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Sulfate removal from nanofiltration concentrate of alkaloid wastewater by electrodialysis

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ABSTRACT

Treatment of alkaloid wastewater is a challenging task because of its complex mixture of contaminants with high chemical oxygen demand and sulfate concentrations. The aim of this study was to investigate the removal of sulfate from nanofitration (NF) concentrate of alkaloid wastewater by electrodialysis (ED). The effectiveness of ED process was evaluated using synthetic sodium sulfate solutions at three different concentrations (20, 30, and 40 g/L). The removal efficiencies ranged from 95 to 98% at all applied voltages (5–20 V). Energy consumption for 95% sulfate removal was linearly increasing with applied voltage. The influences of diluate and concentrate flow rates on sulfate removal were investigated at 20, 30, and 40 L/h. At least 95% of deionization efficiencies were achieved at all flow rates. The performance of three different NF membranes (NF270, NF90, and NF245) was investigated in order to remove sulfate from biologically treated alkaloid wastewater. Ninety-nine percent of sulfate retained in membrane concentrate in NF90 and NF245 membranes. Finally, the sulfate removal efficiencies from NF concentrate were determined by ED process. Up to 98% of deionization efficiencies were achieved. However, both ED time to teach 95% efficiency and the energy consumptions for the same degree of treatment were much greater that those obtained using synthetic wastewater.

Keywords: Alkaloid wastewater; Electrodialysis; Desalination; Sulfate removal

1. Introduction

Attaining proper water resources is a challenging task for industries because of the growing water scarcity. Many industries use large amount of water and generate wide range of wastes. Therefore, advanced wastewater treatment plants for water reuse have been constructed by many industries in recent years [1]. Among those, opium alkaloid industry is an example in which large quantities of water are used and high pollution load is generated. The licensed opium alkaloid processing industries currently reside in 12 countries around the world, including four main producers: India, Australia, Turkey, and France [2]. The alkaloid factory in Turkey processes 72 tons of opium straw daily and producing 3.3 kg morphine per ton of opium. The specific wastewater production of the industry is around 6.7 m^3 per ton of opium capsule [3]. The opium is obtained from crude seed capsule of the opium poppy that contains sugars, proteins, fats, ammonia, latex, plant wax, lactic acid,

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and a wide variety of alkaloids. Alkaloids are partially chemically bonded to meconic acid and a group of complex nitrogen-containing product. Morphine contains more than 40 individual alkaloids. Morphine is the most prevalent and important constituent besides base codeine, base ethyl morphine, codeine phosphate, and dionin [4,5]. The information about characterization, treatment, and disposal of the alkaloid wastewater is limited in the literature. Various treatment options have been reported including both anaerobic and aerobic biological treatment, aerobic treatment with catalytic wet air oxidation, and anaerobic treatment with membrane treatment [6]. Physicochemical treatment combined with activated sludge process has also been investigated [7]. As a post-treatment method, Fenton oxidation and membrane processes have also been investigated [8]. Based on the previous studies, chemical oxygen demand (COD) removal efficiencies were about 70% with anaerobic treatment [9]. It was also reported that 95% of COD and complete color removal were obtained by nanofitration (NF) and RO membranes [9].

Membrane technologies are attractive for industrial wastewater treatment due to the advantage of enabling both separation and concentration operations without the addition of chemicals. However, the membrane concentrate is a major problem in the process. Based on our previous treatability studies in the laboratory, an aerobic biological reactor and a nanofiltration process were suggested for the treatment of alkaloid wastewater. As a biological treatment process, membrane bioreactors (MBRs) integrate the biological degradation of waste products with membrane filtration, ensuring effective removal of organic contaminants and nutrients from industrial wastewaters [10]. Therefore, MBRs were used for the treatment. Following MBR, the effluent was treated by an NF unit in which sulfate and remaining COD were removed. The sludge from MBR unit was treated in an anaerobic digester. The concentrate from the NF unit was planned to be treated in the digester unit as well. However, it contained large quantities of sulfate which inhibited the anaerobic process. Therefore, prior to the anaerobic digester, sulfate was removed from the concentrate by electrodialysis. ED is a membrane separation process based on the selective migration of aqueous ions through ion-exchange membranes as a result of an electrical driving force. ED process was first developed for the desalination application. However, other applications are also in progress [11–13].

The objective of this study was to investigate the sulfate removal performance of ED from alkaloid wastewater. First, the effectiveness of ED process was evaluated using synthetic wastewater containing varying concentrations of sodium sulfate. Flow rate of concentrate and diluate and applied voltage values were optimized. Then, the effectiveness of three different membrane materials was evaluated to remove sulfate from biologically treated alkaloid wastewater. Finally, ED studies were conducted with NF concentrate.

2. Material and methods

2.1. Experimental methods

Electrodialysis experiments were performed by a commercial ED system (ED 64002, PCCell GmbH, Heusweiler, Germany) consisting of five cell pairs with five pieces of anion-exchange membranes and six pieces of cation-exchange membranes. PCA standard cation-exchange membranes (PC-SA) and PCA standard anion-exchange membranes (PC-SK) were used in the stack which were provided by the same manufacturer of ED cell. The effective area of the membranes was 64 cm^2. The detailed information about the membranes is given in Table 1. The membranes were arranged between an anode (mixed metal oxides (Pt/Ir)-coated Ti-stretched metal) and a cathode (the same material as anode). Both electrodes were connected to a direct current power supply (Manson, HCS-3202). The distance between electrodes and membranes were 1 mm and inter-cell spaces were 0.5 mm. The diluate and concentrate compartments were separated by silicone polyethylene spacers with a thickness of 0.7 mm, and each compartment was connected to an external pump (Gemu 617, with the maximal speed of 100 L/h).

The ED system was operated at a constant voltage in a batch mode. The corresponding current values were monitored online through the experiments and conductivity measurements were carried out at 10 min intervals. In order to optimize the operating conditions of the ED system, four different voltage values (5, 10, 15, and 20 V) were applied at three different Na_2SO_4 concentrations (20, 30, and 40 g/L). The flow rate was

Table 1
Properties of PCA cation- and anion-exchange membranes

	PC-SK	PC-SA
Thickness (μm)	130	90–130
Ion-exchange capacity (meq/g)	ca. 1	ca. 1.5
Chemical stability pH	0–11	0–9
Permselectivity	>0.96	>0.93
Functional groups	$-SO_3Na$	$-NR_4Cl$
Surface potential (Ωcm^2)	0.75–3	1–1.5

fixed at 30 L/h in the first part of the study. After determining an optimum voltage value, the flow rates of diluate and concentrate were optimized at 20, 30, and 40 L/h. The optimum voltage value and the flow rate were determined considering both the desalination rate and energy consumption. The effect of initial concentration on sulfate removal was also investigated. The ED unit was operated at 15 V and the flow rate was fixed at 30 L/h with 20, 30, and 40 g/L Na_2SO_4 solutions. To reduce the electrical resistant on electrodes, a rinse solution was prepared with Na_2SO_4 at 0.25 M. Each channel was connected to a separate external reservoir, allowing continuous recirculation. The feedwater was recirculated from the tank through the spacers of the membrane stack and back to the feed tank until the desired removal efficiency was obtained. The concentrate stream was also recirculated to reduce wastewater volume. The solution volumes were determined at the beginning and at the end of every experiment. To balance initial pressure, initial volume of the solution in each compartment was arranged at same value. The initial volumes of the diluate and concentrate solutions were 1 L and electrode rinse solution was 4 L.

The ED system was not equipped with a temperature controller hence the temperature was allowed to rise. Approximately 5–6°C of temperature increase was observed in the experiments. Temperature increase was similar at all voltages since the duration was longer at lower voltage values. Voltage and current data were monitored online. The conductivities and pH of the diluate and concentrate solutions were recorded at 10 min intervals. Before the current was applied, the solution in each compartment was circulated for 30 min to eliminate the gas bubbles in the ED stack. Bubbles are the reason for the increase in voltage drop, resistance, and energy consumption of the system [14].

After determination of optimum operating conditions for ED system with synthetic solutions, studies with biologically treated alkaloid wastewater were performed. Three different NF membranes were evaluated for COD and sulfate removal efficiencies. The characteristics of the NF membranes used in the experiments are presented in Table 2. The nanofiltration studies were performed using a laboratory-scale membrane filtration setup (Sterlitech HP4750) with an effective membrane area of 14.6 cm^2. Biologically pretreated wastewater was transferred into 500 mL of membrane module. Permeate was collected in a beaker and was weighted at prescribed intervals using a digital balance (Precisa 6200D) connected to a computer. Concentrate flow of the system was collected inside the membrane module. Temperature was constant at 20 ± 2°C during the experiments. Conductivity, pH, and temperature of permeate were measured.

2.2. Analytic methods

The chemicals used in the experiments were of analytical grade and used without any purification. COD, chloride, and sulfate were determined according to the Standard Methods [15]. Solution pH was determined by a pH probe (WTW3210), and conductivity measurements were performed by a conductivity meter (WTW340i).

2.3. Characteristics of wastewater

The wastewater was obtained from the opium alkaloid processing plant which is located in Afyon Province in Turkey. Analysis of selected contaminants and water treatment discharge standards are presented in Table 3.

3. Result and discussion

3.1. Influence of operational parameters on electrodialysis process

Experiments were conducted using a synthetic wastewater in order to optimize voltage and flow rate of ED. The influences of initial concentration of the feed solution, the applied voltage, and the flow rate on the effectiveness of the sulfate removals were investigated.

3.1.1. Limiting current density

Limiting current density (LCD) is one of the important parameters in the operations of electrodialysis (ED) systems. The ED systems must be operated with the highest possible current densities in order to obtain the maximum ion flow per unit of membrane area. When the ions are transferred to the cathode and to the anode through the cells, the ion concentration in the diluate compartment approaches zero at the membrane interface, and the current density attains a maximum [16]. This maximum current density, also called LCD, enables to determine the electrical resistance and current utilization of the systems [16,17].

Before the experiments, the limiting current measurement was carried out for each feed solution containing different concentrations of Na_2SO_4. The current-voltage method is a commonly used method among various methods including current–pH

Table 2
Properties of NF membranes used in the experiments

	NF270	NF90	NF245
Material	Polyamide thin-film composite	Polyamide thin-film composite	Polyamide thin-film composite
MWCO (Da)	200–300	200	200–400
$MgSO_4$ rejection (%)	98	98	99
Max. temp. (˚C)	45	45	48.6
pH	2–11	2–11	2–11

Table 3
Characterization of alkaloid wastewater

Parameter	Minimum	Maximum	Discharge standards[a]
Total COD (mg/L)	18,300	43,000	1,000
Soluble COD (mg/L)	17,000	40,000	
BOD_5 (mg/L)	4,250	25,000	
TSS (mg/L)	555	2,295	500
VSS (mg/L)	310	1,775	
TP (mgP/L)	3.1	15	–
TKN (mgN/L)	380	1,030	15
NH_4 (mgN/L)	61	173	
NO_3 (mgN/L)	–	–	
pH	4.5	6.3	6–12
Sulfate (mg/L)	800	10,000	1,700
Color (Pt-Co)	2,150	4,750	
Alkalinity (mg$CaCO_3$/L)	144	4,450	

[a] Water Pollution Control Regulations of Turkey.

method, over voltage method, noise spectra method, and reflective index method [18]. The variations in electrical current with applied voltage at three different Na_2SO_4 concentrations are shown in Fig. 1. The LCD of alkaloid wastewater was also determined and the results are also shown in Fig. 1. The applied current densities did not reach the LCD level in all experiments.

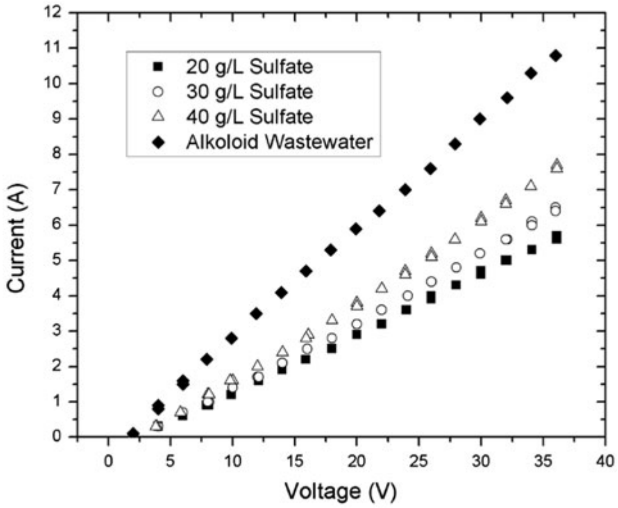

Fig. 1. LCD determination lines.

3.1.2. Effect of voltage on sulfate removal

The experiments were performed at three different Na_2SO_4 concentrations (20, 30, and 40 g/L) and at 30 L/h of flow rate. When the applied voltage increased, the electric field becomes greater causing greater ion transfer due to the formation of larger electrical field. On the other hand, the greater voltage values leads to a higher concentration polarization across the membrane surface and therefore the deionization efficiency decreases.

The ED cell was operated until at least 95% sulfate transported to the concentrate department. Variation in sulfate removal efficiencies and current densities at various initial solution concentrations and applied voltages are shown in Fig. 2. Energy consumption for 95% sulfate removal, time to reach 95% of sulfate removal efficiency, as well as the final diluate and concentrate volumes are summarized in Table 4. The increase in applied voltage caused an increase in

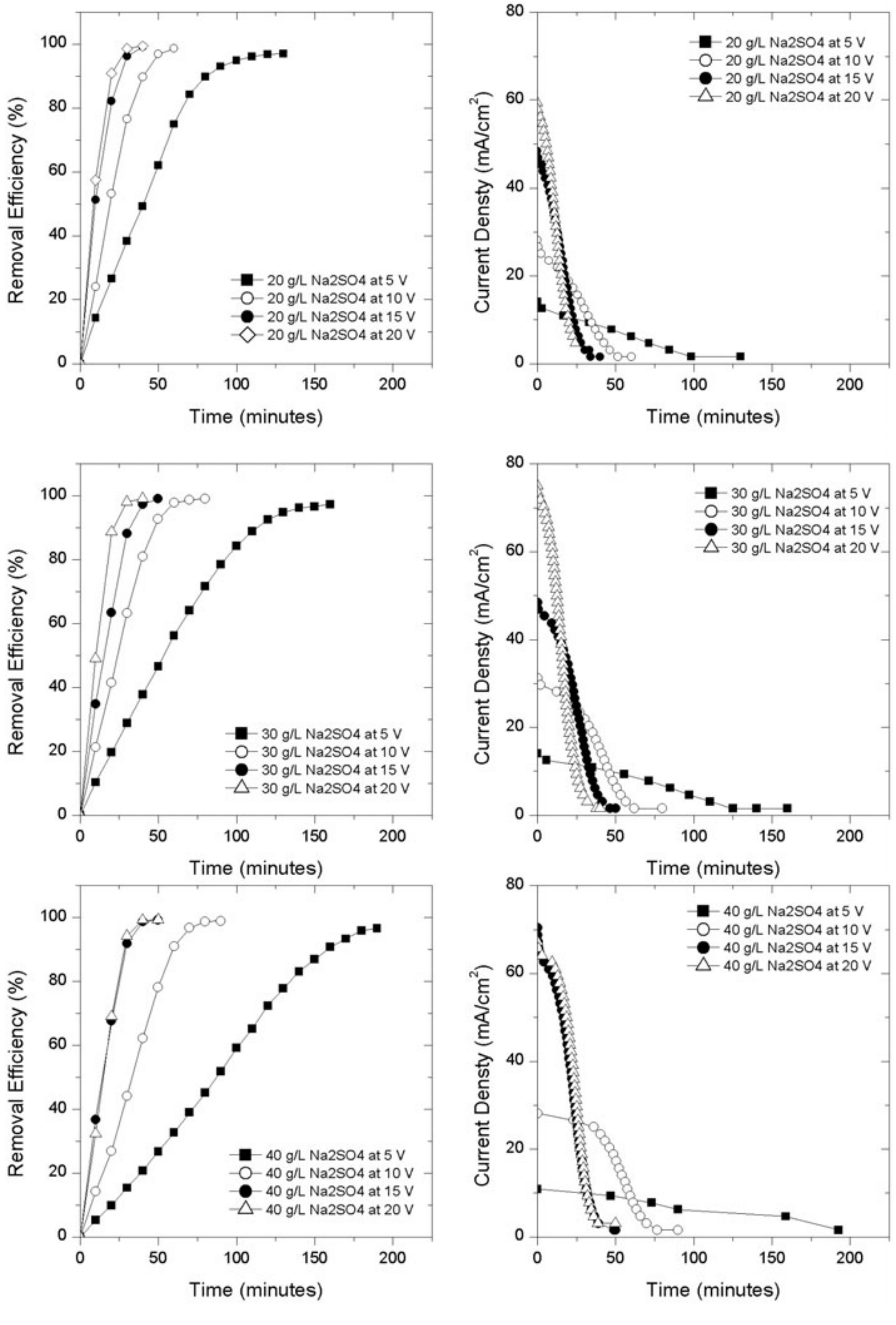

Fig. 2. Effect of applied voltage on desalination performance and time-dependent current density values of Na_2SO_4 solutions at different concentrations.

deionization performance. It was obvious that both the removal efficiency and the removal rate at 5 V experiment were different than those at 10, 15, and 20 V experiments. Time required to achieve greater than 95% of deionization was two to three times longer at 5 V than at the other voltages. As the voltage increased, the duration of the process reduced for the same degree of sulfate removal. The duration of ED was in between 25 and 179 min depending on the applied voltage at different Na_2SO_4 concentrations. The removal efficiencies ranging from 95 to 98% were achieved in the first 40 to 60 min except for at 5 V. After that, the removal efficiencies started to decelerate. The decrease in ion transfer was attributed to the

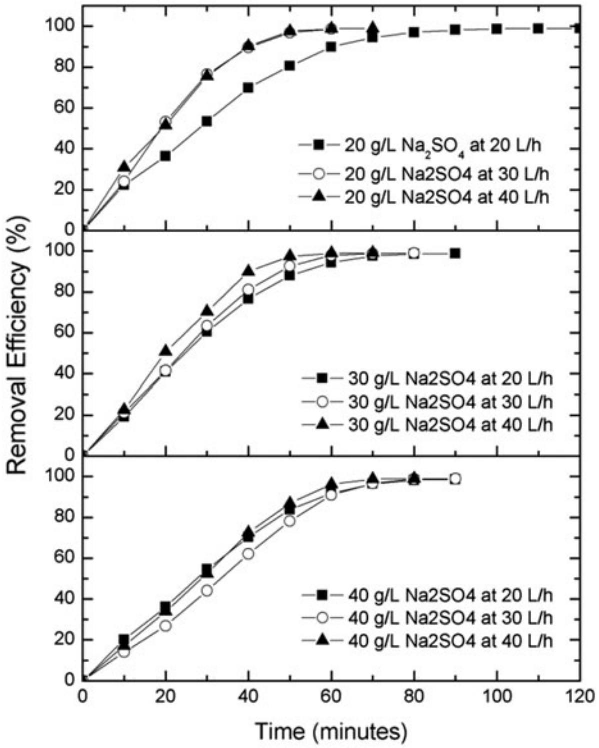

Fig. 3. Effect of feed flow rate on desalination performance of Na_2SO_4 solutions with different concentrations at 10 V.

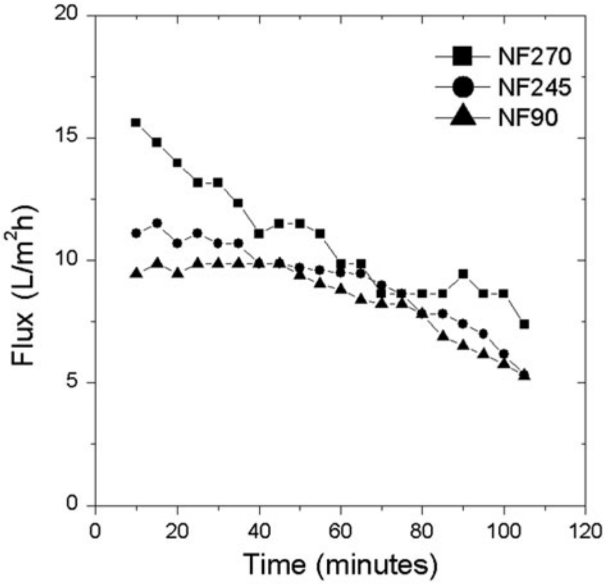

Fig. 5. Time-dependent flux values for NF270, NF245, and NF90.

increased concentration gradient between concentrate and diluate [19].

From Fig. 2, it can be seen that the current density decreased gradually during the batch runs. There was a sharp decrease in 15 and 20 V experiments which was different than those in 5 and 10 V experiments. The ED duration reduced as the current density increased.

The maximum deionization efficiency was achieved at 20 V at all Na_2SO_4 concentration. The removal efficiencies were 99.4, 99.2, and 99.3% for 20, 30, and 40 g/L of Na_2SO_4, respectively. However at 15 V, the deionization performance and the run time was nearly the same as 20 V experiment. Almost 98% of removal efficiencies were reached in 30 min at both

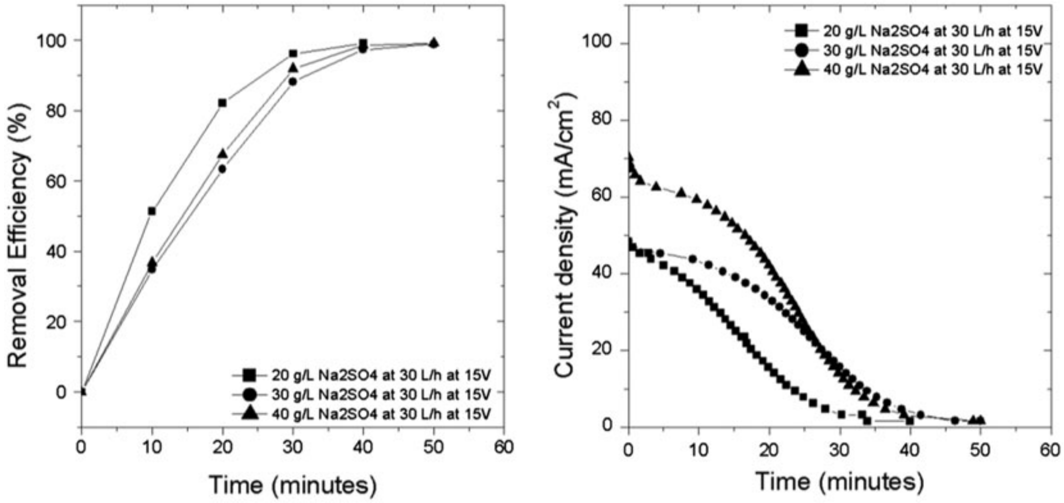

Fig. 4. Effect of inital Na_2SO_4 concentrations on desalination performance and time-dependent current density values for Na_2SO_4 solutions with different concentrations at 15 V applied voltage and 30 L/h flow rate.

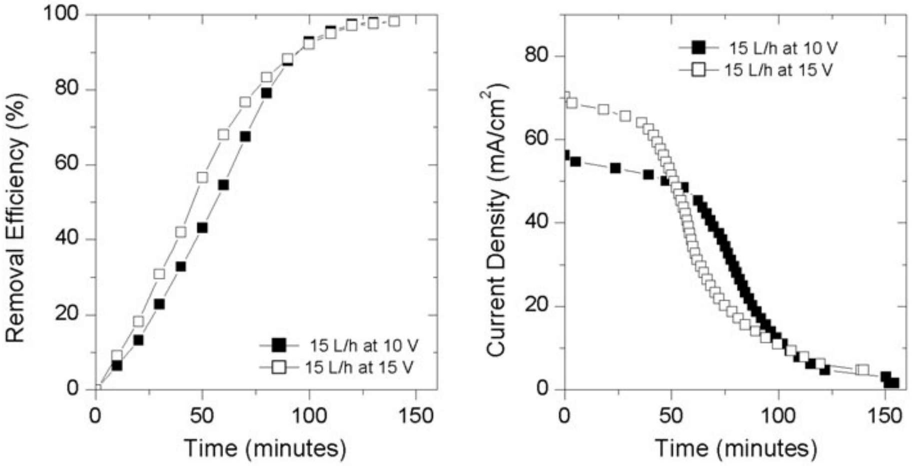

Fig. 6. Effect of applied voltage on desalination performance and time-dependent current density values of NF concentrate.

15 and 20 V. The maximum recorded conductivity value of the concentrate stream was 54 ms/cm. When the voltage is raised, the energy consumption increases and irreversible energy loss occurs through the generation of heat [20]. High temperature can shorten the life of ion-exchange membranes [19]. As seen in Table 4, the energy consumption per sulfate removal was linearly changing with increasing voltage. The lowest energy consumption was achieved at 5 V experiment. However, time to reach 95% of sulfate removal efficiency was significantly higher at 5 V. For example, energy consumption values at 40 g/L of Na_2SO_4 were 1.1, 2.36, and 3.50 kJ/gSO_4^{2-} at 5, 10, and 15 V, respectively. However, time taken for 95% of sulfate removal efficiencies was 179, 68, and 39 min. Therefore, the operation voltage was chosen as 10 and 15 V for the treatment of NF concentrate.

3.1.3. Effect of flow rate

Theoretically, the flow rate can increase the desalination efficiency but this increase is limited. Therefore, the operation flux must be determined and controlled at a suitable range. The flow rate of the electrode rinsing solution was fixed at 100 L/h in all experiments. Because of the reactions at anode and cathode compartments, H_2 and O_2 gasses form. These gases have negative effect such as an increased electrical resistance on the electrodes, which may damage the membranes. Consequently, these gases should be removed from the system by applying higher flow rates [21].

A series of experiments were conducted to investigate the effect of diluate and concentrate flow rate at constant voltages. Three different flow rates (20, 30, or 40 L/h) were investigated. The results at 10 V are presented in Fig. 3. Energy consumption values at 10 and 15 V are also presented in Table 4. The results showed that as the flow rate of diluate and concentrate increased, time to reach 95% sulfate removal efficiency decreased. At 20 L/h of flow rate, sulfate removal was noticeably slower than those at 30 and 40 L/h. Slightly faster rates were observed at 40 L/h than that at 30 L/h (Fig. 3 and Table 4). Low flow rates can cause concentration polarization at boundary layer of the membrane surface. Accordingly, the low flow of the feed solution gives enough time to organic or inorganic ions to accumulate on the membrane surface. On the other hand, at higher flow rates the effect of the concentration polarization is reduced because of the turbulence through the stack. In the present study, it was observed that the operation time was shorter as the flow rate increased. This observation was similar to the studies of Chandramowleeswaran and Palanivelu [21] and Jing et al. [22]. At least 95% deionization efficiency was achieved at all flow rates. The energy consumption values were similar at each flow rate (Table 4). It was concluded that the desalination performances were nearly the same at 30 and 40 L/h experiments. Therefore, the 30 L/h of flow rate was chosen as the optimum flow rate for the rest of the experiments.

3.1.4. Effect of initial sulfate concentration

To study the effect of initial sulfate concentration on its removal, three different Na_2SO_4 concentrations (20, 30, and 40 g/L) were studied at 15 V and 30 L/h. The results are shown in Fig. 4. It was observed that

Table 4
Energy consuption and final diluate and concentrate volumes at various operating conditions

Voltage (V)	Na_2SO_4 Conc. (g/L)	Q (mL/min)	$t_{95\%}$ (min)	Energy consuption (kJ/g sulfate)	Final volume (mL)[a] diluate	concentrate
5	20	30	100	1.27	825	1,180
10	20	30	48	2.46	885	1,100
15	20	30	29	3.65	900	1,120
20	20	30	25	4.87	920	1,100
5	30	30	130	1.17	780	1,230
10	30	30	58	2.47	840	1,180
15	30	30	38	3.77	845	1,145
20	30	30	28	4.98	860	1,140
5	40	30	179	1.10	665	1,220
10	40	30	68	2.36	740	1,180
15	40	30	39	3.50	750	1,150
20	40	30	31	4.81	760	1,140
10	20	20	72		840	1,120
10	20	30	48	2.46	885	1,100
10	20	40	46	2.11	820	1,100
10	30	20	62	2.38	830	1,180
10	30	30	58	2.47	840	1,180
10	30	40	46	2.41	800	1,100
10	40	20	68	2.42	740	1,180
10	40	30	68	2.36	740	1,180
10	40	40	58	2.33	760	1,180
15	20	20	50	3.58	820	1,100
15	20	30	28	3.65	900	1,120
15	20	40	36	3.57	860	1,060
15	30	20	42	3.74	830	1,190
15	30	30	38	3.77	845	1,145
15	30	40	33	3.61	800	1,110
15	40	20	51	3.53	750	1,180
15	40	30	35	3.50	750	1,150
15	40	40	32	3.63	800	1,180

[a] Initial diluate and concentrate volumes were approximately 1,000 mL each.

the removal of Na_2SO_4 was almost the same. Ninety-nine percent of desalination was obtained within the first 50 min at all three concentrations. However, for the lowest initial concentration, the removal efficiency was slightly different than the other two experiments. For the first 30 min of the experiments, the desalination of 96.2, 88.2, and 91.8% were recorded for 20, 30, and 40 g/L, respectively. After that, the change in the effluent conductivity values became stable and reached to 99% of its initial value at the end of the runs. Higher desalination was achieved at lower feed concentrations similar to the studies reported in the literature [23].

As the initial concentration increased, the total number of ions in the solution and the conductivity values were higher. When the ion concentration of the feedwater increased, the current density values increased as well. The run time of three batch experiments were about 50 min.

From Fig. 4, it can be seen that the current density values decreased with time in all experiments due to the total cell resistance. During the process, the total resistance of the cell increased when the ion transferred from feed compartment to the concentrate compartment. Therefore, the current density values decreased. When Na_2SO_4 concentration increased, the number of ions in the solution increased and the total electrical resistance of the cell decreased, hence the current density was enhanced. The higher concentration of the feedwater leads to an increase in water diffusion rate [24]. The generated hydrogen ions in the feed compartment compete with sodium ions, so the desalination performance slightly decreases [25].

3.2. *NF studies of aerobically treated alkaloid wastewater*

The NF experiments were carried out using NF90, NF245, and NF270 membranes at the operating transmembrane pressure of 20 bar. During the nanofiltration experiments, permeate samples were collected and analyzed for the sulfate, pH, COD, and conductivity. The operational conditions were kept the same for all membrane types.

The change in permeate flux with time are shown in Fig. 5. It was seen that the flux was significantly affected by the concentration of pollutants in wastewater. The highest steady state flux value was recorded as 17.3 L/m^2 h for NF270 membrane. The flux values of NF90 were lower than those of NF270 and NF245. The lowest flux was obtained as 5.8 L/m^2 h with NF90 membrane. These three membranes were all made of polyamide thin-film composite with different MWCO (Table 1). MWCO of NF270 is 200–300 Da while MWCOs of NF90 and NF245 are 200 Da and 200–400 Da, respectively. NF270 and NF245 membranes have looser structure than the NF90. It was concluded that the pollutants with molecular weight ranging from 200 to 400 Da could pass through the NF270 and NF245; however, NF90 membrane did not allow those molecules to pass through the membrane. Although the permeate quality of NF90 was better than NF270, the flux values of NF90 were lower.

The characteristics of raw water, MBR effluent, and NF permeate are given in Table 5. The biological process was not affected by high sulfate concentration. The COD content decreased from 13,500 to 3,300 mg/L. The sulfate removal efficiencies of NF90 and NF245 reached up to 99%, while NF270 had the worst sulfate removal efficiency amongst three membranes. The average effluent sulfate concentrations were 400, 2,700, and 400 mg/L for NF90, NF270, and NF245, respectively. Conductivity values also showed decreases; however, the decrease in conductivity was not as high as the decrease in sulfate concentrations. This was attributed to the presence of significant amount of monovalent ions in wastewater. Significant reductions in COD were also obtained by all three membranes. The influent COD of 3,300 mg/L reduced down to 50 mg/L, ranging between 50 and 130 mg/L. In light of these findings, NF245 membrane was chosen for the process due to its higher flux values and better removal efficiencies.

3.3. *ED of NF concentrate*

The optimum operating voltage was determined to be 10 V in experiments with synthetic wastewater. However, the effectiveness of ED on the removal of sulfate from NF concentrate was also tested at 15 V. The experiments were performed at a constant voltage of 10 and 15 V and the duration of the process was 140 min. The initial flow rate decreased to 15 L/h under the same conditions as the previous experiments. This was attributed to the existence of high organic content of NF concentrate, causing membrane fouling. The existence of organic substances in the influent water of ED can cause an increase in electrical resistance because of the deposition tendency across the membrane surface [23].

The change in conductivity of the diluate with time and the current density are shown Fig. 6 as a function of time for both 10 and 15 V experiments. The electrical current decreased as a function of time as more ions are removed from the desalting compartments for both experiments. When the applied voltage of the system was 10 V, 98.2% desalination efficiency was achieved and the conductivity value of feedwater was decreased from 68.7 to 1.24 mS/cm. At 15 V,

Table 5
Analysis of raw wastewater, MBR effluent, and NF permeates

	Conductivity (mS/cm)	Sulfate (mg/L)	COD (mg/L)	pH
Wastewater	32	30,780	13,552	5.5
MBR effluent	31.6	29,950	3,287	7.1
NF90 permeate	2.5	400	49.2	7.5
NF270 permeate	8.25	2,700	128	7.8
NF245 permeate	5.5	300	98.4	8.1

Table 6
Analysis results of the wastewater, after nanofiltration membrane and ED process

	NF245 concentrate	ED diluate	ED concentrate
Conductivity (mS/cm)	68.5	1.18	81.6
Sulfate (mg/L)	40,000	1,000	58,000
COD (mg/L)	5,272	6,240	4,912
pH	8.7	5.4	8.4

the conductivity of feedwater was decreased to 1.18 mS/cm from 68.1 mS/cm which corresponded to a desalination efficiency of 98.3%. Meanwhile, the conductivity of concentrate stream increased to 80.2 and 81.6 mS/cm at 10 and 15 V, respectively. It was clear that almost all the sulfate and most of the other ionic species were removed from the diluate stream.

The higher voltage refers to the higher driving force, hence the migration rate of the ions increases. Therefore, the desalination efficiency was slightly better in the first 20–90 min time interval at 15 V with the final removal efficiency remaining around approximately 98% at both 10 and 15 V. The membrane fouling had no direct effect on desalination efficiency.

In Table 6, the characteristics of concentrated flow of NF245 nanofiltration membrane and diluate and concentrate flows of ED process are given. Sulfate concentration in the NF concentrate reduced from 40,000 to 1,000 mg/L. The sulfate removal efficiency was slightly lower than the conductivity removal efficiencies. This was attributed to the larger size of sulfate. Chao and Liang [17] reported similar results as they achieved desalination efficiency of 92%, chloride removal efficiency of 98%, sulfate removal efficiency of 80%, calcium removal efficiency of 99%, and COD removal efficiency of 51% with an ED reversal process and they reported that the process was less efficient in sulfate removal [17]. This was attributed to the larger hydrated radius of sulfate. Sulfate ions undergo a higher resistance during the migration through the membrane [26]. For charged species the transport process results from the combination of diffusion and migration [27].

Time to reach 95% of sulfate removal efficiency was almost the same as 110 min at 10 and 15 V. However, the energy consumption values for the same degree of removal at 10 and 15 V were 6.9 and 10.7 kJ/g sulfate, respectively. These values were substantially higher those obtained using synthetic wastewater. This was attributed to both the existence of other ions as well as the membrane fouling. Membrane fouling likely decreased the ion transfer efficiency across the membrane causing longer durations with high energy consumption. Diluate volumes at the end of experiments (approximately 140 min) were 350 and 400 mL at 10 and 15 V.

The final COD concentration remained as 4,912 mg/L (Table 6). Both experiments showed that sulfate was removed from dilute solution within 140 min. The conductivity value of the concentrate was 81.6 mS/cm and the conductivity value of the diluate was 1.18 mS/cm which corresponded to 98.3% removal efficiency.

4. Conclusion

The results can be summarized as follows.

(1) The experiments conducted using synthetic sodium sulfate solutions showed that increase in applied voltage increased the deionization performance. In the first 40–60 min, the removal efficiencies ranged from 95 to 98%, except for at 5 V experiments. The maximum deionization was achieved at 20 V at all Na_2SO_4 concentration. The removal efficiencies

were 99.4, 99.2, and 99.3% for 20, 30, and 40 g/L of Na_2SO_4, respectively. Ninety-nine percent desalination was obtained within the first 50 min at all three concentrations. Deionization efficiencies were almost the same at all flow rates (20, 30, and 40 L/h). However, deionization rate at 30 and 40 L/h was slightly better than that at 20 L/h. Energy consumption for 95% removal was the lowest at 5 V with linear increase as the voltage increased. However, time to reach 95% of removal efficiency at 5 V was two to three times longer that at 10 V.

(2) Biologically pretreated wastewater was filtered by three different NF membranes to investigate the removal efficiencies of organics and sulfate. The sulfate removal efficiencies of NF90 and NF245 were reaching up to 99%. Conductivity values were also decreased but the decrease was not as high as sulfate concentrations. This was attributed to the presence of significant amount of monovalent ions in wastewater. Significant reductions in COD were also obtained by all three membranes.

(3) The deionization efficiency was around 98% at both 10 and 15 V for the ED of NF concentrate. In addition, membrane fouling had no direct effect on desalination efficiency. However, the energy consumption and time to reach 95% efficiency increased substantially, which was attributed mainly to the membrane fouling and the existence of other ions.

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