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Generation of acid–base by bipolar membrane electrodialysis process during desalination of pesticide containing wastewater

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ABSTRACT

The high salinity pesticide wastewater was generated during the production process of 2,6-Difluorobenzamide (DB), which would cause a severe environmental pollution problem. In this study, BP-A-C-BP style bipolar membrane electrodialysis (BMED) process was applied for the zero-liquid discharge of pesticide wastewater. The end point of BMED process, the effect of operational voltage, and initial concentration of base and acid were investigated. The membrane fouling analysis has further verified the feasibility of the BMED process on the recovery of DB from pesticide wastewater. The results indicated that when the operational voltage 30 V and initial concentration of acid and base 0.10 mol/L, 99% of Na_2SO_4 was removed and 97% of DB was recovered. The energy consumption and current efficiency of BMED process were 2.89 kWh/kg Na_2SO_4 and 79.82%, respectively. Thus, BMED was a suitable method for DB recovery and desalination of pesticide wastewater with the aim of zero discharge and resource recycling in industrial application.

Keywords: Bipolar membrane electrodialysis; Reclamation of 2,6-difluorobenzamide; Industrial wastewater treatment; Zero liquid discharge process

1. Introduction

Fluorinated benzoylurea insecticides (FBUs), a novel broad-spectrum pesticide that possesses the ability to interfere with the synthesis of chitin in target pests, is widely used in the world for controlling numerous pest species because of its insecticidal activities, tremendous selectivity, and rapid degradation [1]. During the past two decades, the FBUs have received extensive attention and occupied 12% of the global agrochemical market. Due to the rapid development of FBUs, 2,6-difluorobenzamide, which is the most significant intermediate in the synthetic process of FBUs, has gained widely attention as well. The chemical structure of 2,6-difluorobenzamide is shown in

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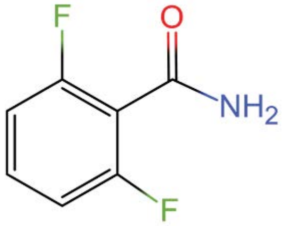

Fig. 1. Chemical structure of 2,6-difluorobenzamide.

Fig. 1, can cause water pollution after entering the water body. However, as the important pesticide intermediate the demand for 2,6-difluorobenzamide will achieve more incensements in the coming years.

At present, the synthesis methods of 2,6-difluorobenzamide mainly include the hydrolysis of 2,6-difluorobenzonitrile and ammonolysis of 2,6-difluorobenz and its derivatives. Both synthesis processes contain acid–base neutralization reaction, and thus large amounts of pesticide wastewater which occupied as 0.5% 2,6-difluorobenzamide and 2.5% Na_2SO_4 were generated during the production process 2,6-difluorobenzamide [2]. If the pesticide wastewater was discharged directly, it would not only waste the high value-added pesticide intermediate, but also lead to chronic exposure and long-term toxicity effects in the environment.

Conventionally, the evaporation crystallization or mechanical vapor recompression (MVR) were applied in the treatment of pesticide wastewater. The processes were generally considered to be effective in the removal of organic pollutants in the pesticide wastewater and the quality of produced water commonly met the industrial wastewater emission standards [3]. Nevertheless, the high energy consumption, high capital, further solid waste management, and toxic chemical by-product generated during the process severely delays their development and application [4]. In recent years, the pressure-driven membrane processes, such as ultrafiltration, nanofiltration, and reverse osmosis, have formed the second trend of widely used technologies for the 2,6-difluorobenzamide and inorganic components removed from the pesticide wastewater [5]. Although the produced water quality has been greatly improved to a great extent compared with the conventional processes, the membrane fouling and concentrated wastewater after the processes containing higher 2,6-difluorobenzamide and sodium sulfate level after the processes requires further consideration. Therefore, it is urgent to find out an eco-friendly technique to reclaim 2,6-difluorobenzamide from the pesticide wastewater.

Electrodialysis (ED) technology is a solution concentration and desalination technology developed in recent years. The ED stack consists of anion and cation exchange membranes (CEMs) arranged alternately between the cathode and anode [6]. Previous research successfully used ED to recover sodium carbonate and sodium bicarbonate from Lake Van [7]. Lin et al. [8] demonstrated the feasibility of using ED combined with a separate recovery system to recover phosphorus from wastewater, achieving a phosphate removal efficiency of 93%. Liu et al. [9] demonstrated that with the applicability of electrodialysis, the L-phenylalanine recovery and salt removal can reach up to 84.3% and 98.5%, respectively. Literature and research proved that proof ED is an energy-saving and environmentally friendly technology that had been widely used in water desalination, resource recycling, and environmental protection. With the development of membrane processing technology, people have produced a composite membrane with a CEM on one side and an anion exchange membrane (AEM) on the other side, and found that this membrane can promote the electrolysis of water during the electrodialysis process. It is called a bipolar membrane. The electrodialysis technology in which bipolar membranes and anion and CEMs are alternately arranged to form a membrane stack is called bipolar membrane electrodialysis (BMED).

BMED is a new type of electrodialysis technology developed based on ion-exchange membrane. Its advantage is that it can split water into H^+ and OH^- and then produce acid and base from the corresponding salt under the direct electric field [10]. BMED attracted more and more attention from all over the world since it was incipiently adapted to the practical industrial application in 1980s. A large amount of [11] experiments had been conducted using BMED technology for the production of organic acids in the previous research. It was reported that alpha-ketoglutaric acid could be produced by using an environmentally friendly EDBM process at a high concentration of 4.83 g/L with high current efficiency and low energy consumption, equal to 71.8% and 3.72 kWh/kg, respectively. Lameloise and Lewandowski [12] investigated the influence of different stack cell configurations on the production of organic acids by the BMED process. The results indicated that the two compartment cell configuration were viable to increase the concentration of aldonic acid to a satisfactory level and the multichambered cell configuration stack was more suitable to produce gluconic acid due to lower energy consumption, higher current efficiency, and higher conversion rate [13]. In recent years, as the increasingly serious growing of water resource shortage and industrial water pollution, much more attention has been paid to the application of BMED technology in the treatment of industrial effluents. It was reported that simulated ammonium chloride wastewater could be treated by a lab-scale BMED for the generation of HCl and $NH_3{\cdot}H_2O$ and desalination. The highest concentration of HCl and $NH_3{\cdot}H_2O$ was 57.67 and 45.85 g/L, respectively, at the current density of 48 mA/cm^2 and initial NH_4Cl concentration 110 g/L [14]. The metal washing step water could be treated by BMED for the regeneration of inorganic acid and base and the concentration of acid and base was up to 1.76 and 2.41 mol/L, respectively [15]. These studies presented that BMED technology had a favorable application prospect in organic acid preparation and industrial saline wastewater treatment. However, the related researches and reports on the pesticide wastewater treated by BMED technology have not been found up to now.

In this study, the pesticide wastewater was treated by a lab-scale BMED for the generations of acid and base and desalination simultaneously. The H_2SO_4 and NaOH generated in the BMED could be reused in the synthesis process of 2,6-difluorobenzamide. Whilst the reclaimed 2,6-difluorobenzamide solution could be applied in the synthesis process of FBUs directly. A zero liquid discharge process was then formed. The influence of operational voltage, initial acid, and base concentrations on the treatment of pesticide wastewater by BMED were investigated. The current efficiency, energy consumption, acid, and base concentration, recovery of 2,6-difluorobenzamide and the membrane fouling were examined to test the application feasibility of BMED process in the treatment of pesticide wastewater and the optimized conditions of the system were obtained.

2. Materials and methods

2.1. Reagents and membranes

The following reagents were used in the experiments: sodium sulfate (Sinopharm Chemical Reagent Co., Ltd., Beijing), 2,6-difluorobenzamide (Macklin Biochemical Technology Co., Ltd., Shanghai), sodium hydroxide (Sinopharm Chemical Reagent Co., Ltd. , Beijing), sulfuric acid (Merck Serono Co., Ltd., China), methyl orange (Sinopharm Chemical Reagent Co., Ltd., Beijing), phenolphthalein (Guangfu Fine Chemical Research Institute), absolute ethyl alcohol (Fuyu Fine Chemical Co., Ltd. , Shanghai). All the reagents are analytical pure and de-ionized water (Millipore Milli-Q 18 MΩ) was used throughout the experiment. The main components of wastewater are 2,6-difluorobenzamide and sodium sulfate (the concentration are 3.2×10^{-2} and 0.18 mol/L, respectively).

Three ion exchange membranes (CEM, AEM, and bipolar membrane) were used in the experiment. CEM and AEM were purchased from ASAHII Glass Co., Ltd., Japan. The bipolar membrane (BM) was provided by the Beijing Tingrun Membrane Technology Co., Ltd., China. The main characteristics of ion exchange membranes provided by the manufacturers are presented in Table 1.

2.2. Experimental set-up

In this paper, a laboratory-scale experimental BMED apparatus provided by Beijing Tingrun Membrane Technology Co., Ltd., China was used to perform the experiment. The style of bipolar membrane configuration in this study was BM-A-C-BM namely four-compartment electrodialysis system which includes base, salt, acid, and electrode compartments. It can be seen from Fig. 2 that sodium hydroxide solution, the pesticide wastewater, sulfuric acid solution, and electrode rinsing solution were circulated in the separated circuits which contains a 2 L tank, a rotameter, and a gauge driven by four peristaltic pumps. Each ion exchange membrane has an effective surface area of 100 cm^2 and the membrane triples were five in the stack. The thickness of the spacers between two membranes was 0.5 mm. The titanium electrode coated with ruthenium was applied as both the anode and cathode and 0.2 mol/L sodium sulfate solution were used as electrode rinsing solution for all experiments.

2.3. Sample analysis

The samples from the different BMED compartments were taken every 2.5 min. The conductivity of the pesticide wastewater was continuously measured with an YSI conductivity meter (DDS-307A, Shanghai Instrumental Analysis Scientific Instrument Co., Ltd., Shanghai). The concentration of the 2,6-difluorobenzamide in the salt compartment was measured with a spectrophotometer (UV2450, Shimadzu Corporation Ltd., Japan) at wavelength 289.5 nm. SO_4^{2-} concentration was measured with ion chromatography (ICS-900, Dionex, HITACHIS, Shanghai). The acid concentration was determined by titration method with a standard sodium hydroxide solution (1 mol/L) using phenolphthalein as indicator. Similarly, base concentration was determined using a standard hydric sulphate solution (1 mol/L) with methyl orange indicator. The fouling of bipolar membranes and ion exchange membranes was analyzed by scanning electron microscopy (SEM, HITACHIS-4800).

2.4. Data analysis

The efficiency of sodium sulfate removal by BMED process was calculated as Eq. (1) shows:

$$\eta_{Na_2SO_4} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

Similarly, the coefficient of 2,6-difluorobenzamide recovery after BMED process was calculated as Eq. (2) shows:

$$\eta_{DF} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \tag{2}$$

where C_0 is the initial sodium sulfate concentration of pesticide wastewater (mol/L), C_t is the sodium sulfate concentration of pesticide wastewater at time t (mol/L). C_{in} is the initial 2,6-difluorobenzamide concentration of pesticide wastewater (mol/L), and C_{out} is the concentration of 2,6-difluorobenzamide after desalination of BMED process (mol/L).

The energy consumption and the current efficiency are the significant parameters for evaluating the performance of BMED used in recovery of 2,6-difluorobenzamide from

Table 1
Main characteristics of ion exchange membranes used in the experiment

Membrane	Model number	Thickness (mm)	Area resistance (Ω·cm^2)	Transport number	Burst strength (kPa)	Water splitting voltage (V)	Ion exchange capacity (mol/kg)
CEM	Selemion standard	0.12	3.0	>0.96	200	–	2.0–2.5
AEM	Selemion standard	0.12	2.8	>0.96	200	–	2.0–2.5
BM	TRJBM	0.16–0.23	–	–	250	0.8–2.0	/

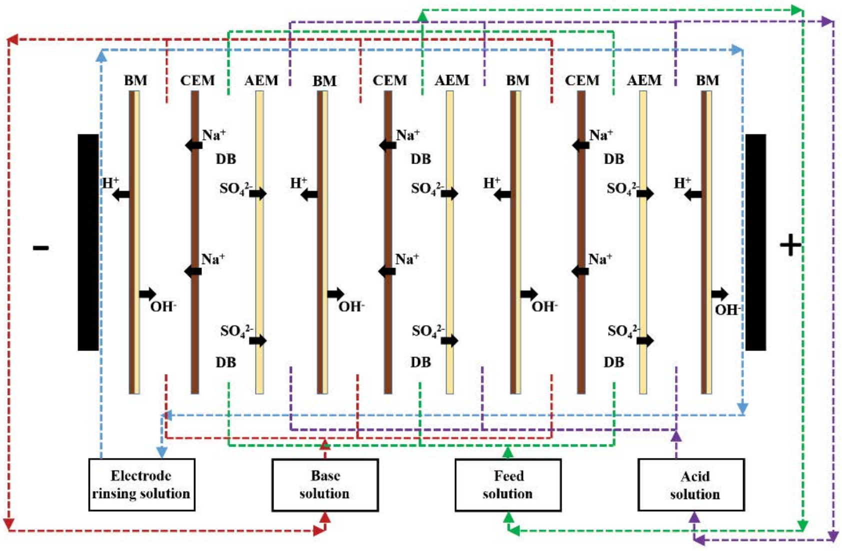

Fig. 2. Schematic diagram of the cell configuration of BMED stack.

pesticide wastewater. The energy consumption was calculated as Eq. (3).

$$E = \frac{\int_0^t UIdt}{60M\left(C_t V_t - C_0 V_0\right)} \quad (3)$$

where E is the energy consumption (kWh/kg), U is the potential across the membrane stack (V), I is the current (A), t is the time (min), M is the molar weight of sodium sulfate, acid/base (g/mol), C_t and C_0 (mol/L) are the concentration of acid, base and sodium sulfate in the acid, base and salt compartment at time t and 0, respectively. V_t and V_0 are the volumes of the solution at time t and 0.

The current efficiency was calculated as Eq. (4) shows:

$$\text{CE} = \frac{z\left(m_t/M\right)F}{nIt} \times 100\% \quad (4)$$

where CE is the current efficiency, z is the ion valence, m_t is the weight of the transferred ion (g), M is the molar mass of the ion (g/mol), F is the Faraday constant (96,500 C/mol), n is the number of cell pairs, I is the current (A), and t is the time (s).

2.5. Experimental procedures

The pesticide wastewater was circulated in the salt compartment and different concentrations of H_2SO_4 and NaOH solutions were circulated through acid and base compartments respectively driven by different pumps at a constant flow rate of 15 L/h in the BMED system. A 0.2 mol/L Na_2SO_4 solution was circulated through the electrode compartment as electrode rinsing solution at flow rate of 50 L/h. Ten-milliliter pesticide wastewater, acid solution, and base solution samples were taken from salt compartment, acid compartment, and base compartment, respectively, every 2.5 min. The fouling of bipolar membranes, AEMs and CEMs were analyzed by SEM.

3. Results and discussion

3.1. Determination of the end point of the BMED process

The purpose of the experiment is to reclaim the 2,6-difluorobenzamide from the pesticide wastewater for the larger molecular radius and lower valence compared to SO_4^{2-}. We are looking forward that the sodium sulfate which impedes the synthesize of the FBUs could be reduced as much as possible. The variation of the solution concentration in each compartment will lead to the rise of stack resistance of BMED [16]. In Fig. 3, the energy consumption and conductivity of the BMED process have been demonstrated. The energy consumption almost remains stable during first 25 min at constant voltage mode though the conductivity of the pesticide wastewater decreases continuously. The main reason is that the exhaustion of salt solution leads to the increase in the resistance of salt compartment while the increase in acid/base concentration results in a decrease in the resistance of acid/base compartment. Therefore, the constant electrical resistance of stack leads to a constant current density. Finally, the almost constant energy consumption was obtained. However, after the salt content becomes inadequate for maintaining the constant current density with the previously stable voltage, the energy consumption increases abruptly.

Fig. 4 shows that the concentrations of acid and base generated during the BMED were increased generally when the initial acid/base concentrations were 0.1 mol/L under an operating voltage of 30 V. It can be found that the yields of acid and base increased identically at the beginning of the experiment. After that, the base concentration was always higher than acid concentration due to the proton leakage of the AEM. That is, the protons can be easily transported across AEM by the so-called tunnel transport mechanism which is practically in agreement with the recent researches [17]. It was shown that the concentrations of acid and base remained constant after 25 min. The main reasons should be that (1) the decrease of salt concentration in the pesticide wastewater and (2) more OH^- and H^+ in the base/acid compartment increased the driving force for diffusion according to Fick's first law [18]. Above all, the point at 25 min which is called the "inflection point" should correspond to the bottom line of the salt content when the conductivity was 1 ms/cm and the removal rate of Na_2SO_4 was 99.2% for the BMED process.

3.2. Effect of operational voltage

The effect of different operational voltages (15, 20, 25, 30, and 35 V) on conductivity, current density, acid/base yield, current efficiency, and energy consumption in the BMED process were examined at the initial acid/ base concentration 0.1 mol/L. It is shown in Fig. 5a that the conductivity of the solution in the salt compartment decreased gradually at different voltages to the inflection point concentration 1 ms/cm which was proved to be the bottom line of BMED process in the last section, suggesting that Na_2SO_4 in the salt compartment had been almost depleted at the end of the experiments. It illustrated that the proper increase of operational voltage was helpful to shorten the operation time [19].

Fig. 5b presents the variation of current density at different operational voltages in the BMED system. It was found that the higher operational voltage was a favor to increase the current density according to Ohm's law [20]. The variations of current density at different operational voltages were similar. They were increased to a local maximum and then gradually decreased until the end of the experiments. The main reason should be that the initial concentrations of acid and base were relatively low, which resulted in the higher membrane stack resistance in the BMED system at the beginning of the experiment. Along with the yield of acid and base, the resistance of the membrane stack was decreased and led to an increase of the current density. When the decrease of the acid/base compartment resistance resulted from the increase in acid/base concentration was equal to the increase of salt compartment resistance resulted from the exhaustion of salt solution, the maximum was reached. After that, the continuously increase of salt compartment resistance and high concentration gradient increased the membrane stack resistance and reduced the ions' electrical migration [21]. The current density was then decreased gradually.

Fig. 6 shows the effect of the operational voltage on the yield of base and acid in the BMED process. It was found that the proper increase of operational voltage was helpful to improve the performance of BMED process to produce base and acid. The base and acid concentrations were increased from 0.306 to 0.32 mol/L and 0.195 to 0.225 mol/L, respectively, as the operational voltage was increased from 15 to 35 V. The main reason should be that higher operational voltage increased the mass transfer rate of Na^+ and SO_4^{2-} ions through the ion exchange membrane. Moreover, the higher operational voltage split more water into protons and hydroxide ions at the surface of bipolar membrane according to the Second Wien effect [22].

Fig. 7 presents the energy consumption and current efficiency at different operational voltages during the BMED process. It is well-known that the energy requirements are mainly resulted from water dissociation and ion migration through ion exchange membranes and solution. A large part of the total electrical energy was consumed to overcome the electrical resistance as the operational voltage increased. That is the main reason that energy consumption will be improved with the increase of the operational voltage [23]. It was observed that the current efficiency of the BMED process was increased when the operational voltage was increased from 15 to 30 V. The highest current efficiency occurred at the operational voltage was 30 V when the removal of Na_2SO_4 was 79.82% and the yield of base/acid were 52.75% and 57.54%, respectively. This should be mainly attributed to the higher operational voltage which could accelerate the transmembrane migration of ions and the dissociation of water. Moreover, the higher operational voltage was favorable to inhibit reverse diffusion of ions, especially at the end of the experiments when there was a large concentration gradient between the adjacent compartments of salt and base/acid. However, the exorbitant

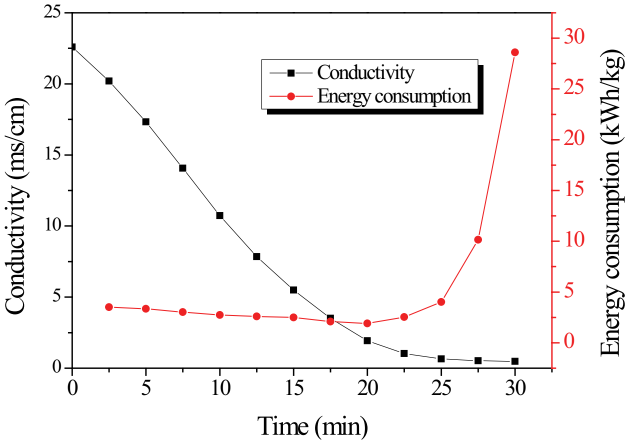

Fig. 3. Relation between the conductivity and energy consumption of the pesticide wastewater at the end of the BMED process at 30 V.

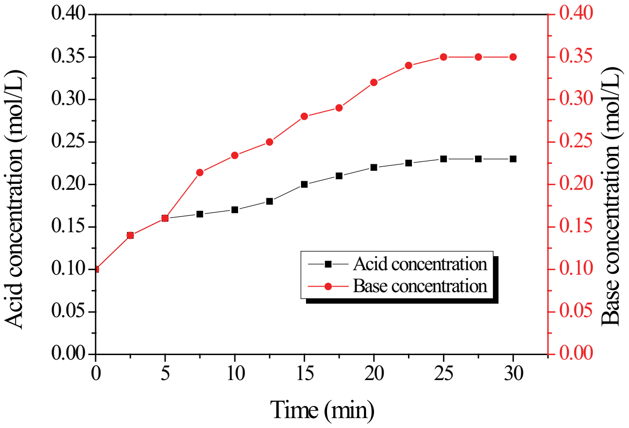

Fig. 4. Concentration of acid and base generated from pesticide wastewater by BMED.

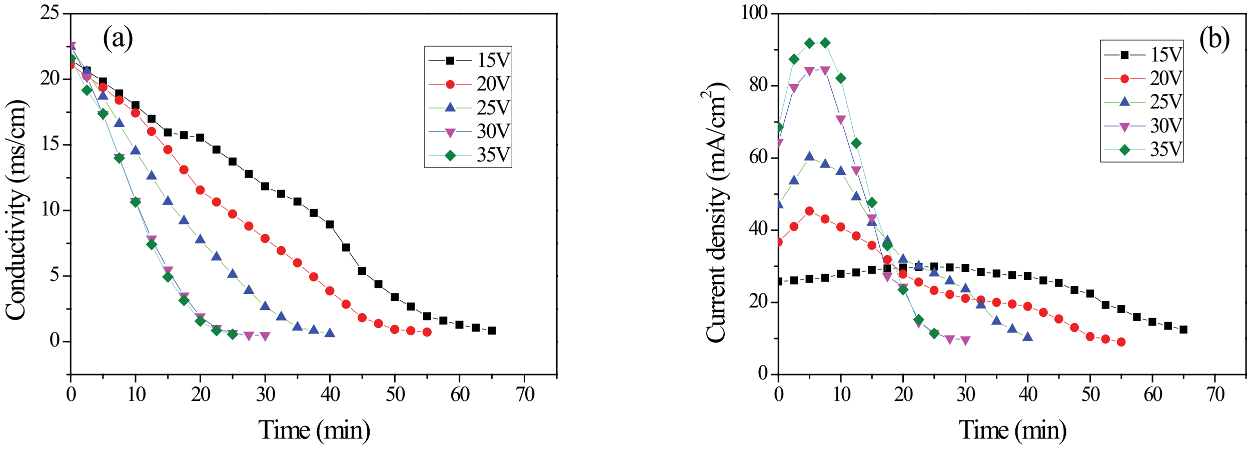

Fig. 5. Conductivity (a) and current density (b) of the BMED process under different operational voltages.

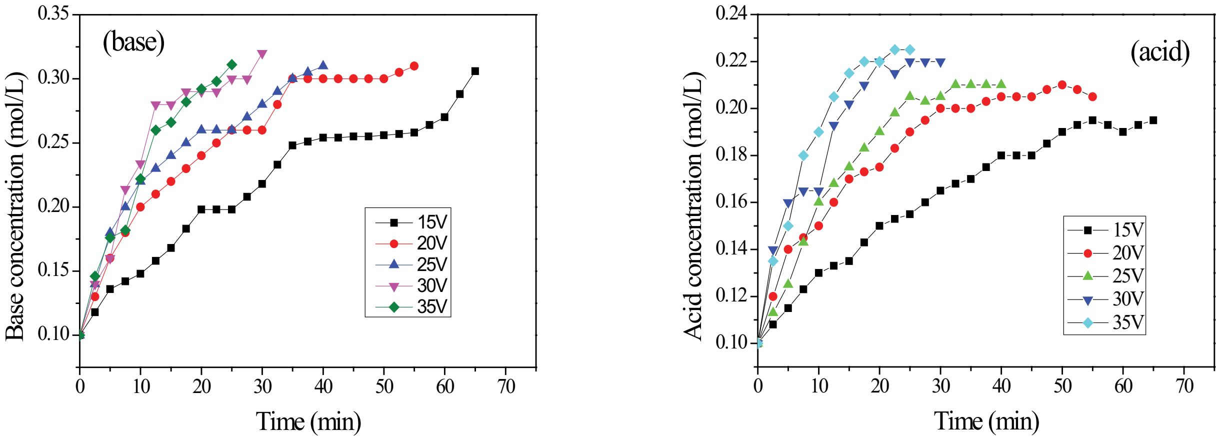

Fig. 6. Concentrations of acid and base generated by BMED process at different voltages with initial acid/base concentration 0.1 mol/L.

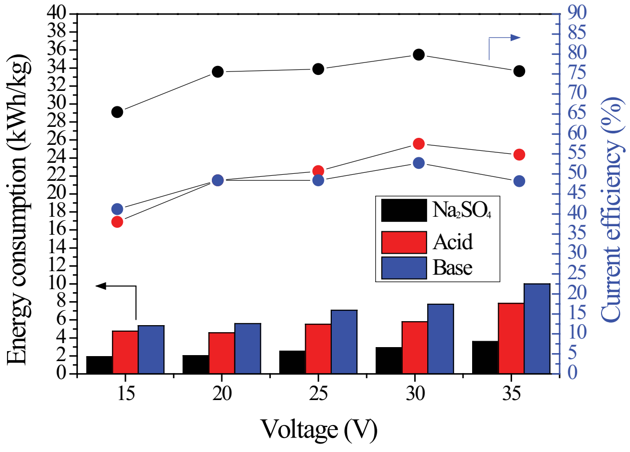

Fig. 7. Current efficiency and energy consumption of BMED process with different operational voltages.

operational voltage can exceed the limiting current efficiency which leads to the occurrence of side reactions and high energy consumption. It is proved in Fig. 6 that the current efficiency was decreased and the energy consumption was increased in the BMED process after the operational voltage exceeding 30 V. It was easy to understand that the appropriate high operational voltage was suitable for BMED process because it will not only increase the treating ability to pesticide wastewater but also reduce the investment cost. Therefore, the 30 V was chosen to be the optimized operational voltage after a comprehensive consideration.

3.3. Effect of initial concentration of base and acid

The experiments with 0.05, 0.10, 0.15, and 0.20 mol/L acid/base were taken at operational voltage 30 V to investigate the influence of initial concentration of base and acid on the BMED process. It can be found from Fig. 8a that the operation time was shortened when the initial concentration of acid/base increased from 0.05 to 0.10 mol/L. It was because the proper increase of initial concentration of acid/base was could decrease the electrical resistance of membrane stack and accelerate the ions transmembrane migration. However, when the initial acid/base concentration continuously increased, the salt removing dropped again. This was mainly caused by the high concentration gradient between the adjacent compartments. Fig. 8b shows the effect of the initial concentration of acid/base on the

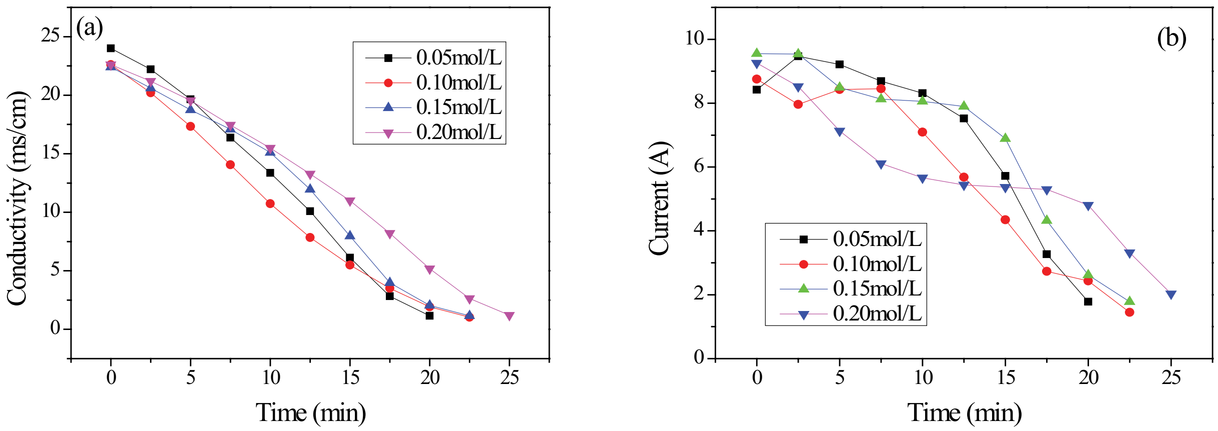

Fig. 8. Conductivity (a) and current density (b) of the BMED process with different initial base and acid concentrations.

current density during the BMED process. At the beginning of the experiment, the initial current densities were improved with the increase of initial concentrations of acid/base due to the low concentration of acid/base, which led to a high electrical resistance. After that, the concentration of split protons and hydroxide ions at the interface layer of the bipolar membrane was increased as a function of time under the electrical field, resulting in a high concentration gradient between the acid/base and salt compartments. The opposite potential reduced current densities until the end of the experiments.

Fig. 9 shows the effect of the initial concentration of acid/base on the acid/base yield. It could be seen that the higher initial concentrations of acid and base helped to get a higher concentration of final acid and base concentration. However, the acid yield was decreased slightly as the initial acid concentration was increased. This was caused by the fact that protons leaked through the AEM under the high concentration gradient between the adjacent compartments. The base yield was increased at the beginning of the experiment and then decreased after the initial base concentration exceeded 0.10 mol/L. The decrease was also caused by the ions back diffusion from the base compartment to the salt compartment. The increase was due to the lower leakage of hydroxide through the CEM than proton through the AEM [18]. Therefore, the higher initial concentration of acid and base may be a method to increase the concentrations of acid and base generated with BMED, but it was not a suitable way to improve the yield of acid and base from pesticide wastewater [24].

Fig. 10 shows that the current efficiency was increased with the initial concentration of acid and base increased from 0.05 to 0.10 mol/L. It has already been attributed to the proper increase in initial concentration of acid and base could decrease the transfer resistance of the membrane stack. Therefore, more current was used for ion migration rather than overcoming the electrical resistance. So that the current efficiency increased. Along with the continuous increase of initial concentration of acid and base, the high concentration gradient between the adjacent compartments could cause the ions back diffusion from acid and base compartments to salt compartment [21]. This was the main reason that the current efficiency was decreased with the increase of initial concentration of acid and base when it exceeded 0.10 mol/L. Although the current density decreased with the operate time, the acid and base yields

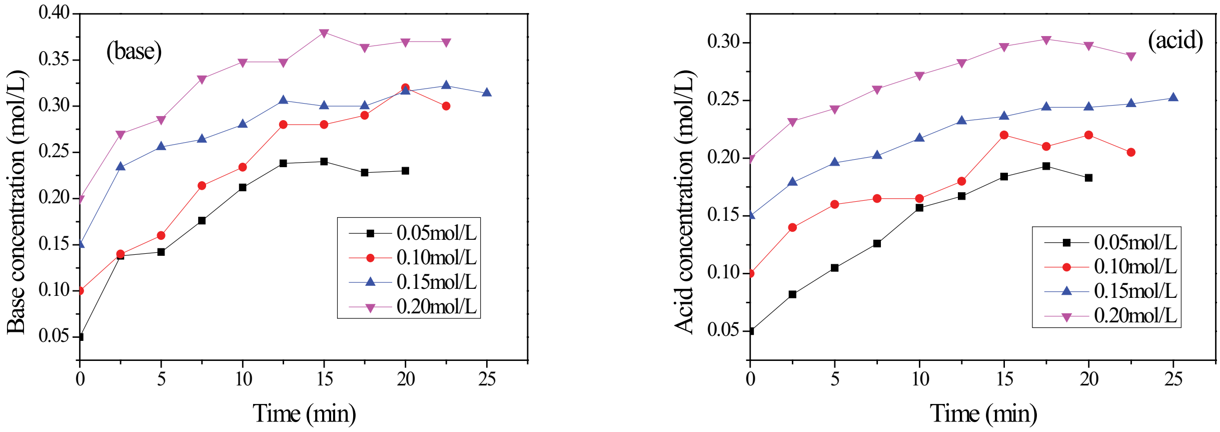

Fig. 9. Concentrations of acid and base generated by BMED process at different initial acid/base concentrations with voltage 30 V.

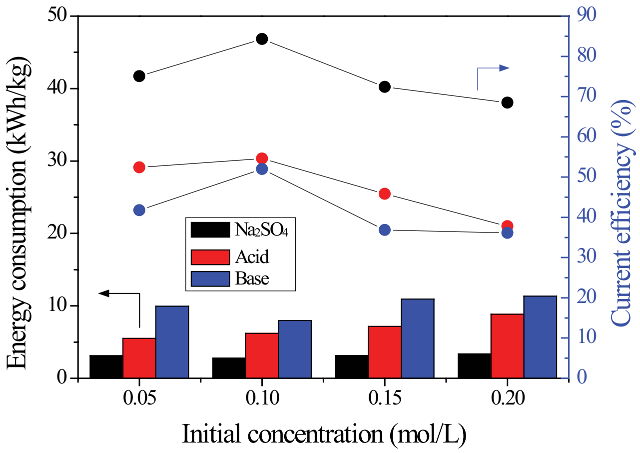

Fig. 10. Current efficiency and energy consumption of BMED process with different initial concentrations of acid and base.

were also decreased. Therefore, the energy consumption of BMED process with different initial concentrations of acid and base was almost constant, which is shown in Fig. 10.

3.4. Overview of the performance of BMED process for 2,6-difluorobenzamide recovery

The BMED process had been proved to be feasible and efficient to produce acid and base from pesticide wastewater. However, the recovery of DB from the produced wastewater with inorganic salts was the core of the BMED process, with no related experiments and research reports. In order to evaluate the feasibility of the BMED process for DB recovery from pesticide wastewater, the performance of the BMED process was summarized in Table 2.

Table 2 presents the DB recovery by BMED process which was around 97% and the removal rate of Na_2SO_4 which was above 99%. The content of Na_2SO_4 was around 0.3% in the pesticide wastewater after treating by BMED process, which was acceptable for industrial application. Furthermore, the produced acid and base had a high purity and only traces of DB were present in the acid and base compartments of BMED process. Due to the weakly charged characteristics of DB which was allowed to transfer through ion exchange membranes by diffusion [21], the base solution contained a larger amount of DB than the acid solution. Therefore, the high DB recovery and removal of Na_2SO_4 indicated that BMED process has the technical potential for DB recovery from pesticide wastewater and wastewater desalination.

3.5. Fouling investigation of ion exchange membranes

The membrane fouling is a significant limitation for BMED process due to the fouling on the membrane surface which would block the gallery between membrane functional group and solutions and then increase the membrane area resistance. To investigate the membranes fouling during the BMED process, the SEM was used to observe the morphology changes of bipolar membranes, CEMs and AEMs after finishing the experiments. Fig. 11 presents the SEM images of BM used in the membrane stack at cation side (a) and anion side (b). There was rarely no change on the both sides of BM surface pre-and post the experiments. The reasons should be that, on the one hand, there was traces of DB in the acid and base compartments and on the other hand, it confirmed the BM has anti-fouling ability toward DB ions [25].

It was found from Fig. 11 that CEMs were polluted heavily than AEMs during the treatment of pesticide wastewater by BMED process. This was caused by the fact that the DB ions possess positive electricity which made them migrate to the surface of CEMs under the direct current electrical field. Due to the sieve effect of the CEM, the DB ions could not pass through the CEMs and then enriched on the surface of the CEMs. However, the fouling of ion exchange membranes didn't significantly affect the current efficiency and energy consumption of the BMED process. Almost all of DB ions on the surface of CEM and AEM were removed after backwash. This indicated that the DB ions had not entrapped inside the membranes. Therefore, both CEM and AEM which exhibited excellent anti-fouling property, high desalination efficiency and DB recovery ratio were suitable for the treatment of pesticide wastewater.

Table 3 shows the change of AM and CM in the experiment. It can be seen from the table, no matter the AM or the CM, the ion mobility of the membrane drops significantly after use. After the backwash, the ion mobility recovered and this also proved that DB ions had not entrapped inside the membranes. To a certain extent, it reflected the pollution of the membrane during the experiment. Table 4 also illustrated this issue. Since DB will accumulate on the membrane surface during the experiment, it will also cause a slight increase in membrane resistance. Similarly, after scouring, the membrane resistance returned to its original level, demonstrating the better anti-pollution ability of the ion exchange membrane for DB ions.

Table 2
Performance of BMED process for 2,6-difluorobenzamide recovery with various initial concentrations of acid and base at 30 V

Initial concentration of acid and base (mol/L)	DB recovery (%)	SO_4^{2-} in the salt compartment (%)	Acid compartment DB content (%)	Base compartment DB content (%)
0.05	97.1	0.31	0.0032	0.014
0.10	97.8	0.34	0.0023	0.018
0.15	96.9	0.33	0.0036	0.011
0.20	97.4	0.35	0.0025	0.014

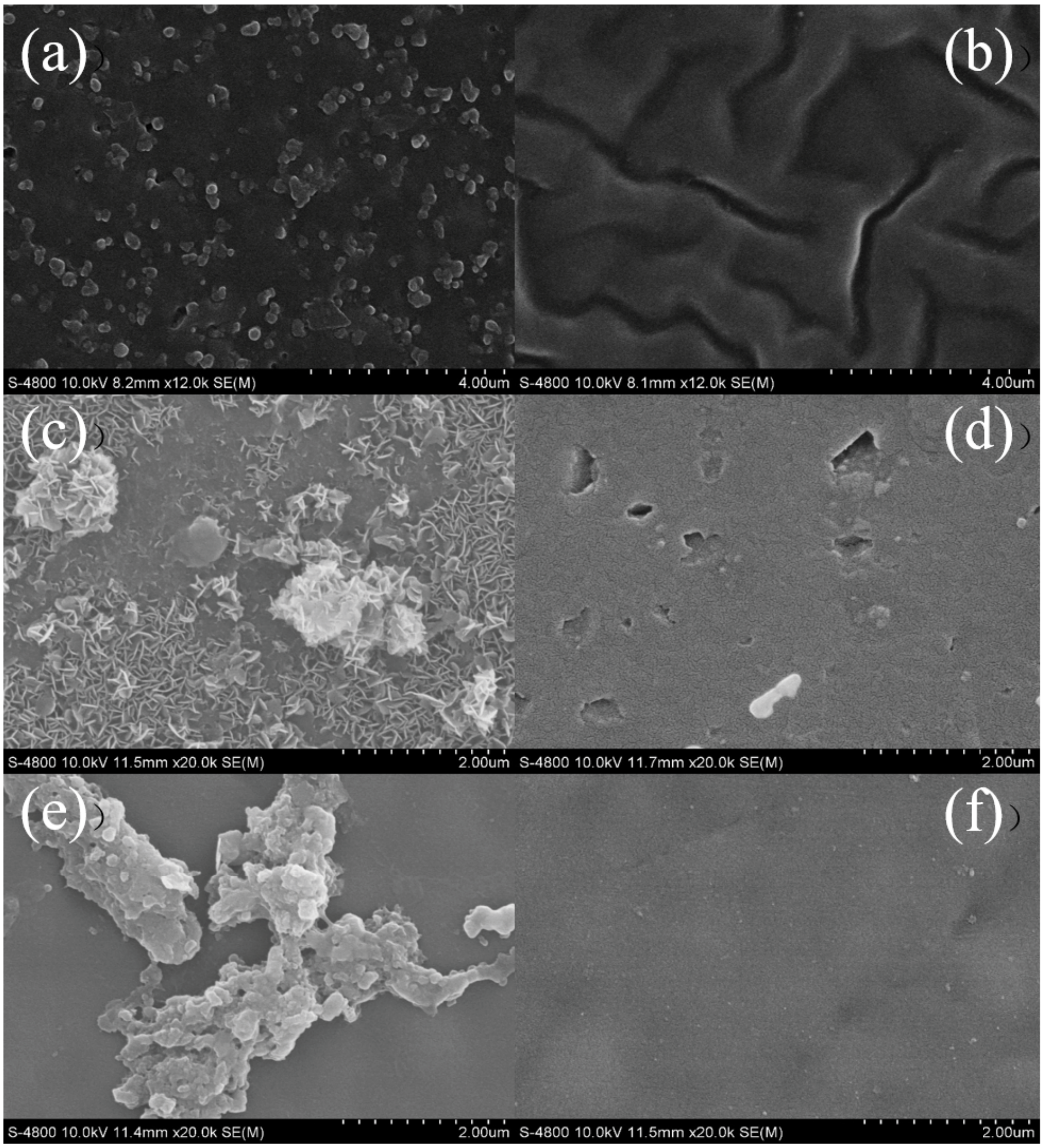

Fig. 11. SEM images of BM, CEM, and AEM in the treatment of pesticide wastewater by BMED process and after the backwash. (Cation side (a) and anion side (b), polluted CEM (c), CEM after backwash (d), polluted AEM (e), and AEM after backwash (f).

Table 3
Ionic mobility of AM and CM in the experiment

	Before use	After use	After backwash
Ion mobility (AM)	0.948	0.942	0.947
Ion mobility (CM)	0.985	0.971	0.983

Table 4
Area resistance of AM and CM in the experiment

	Before use	After use	After backwash
Area resistance (AM) Ω/cm	2.57	3.21	2.56
Area resistance (CM) Ω/cm	2.39	3.49	2.40

4. Conclusion

The application feasibility of a lab-scale BMED system in pesticide wastewater treatment was proved in this study. The zero-discharge process was created for the reclamation of 2,6-difluorobenzamide and production of H_2SO_4 and NaOH. The influence of operational voltage and initial concentration of acid and base on the DB recovery ratio, desalination ratio, and acid/base yield were investigated by the analysis of absorbance of the solution, the conductivity, and acid/base concentration, respectively. The membrane fouling was also investigated by SEM analysis. The results indicated that at an operational voltage 30 V and initial concentration of acid and base 0.10 mol/L, the energy consumption was 2.89 kWh/kg Na_2SO_4 and the current efficiency was 79.82%. The DB recovery was more than 97%, whilst the desalination ratio could be above 99%. The H_2SO_4 and NaOH with high purity could be recycled to synthesis 2,6-difluorobenzamide and produce downstream products. The membrane fouling analysis further proved that the CEM, AEM, and BM were suitable for the treatment of pesticide wastewater by BMED with excellent anti-fouling property, high desalination efficiency, and DB recovery ratio. It was concluded that the BMED is a feasible and environmental process for the application of DB recovery. This process may also be applicable for the wastewater with high salt concentration from the other industrial fields.

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