.07)
pH	–	6.18
Ammonium (NH_4^+)	(mg/L)	31.48 ($\pm$0.9)
Hydrogen cyanide (HCN)	(mg/L)	0.20 ($\pm$0.02)
Thiocyanate (SCN^-)	(mg/L)	6.55 ($\pm$0.13)
Dissolved organic carbon (DOC)	(mg/L)	93.11 ($\pm$2.05)
Dissolved inorganic carbon (DIC)	(mg/L)	6.08 ($\pm$0.28)
Color	(CU)	1225.30 ($\pm$14)

N.D., not detected.

All the analytical methods, which were used to evaluate the removal efficiency of membrane and activated carbon, were implemented according to the Standard Methods for the Examination of Water and Wastewater. The COD and ammonium analyses were carried out according to the STM 5220 C and STM 4500-NH_3 methods, respectively (APHA 2005). The T-CN, SCN^- and CN^- concentrations were determined according to STM 4500-CN^--C, STM 4500-CN^-M, and STM 4500-CN^--D methods, respectively (APHA 2005). The phenol concentration was determined by high-performance liquid chromatography (HPLC) using a UV/VIS detector (Perkin Elmer) and C18 column, 150 × 4.60 mm–5 μm. A 30% methanol solution buffered with 1/1,000 acetic acid was used as the mobile phase at a flow rate of 0.8 mL/min. Oil grease concentration was measured according to the partial gravimetric method (STM 5520 B) (APHA 2005). DOC and DIC were analyzed using Shimadzu TOC-L. Color was measured with a spectrophotometer (Hach, dr6000) according to STM 2120-C (APHA 2005). All analyses were performed at least three times.

2.1. Materials

All chemicals used were at reagent grade and deionized water was produced from a Millipore Milli-Q unit. In all filtration studies, a Sterlitech brand HP4750 model dead-end membrane module made of stainless steel was used. In the experiments, two different NF membranes were used, which are NP010 and XN45 membranes (Microdyn Nadir, Trisep). The technical specifications of the NF membranes used are given in Table 3. MF-PAC experiments were carried out with a 0.2 μm MF membrane made of polypropylene (Microdyn-Nadir, MD 063 TP 2N). The effective surface area of all membranes used is 14.6 cm^2. The PAC of TechCarb PU800 was used and its technical specifications are given in Table 4. The precision balance used in all studies was AND brand ej–6100. The pressure required for all the experiments was met through the nitrogen tube.

2.2. NF experiments

The NF system was operated with 1,000 and 2,000 kPa pressures at room temperature. The membrane flux was recorded and calculated at regular intervals via a digital precision balance connected to the PC. The flux (J) was calculated by the following formula:

$$J = \frac{dV}{A \times dt} \tag{1}$$

where A is the effective area of the membrane (m^2), V is the volume of feed (L), and t is the recorded time (hour).

2.3. MF-PAC experiments

In MF-PAC hybrid experiments, before filtration, 250 mL of coking wastewater was treated the PAC in a beaker at 250 rpm, room temperature for 60 min. Nine different PAC concentrations (0.1, 0.2, 0.5, 1, 2, 4, 6, 8, and 10 g PAC/L) were applied in

Table 3 | NF membranes and some properties

	Membrane properties	
	NP010 (Microdyn Nadir)	**XN45 (Trisep)**
Membrane type	Flat sheet	Flat sheet
pH range	0–14	1–12
Flux (gfd-LMH)/psi	>200 LMH/4,000 kPa	35 gfd/110 kPa
Molecular weight cut-off value (MWCO)	1,000–1,400 Da	250–500 Da
Polymer	Polyethersulfone	Polypiperazine-amide
Max temperature (°C)	50	45
Max operating pressures	4,000 kPa (580 psi)	4,100 kPa (600 psi)
Surface charge	Negative	Negative
Zeta potential at		
pH 6–7–8	~−5/ ~ −11/ ~ −17	~−15/ ~ −22/ ~ −28
Average pore size (nm)	~2.66– ~ 2.84–1.49	3.5–4/2.64–3
Contact angle (°)	65.91–72	44–57–60
Roughness – R_q (nm)[a]	1.3	13.9–21

[a] R_q is referred to as the root-mean-square roughness.

Table 4 | Properties of the PAC

Specifications of TechCarb PU 800	
Raw materials	Coconut
Manufacturing process	Steam activation
Min. iodine number (mg/g)	700
Surface area (m^2/g)	1,050
Max. moisture content (%)	5
Max. ash content (%)	5
Apparent density (kg/m^3)	540
Particle size distribution (mesh)	<200
Dominant surface charge	Positive

this system. MF experiments were carried out at 175 kPa pressure. The permeate flow rate was monitored using a digital precision balance connected to a PC, and the J was calculated in Equation (1).

2.4. NF-PAC experiments

In NF-PAC hybrid experiments, before filtration, 250 mL of coking wastewater was treated by the PAC in a beaker at 250 rpm, room temperature for 60 min. Five different PAC concentrations (0.1, 0.2, 0.5, 1, and 2 g PAC/L) were tried for the NP010 membrane, as for XN45, three different PAC concentrations (0.1, 0.2, and 0.5 g/L) were tested. All NF filtrations, after contacting with PAC, were implemented under 1,000 kPa pressure. The permeate flow rate was monitored using a digital precision balance connected to a PC, and the J was calculated in Equation (1).

3. RESULTS AND DISCUSSION

3.1. Treatment studies by NF

The pollutant analysis of the filtrate of two different NF membranes (NP010, XN45) at two different operating pressures (1,000 and 2,000 kPa) are shown in Figure 1.

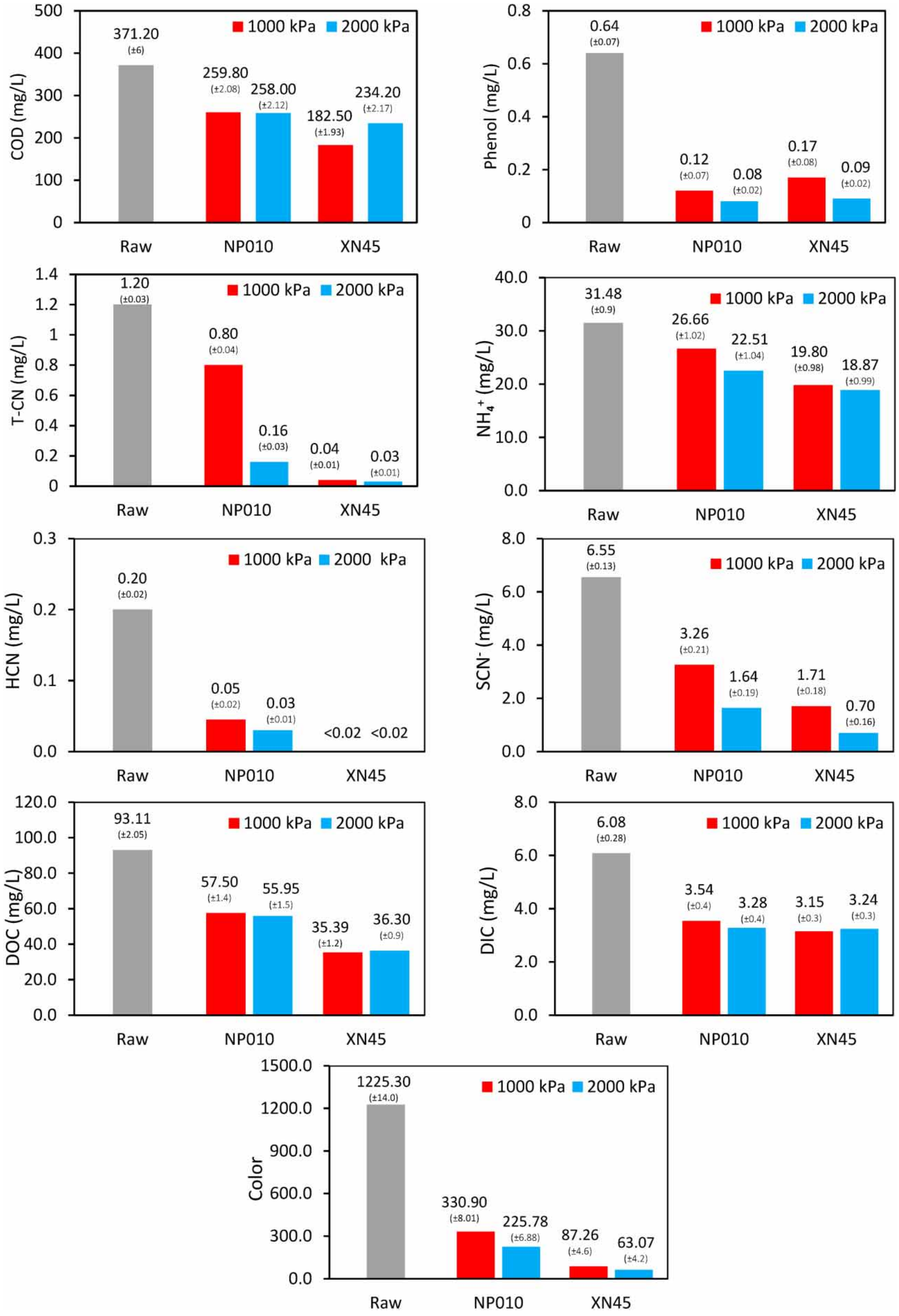

Figure 1 | The pollutant concentrations in effluents of the NF process.

NF membranes were effective in removing COD from coking wastewater treated. However, it is observed that an increase in operational pressure does not directly correlate with enhanced COD removal, as reported by other studies (Gozálvez-Zafrilla *et al.* 2008). In this study, the results show that COD removal was independent of the increase in pressure for the NP010 membrane and inversely proportional to the increase in pressure for the XN45 membrane. This is because, when some types of pollutants in the adsorptive force formed between the pollutants and the membrane cannot overcome the mechanical force of the increasing flux due to the effect of increasing pressure; so, instead of being adsorbed pollutants to the membrane, the pollutants are ensuring inhaled transport by the membrane and it is thought that it causes a decrease in removal efficiency (Hu *et al.* 2020). The XN45 membrane showed higher removal efficiency than the NP010 membrane. However, COD discharge standards were not reached in these experiments.

Both NF membranes, used this study, meet the phenol discharge values at two different pressures. Since phenol is a neutral pollutant, its removal is not affected by Donnan and Dielectric exclusion. The steric sieving force in the both NF membranes contributed sufficiently to the removal of phenol (Lorenc-Grabowska 2016). Considering both NF membranes, adsorption cannot adequately explain the removal efficiency of this pollutant. Because even when the pore size of the membranes was compared with the molecular size of phenol, the efficiency could not be explained clearly. These abnormal removal percentages of phenol may be due to its physical interaction with some organics and salts and forming lumps and masses close to the pore sizes of the NP010 membrane (Monruedee *et al.* 2012). From this aspect, it was thought to increase steric removal. In addition, although it is known that increasing pressure creates a narrower pore size (Wang & Chung 2005), we could not see an increase in the efficiency of other parameters due to steric elimination. This supports the thesis that phenol forms masses with larger size than pores. Similar removal efficiencies were seen in the other studies in the literature (Arsuaga *et al.* 2006; Bódalo *et al.* 2009).

It was reported in the literature that high removal efficiency of T-CN was obtained in the second and third stage NF processes (Jin *et al.* 2013). Yet, the results obtained in this study, except for the NP010 membrane operated at 1,000 kPa, met the discharge standards. Considering COD, all NF effluents could not be provide discharge standards.

Considering the pH of raw wastewater, the dominant species (>99%) of the total measured ammonia ($pK_a = 9.24$) was ammonium. Since this type was ionic, separation occurs by size elimination, electrical exclusion, and adsorption. When the pore diameters of the two membranes in the literature were compared, the NP010 membrane was expected to achieve higher efficiency. However, in the literature, although the ion diameter of the ammonium ion is 0.296 nm, its hydrated diameter is 0.662 nm (Volkov *et al.* 1997). This indicates that ammonium can pass through the pores and its possible removal depends on electrical balance and adsorption. The fact that cations have a higher energy barrier than anions during intrapore diffusion a little prevented them from moving through the membrane to the filtrate (Zhai *et al.* 2022). Considering that negatively charged NF membranes can not sufficiently remove +1 charged cations, the results are within the expected values. In literature RO and NF processes were tested with low MWCO values and at a similar pressure for synthetic water-NH_4^+ (31 mg/L) solution, synthetic water-mixed inorganic (Fe,SO_4, Ca, Zn, NH_3 (30 mg/L)) solution and real mine wastewater NH_4^+ (51.1 mg/L) at the end of which ammonium removal efficiency were 10–30%, 75–95%, and 55–65%, respectively (Awadalla *et al.* 1994). Another researcher reported high removal efficiency for ammonia removal from surface water with NF and RO (Koyuncu 2002). In the literature, it was reported that the presence of ammonia with some cyanide species reduced the removal efficiency of ammonia (Korzenowski *et al.* 2011).

Considering the pH of raw wastewater, the dominant type of free cyanide ($pK_a = 9.24$) (>99%) was HCN. Since HCN is not in ionic form, Donnan exclusion or dielectric exclusion cannot contribute to its removal. The diameter of the $H\text{-}C \equiv N$ ($rCH = 0.1064$ nm, $rCN = 0.1156$ nm) molecule is ~0.222 nm. Considering the average pore sizes in the two membranes, the possibility of steric sieving was very low, indicating that adsorption was the main mechanism for HCN. High removal of efficiency in this pollutant was reported for NF membranes at high pH (Kumar *et al.* 2011).

As to SCN^-, it has an ion diameter of 0.426 nm and a hydrated diameter of <1 nm (Mason *et al.* 2003). In the removal of SCN^- due to having a small diameter than the pore size of both NF membranes size elimination was not the determining mechanism in rejection. The surface of most commercial polyamide or polyether sulfone-based NF membranes is negatively charged above pH 3, and higher solution pH proportionally increases their negative charge. The XN45 membrane with higher zeta potential showed higher removal at the same pressure. The fact that the removal efficiency of the NP010 membrane increased proportionally with increasing pressure, indicates that the membrane becomes tight (its pores become narrower) with increasing pressure (Wang & Chung 2005), resulting in stronger steric sieving than the XN45 membrane. However, the efficiency of the XN45 membrane was better for this ionic pollutant due to Donnan and dielectric exclusion.

DOC results showed that the XN45 membrane had better efficiency, but for both membranes, the results were independent of the driving force. The NP010 membrane with a narrower pore diameter, had less removal, indicating that the dominant sieving was not steric. However, the surface adsorption properties of these two membranes were different. It was thought that the primary adsorption mechanism more contributes to the removal of XN45 membrane. Considering the different pressures of the same membranes, no change in efficiency despite varying surface contact times indicated that the first-order adsorption (surface adsorption) occurred or that adsorption by the intrapore transport mechanism was not the rate-limiting component. In addition, it was possible to remove the charged pollutants in DOC due to Donnan exclusion and dielectric exclusion. In all experiments with the NF process, the high efficiency of color removal was obtained.

3.2. Treatment studies by MF-PAC

Removal efficiencies of pollutants in coking wastewater treated through the MF-PAC hybrid system versus PAC concentration are given in Figure 2. The removal efficiency in this process was achieved only with PAC because coking wastewater treated was effluent from A_2O-MBR with 0.2 μm pore diameter. The time during which adsorption reached equilibrium on the COD was determined. As a result of the experiments, the system reached equilibrium in the fourth hour. However, there was a difference of around ~1% between the efficiency obtained in the 1-h contact time and the efficiency obtained at the 4 h, hence 1 h was determined as the optimum contact time. Thanks to this series of experiments, in addition to understanding the efficiency of the NF-PAC hybrid process more accurately, the differences in removal efficiency between it and other NF and MF-PAC processes were revealed.

Although pH was 6.44 at 0.1 g/L PAC concentration, it increased continuously until the final PAC concentration and reached pH 8.02. The increase in the removal efficiency of COD and pH with increasing PAC concentration indicated that the pollutants adsorbed by PAC were more anionic.

As shown in Figure 2, COD removal initially increased and then decreased significantly, but the COD removed per 1 g PAC constantly decreased due to a decrease in the amount of COD adsorbed into a unit of PAC with an increase in PAC concentration. The least phenol concentration in the filtrate obtained from the experiments with nine different PAC concentrations and a 0.2 μm MF membrane at 175 kPa was <0.05 mg/L at 8 g PAC/L.

It was observed that phenol removal efficiency escalated with an increase in PAC concentration (Liu *et al.* 2020). On the other hand, T-CN removal remained constant with an increase in PAC dose. After a certain CN species was adsorbed, another pollutant group may have preferred it in adsorption because its affinity was higher than the affinity of the remaining CN species (Liu *et al.* 2020). Contrary to the literature, the T-CN removal efficiency of the PAC used was low, in this study. The dominant T-CN species may be composed of cationic species. The maximum removal efficiency of T-CN per 1 g PAC

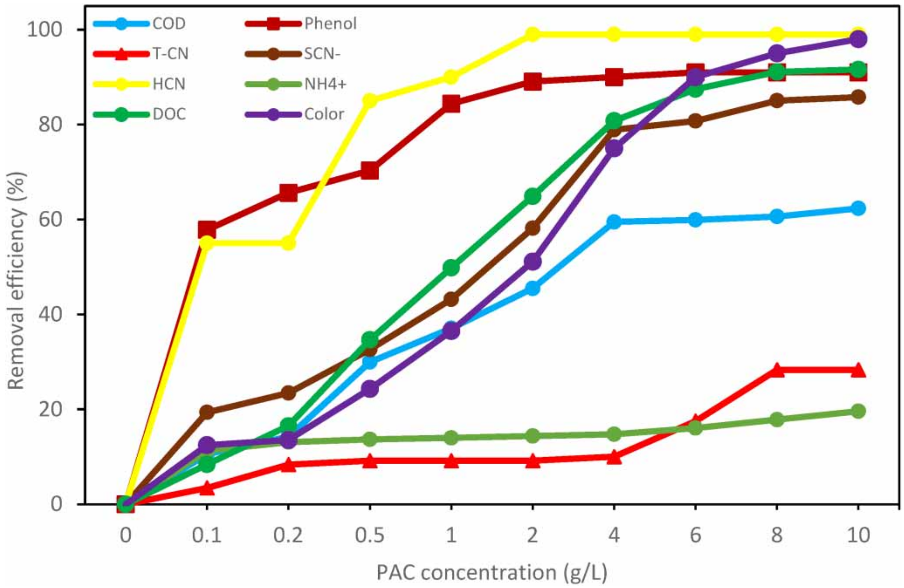

Figure 2 | Removal efficiencies of the MF-PAC hybrid system.

occurred between 4 and 8 g PAC/L. There was no relationship in the removal efficiency of T-CN with every duplicate increase in PAC concentration. This may be due to a medium-affinity to high-concentration pollutant that decreased between the high-affinity T-CN fractions and the low-affinity T-CN fractions (Liu *et al.* 2020).

The removal efficiency of ammonia increased slightly with increasing PAC concentration, but the removal efficiency obtained per unit PAC decreased dramatically. PAC has very few negatively charged active sites targeting ammonium. Likewise, the time taken for the pollutants to be transported to the inner active zone of the PAC through diffusion was longer than the time determined in this study, and therefore, it was not sufficiently removed. Despite previous reports (Stavropoulos *et al.* 2015) showing the removal efficiency of HCN with PAC increased with rising pH, this correlation was not observable in this work because of the high efficiency attained at all doses. However, this may be due to the low HCN concentration. The removal efficiency of SCN^- increased with increasing PAC amount. The observed results indicated that the main adsorption parameter of this anionic species depends on the PAC concentration, independent of pH. The efficiency of the MF-PAC process for DOC removal varies with the PAC concentration. Removal per unit PAC was highest at the lowest concentration and decreased continuously as PAC concentration increased. COD and DOC removals showed a strong positive correlation ($r = 0.99$). This indicated that some of the species in COD were DOC species. The noteworthy point in the MF-PAC process was that the amount of inorganic carbon and conductivity constantly increased with increasing PAC concentration. This shows that PAC particles smaller than 0.2 μm are mixed into the permeate. Furthermore, color removal was high and proportional to the PAC concentration.

3.3. Treatment studies by NF-PAC

Because effluent COD concentration in the NF process operated, and effluent COD and T-CN concentrations in the MF-PAC process could not meet the discharge standard, the adsorption process and the NF process were operated as a hybrid. Therefore, NP010 and XN45 membranes were tested with five and three different PAC concentrations, respectively. Figure 3 depicts the removal efficiencies of the pollutants obtained from these filtration experiments.

As in the MF-PAC hybrid system, the removal efficiency of the COD increased with the added increasing of PAC concentrations on NP010 and XN45 membranes. However, for the NP010 membrane, it can be seen in Figure 3 that the COD removal efficiency rate decreases at 1 and 2 g/L PAC concentrations. Although the PAC concentration increased, the removal per unit PAC decreased because the pollutants could not be adsorbed by PAC and may have been remained in the bulk. Reductions in removal per unit PAC at NP010-PAC process were observed (1–2 g/L) compared at higher PAC concentrations (6–8–10 g/L) in the MF-PAC study. It was shown that some of the pollutants captured by the NF membrane and PAC are common. Otherwise, it would be expected that the removal efficiency of MF-PAC would not decrease at higher PAC concentrations. For the XN45 membrane, the removal efficiency decreased to 7.89% at the final PAC concentration.

The optimum PAC concentration and membrane type were determined as 0.5 g PAC/L and the XN45 membrane, respectively. Therefore, the filtrate of the XN45-PAC with 0.5 g/L system was collected intermittently into 15 mL tubes and COD analysis was performed to determine the recovery rate with each intermittent sample. According to the results, the recovery rate was determined to meet the discharge criteria. The recovery rate of the filtrate was 78%.

Although NP010-PAC process was not effective enough on T-CN removal, the removal efficiency of XN45-PAC was high due to the high T-CN removal efficiency of the XN45 membrane. For phenol, all NF-PAC processes were reported to have high removal efficiency. In the hybrid processes, PAC played a more important role in the removal of phenol than the membrane because it was processed first.

On the ammonium ion removal efficiency of NP010-PAC was compared with that of the NP010 membrane and MF-PAC process, the removal efficiency of NP010-PAC was higher than that of the others. The concentration of ammonium ion without the NP010 membrane decreased with PAC adsorption, thus its transport rate decreased due to a decrease in concentration difference, the driving force of diffusion that could ensure the adsorption of ammonium to surface and pores of the NP010 membrane.

In the MF-PAC process, the removal efficiency of SCN^- anion increased with increasing the PAC concentration, but removal per unit PAC decreased proportionally. Likewise, the removal efficiency of NP010- PAC for SCN^- increased with increasing PAC concentration. Only at the recent concentration of NP010-PAC, the removal efficiency increased significantly. PAC, which is cationic, increased the removal of anions as can be understood from the pH changing at concentrations of 1 and 2 g PAC/L. These removed anions may be multivalent. The increase in conductivity between 1 and 2 g PAC/L can be interpreted as pH converting some neutral species into ionic or the effect of PAC particles missed through MF membrane. According to the results obtained from the filtration of wastewater treated through the NP010 membrane with 2 g PAC/L,

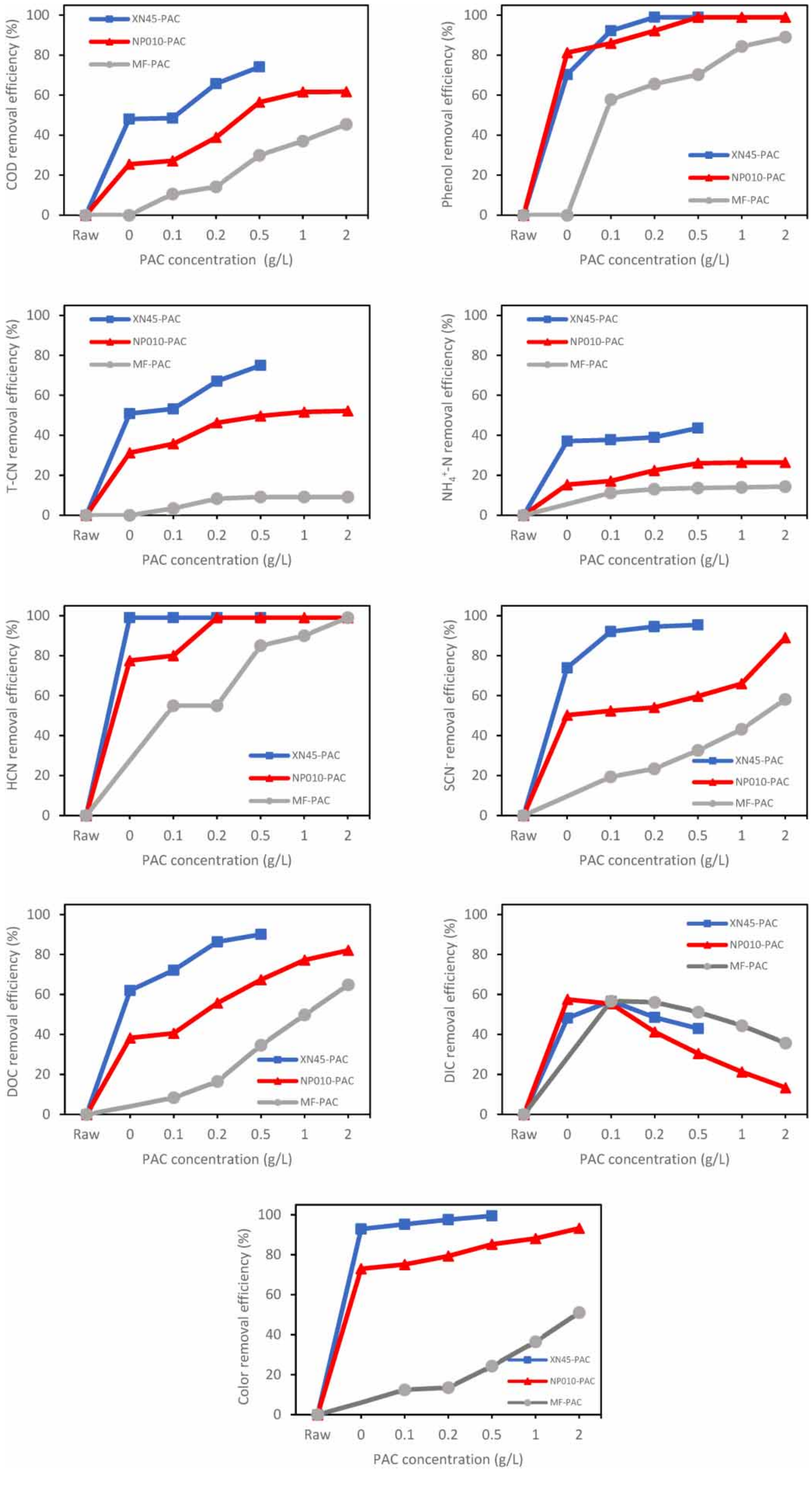

Figure 3 | Removal efficiencies of NF-PAC hybrid system with comparing that of MF-PAC hybrid system.

the removal of anions increased significantly, hence the conductivity decreased. Here, the increased removal efficiency of the NF membrane for SCN^- may have increased the rejection of the SCN^- instead of ions, assuming that PAC adsorbs anions other than SCN^- that NF can hold (more affinity or higher valence) by preferential grouping.

3.4. Flux results of the NF process

In NF experiments, two NF membranes (NP010, XN45) with different MWCO values were operated at two different pressures (1,000 and 2,000 kPa) in the system. The flux changes observed in the system during the experiments are given in Figure 4. Considering the pore sizes and contact angles (Table 3), the flux value of XN45 was expected to be high. However, the results obtained were contrary to expectations. The low flux in XN45, having a high zeta potential, may have been caused by the electroviscotic effect caused by the charged pore surfaces (Childress & Elimelech 2000). In addition, the possibility that the size of pollutants was close to the pore size of the XN45 membrane led to more fouling than the NP010. Furthermore, flux decrease in loose membranes is an expected phenomenon. In addition, polymeric membranes can sometimes be narrow or expand, depending on pH and pressure conditions, which seriously affect flux and rejection efficiency (Wang & Chung 2005).

As the pressure increases in both membranes, their fouling tendency increases (Figure 4). Moreover, the duplicate increase in pressure showed that the flux of the XN45 membrane, having a larger pore size, increased more than that of the NP010 membrane, having a smaller pore size. The tighter membrane (NP010) tended to clog less than the looser membrane (XN45) since the gel layer on the surface increased with the increase in concentration polarization and pressure (Nyström *et al.* 1995). The basic mechanism of more fouling of the looser membrane is that the pollutant passing through the pore can block it completely (adsorption, physical compression, etc.) (Nyström *et al.* 1995). This situation was more observed with an increase in pressure.

The surface charge of both membranes used was negative. If the membrane surface charge is the same as the dissolved substance, membrane fouling is low because of reducing the accumulation of dissolved substances on the membrane surface by the electrostatic repulsion (Mänttäri *et al.* 2000). It was thought that the abundance of negatively charged components (chlorine, CN^-, SCN^-, etc.) (Kwiecińska *et al.* 2017), in the coking wastewater treated may have been contributed to the less fouling. However, an important mechanism for fouling was the accumulation of inorganic salts in the concentrated side, resulting from rejection by the membrane, and when the accumulation of pollutants exceeded their saturation value, a precipitated or crystallized structure was formed on the membrane surface (Antony *et al.* 2011). Moreover, some of the cationic pollutants may have attached to the active layer in the pore, contributing to fouling by narrowing the pores.

3.5. Flux results of the MF-PAC process

Permeate fluxes of the MF-PAC process are given in Figure 5. Because the effluent of the A_2O-MBR system with 0.2 μm pore size was used in the experiment, the main parameter affecting the membrane flux was the used PAC concentration in each experiment.

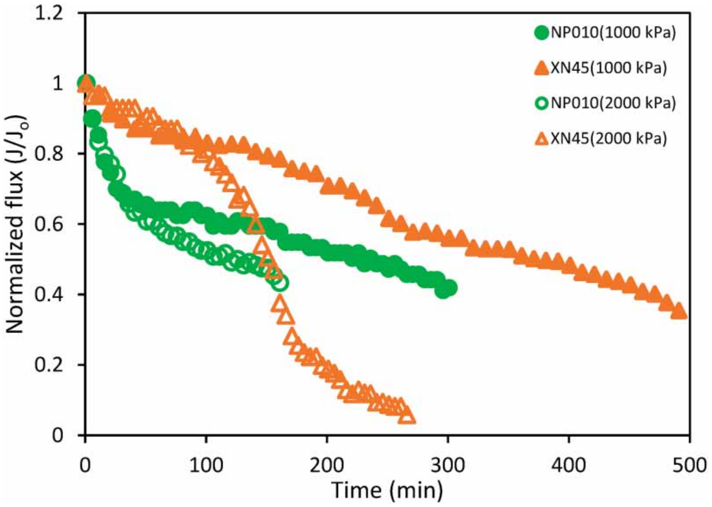

Figure 4 | Normalized flux obtained NF systems.

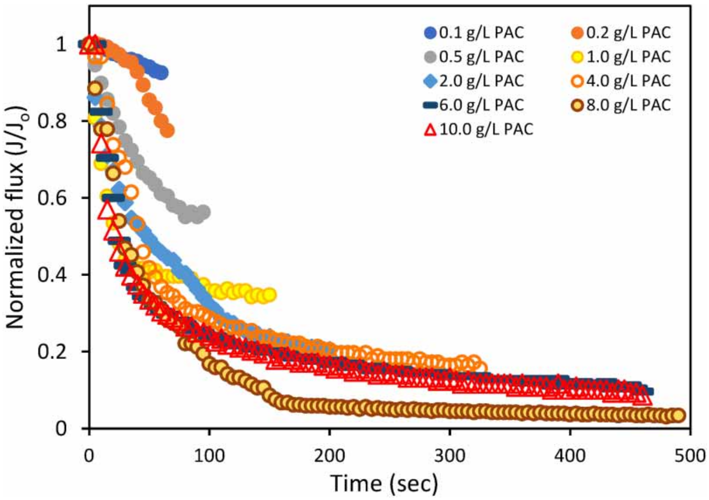

Figure 5 | The normalized flux of MF-PAC hybrid system vs PAC concentration (175 kPa).

In the study, there was a decrease in the flux with an increase in the PAC concentration. However, the rate of decrease in the flux reduced beyond 2 and 4 g PAC/L, even at 10 PAC/L, the flux increased slightly compared to the previous PAC concentration (Figure 5). Since PAC adsorbs dissolved organic matter and colloidal substances, the back diffusion of organic matter at the membrane-liquid interface was thought to increase.

3.6. Flux results of the NF-PAC process

The change rates of the fluxes obtained from NF-PAC experiments are given in Figure 6 and 7.

There are conflicting results in the literature regarding the effect of PAC concentration on membrane fouling. Some researchers have reported increased permeate flux with increasing PAC concentration operating times (Tomaszewska & Mozia 2002; Lee *et al.* 2007). Similar flux values were also found in some studies (Tomaszewska & Mozia 2002; Matsui *et al.* 2006) or severe flux reductions (Lai *et al.* 2007) have been reported. In addition, studies show that the effect of PAC on membrane fouling is a function of membrane properties. These studies showed that PAC either reduced or did not affect the flux drop in hydrophilic membranes but did not reduce the flux in hydrophobic membranes. However, these studies are generally based on the results of studies on UF membranes. Since NF membranes have some properties of UF

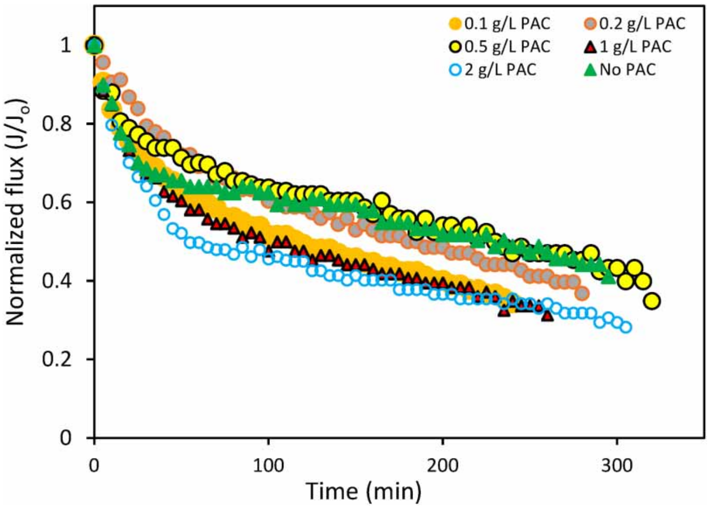

Figure 6 | Normalized fluxes obtained from the NP010-PAC hybrid system (1,000 kPa).

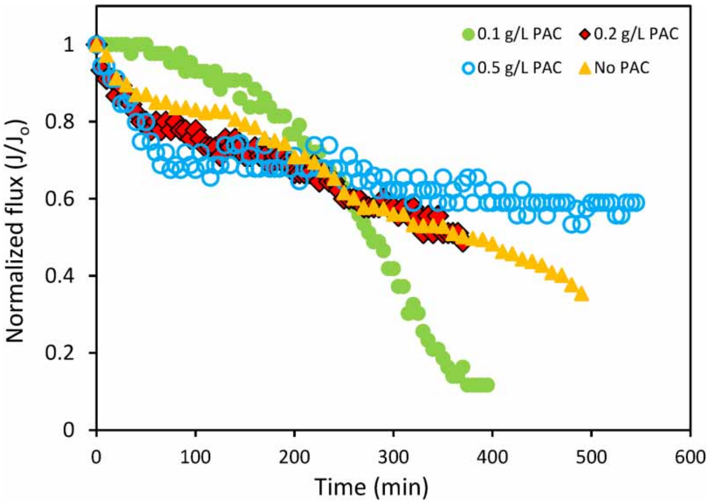

Figure 7 | Normalized fluxes obtained from the XN45-PAC hybrid system (1,000 kPa).

membranes, these results may help explain the fouling mechanisms of NF membranes, but further studies on NF membranes are needed to determine the real situation. In this study, the flux results obtained indicated PAC concentration for NP010 increased the flux in general. At between 0.5 and 2 g/L, there was a slight decrease in flux compared to the only membrane. However, the increase in flux with the PAC concentrations was greater than the decrease, and this general situation can be interpreted as 'it does not change or increases the flux' (Figure 6). Similarly, a high flux increase was observed in the first and second of the three different PAC concentrations tested in the XN45 membrane (Figure 7). However, at 0.5 g/L, the higher PAC concentration tested, a decrease in flux was observed compared to the only membrane (Figure 7). In the literature, both the PAC dynamics in the liquid and the continuous exchange of particles in the particle layer on the membrane surface significantly reduce the thickness of the hydrodynamic layer limiting mass transfer (Winzeler & Belfort 1993). In this study in general, the flux was higher at lower PAC concentrations than both without PAC and at high PAC concentrations. This occurred because of the small amount of PAC supplied, which targets organic and colloidal contaminants that worsen blockage and either increases flux or prevents it. However, when PAC was above a certain concentration, it was thought to accumulate on the membrane surface, resulting from 'the electrical attraction between the anionic membrane and it and the drag force created by transport pressure overcome the 'sweeping effect' provided by the mixer to prevent fouling, causing a decrease in flux by both blocking the pores and increasing the friction in the bulk solution. In the literature, the relationship between PAC and Donnan and dielectric exclusion effects, the basic removal mechanisms of NF membranes, and PAC, and their effects on fouling and flux have not been adequately investigated. But, there are some studies focused on UF membranes and pore size-based removal (Lin *et al.* 2001; Mozia *et al.* 2005). However, it is not clear which of the basic processes in NF membranes with PAC is more effective on fouling and flux.

Another advantage of using the NF-PAC hybrid is that NF rejects ions (especially divalent ions and above) which were not adsorbed by PAC (Meier 2010). In the literature, conductivity removal efficiency of 32.2% in the NF process treating effluent of A_2O-MBR operated for coking wastewater has been reported (Jin *et al.* 2013). However, the raw wastewater conductivity reported in that study was almost one-third of the wastewater treated within the scope of this study. The conductivity removal in the three processes studied was around 17.02 ± ~10%. Hence, it is obvious that the conductivity removal efficiency of the NF process was more stabilized and was better than the MF-PAC process and NP010-PAC. One of the possible reasons why the NF process was better than the NF-PAC processes was that it increased the salt rejection of organic pollutants accumulating on the membrane surface, but in the NP010-PAC process, half of these organics were adsorbed by PAC and could not sufficiently bind the inorganic salts to be pass through the membrane (Seidel & Elimelech 2002).

4. CONCLUSIONS

Further treatment of coking wastewater treated in A_2O-MBR in NF, MF-PAC, and NF-PAC processes was investigated to meet the Ministry of Environment, Urbanization and Climate Change of the Republic of Türkiye discharge standards. According to this research, permeate parameters of XN45-PAC with 0.5 g/L hybrid system (COD = 96 (±1.88) mg/L, T-CN = <0.02 mg/L phenol = <0.05 mg/L) achieved to meet all the discharge standards with recovery of 78%. In this study, other parameters (NH_4^+, SCN^-, HCN, DOC, DIC, and color) in the effluents were also investigated addition to the parameters enacted by the ministry. At the end of the experiments, more than 90% removal efficiency was achieved in all parameters, excluding NH_4^+ (43.65%). This research emphasizes the importance of determining the process and operating conditions considering the target pollutant to achieve high treatment efficiency in the use of NF membranes and PAC. If hybrid processes are to be used, the advantageous and disadvantageous features of the processes must be determined and the hybrid process must be designed to compensate for the disadvantageous features of each other. Likewise, the hybrid use of PAC within NF increased the fluxes of the membrane process at low PAC concentrations. However, with increasing PAC concentration a decrease in flux was observed. Therefore, to elucidate the factors affecting membrane fouling in NF-PAC hybrid system, and also to economic evaluation of the system, further studies should be done.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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