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An economical process to recover sulfuric acid and tetrabutylammonium ions from acidic saline wastewater with organics

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ABSTRACT

Wastewater containing high contents of salt, organics, acids, or other compounds pollutes the environment. It is necessary and important to treat wastewater and recover reusable materials before the discharge. Diffusion dialysis (DD), electrodialysis (ED) and bipolar membrane electrodialysis (BMED) are combined in three different ways in this study. These methods are compared on their operating time, energy consumption, as well as recovery of sulfuric acid and tetrabutylammonium (TBA) ions. Results suggest that DD-ED-BMED is the best combination with the shortest operation time and least energy consumption. The recovery of sulfuric acid reaches 99.6%, while that for TBA^+ is 93.1%. An economical evaluation is discussed. To minimize the total cost of treating 150 L wastewater per hour, the total membrane area of DD process needs to be 179.4 m^2. Total membrane area for ED process is 85.61 m^2. For BMED process, 27.43 m^2 of bipolar membrane and 54.86 m^2 of anion exchange membranes and cation exchange membranes should be used. In this case, the total cost would be 142,474 \$/year, of which equipment investment is 71,292 \$/year and electricity is 71,182 \$/year. Sulfuric acid and TBAOH can be recovered with 315.1 ton/year and 37.40 ton/year, respectively.

Keywords: Diffusion dialysis; Electrodialysis; Bipolar membrane electrodialysis; Sulfuric acid recovery; Tetrabutylammonium ion recovery

1. Introduction

A large amount of acid saline wastewater is generated from industrial process of manufacturing soda, food, medicine and petrochemicals. Discharging this type of wastewater without prior treatment is known to threaten people's health, water quality and agriculture [1]. Conventional treatment of acid saline wastewater is physical–chemical method. Base is first added to the wastewater to react with the acid and produce salt. Then, mechanical vapor recompression method is used to remove the salt. However, the treating cost is particularly high and useful resources are wasted. Nowadays, electrodialysis (ED) and bipolar membrane electrodialysis (BMED) are popular for saline wastewater treatments with following advantages [2]: easy operation, environmental friendly, waste salt utilization and low energy consumption. For ED process, ions can move in certain direction under the electrical field applied between two electrodes. Negative ions pass through the anion exchange membrane (AEM) and are blocked by cation exchange membrane (CEM), while that for positive ions are opposite. Consequently, ions can be removed from dilute compartments and collected in concentrate compartments. Benvenuti et al. [3] applied a lab-scale ED system for nickel salt recovery from a synthetic nickel electroplating effluent. They found that the energy consumption to recover nickel from rinsing waste would be 0.7 kW·h for every kilogram of $NiSO_4{\cdot}6H_2O$. Abou-Shady et al. [4,5] used ED process to reduce Pb^{2+} concentration from 600 to 15 mg/L in dilute solution, and increase Pb^{2+} concentration to 2,600–3,000 mg/L in concentrate solution. They also suggested that at pH 3–5 and voltage of

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10 V the energy consumption is only 0.25 kW·h/L. Kabay et al. [6,7] used ED process to separate the monovalent and divalent ions from binary and ternary mixtures. All the studies show that ED process can efficiently separate and recover different types of ions. Bipolar membrane electrodialysis (BMED) is a type of electrodialysis method with bipolar membrane (BM) in the membrane stack. Water can be split into H^+ and OH^- at the interface of BM [8]. The H^+ ions remain in acid compartments and OH^- ions remain in base compartments. Meanwhile, anions and cations transfer from salt compartments to the acid compartments and base compartments, respectively, under the electrical field. Thus, in BMED stack, conjugate acid and base are produced from the original salt solution without adding new compounds. Furthermore, in the cathode compartment, H^+ ions dissociated in the BM react with OH^- ions from H_2O reduction reaction on the electrode surface to reproduce water. Similarly, water is also reproduced in the anode compartment. The whole process is clean without any pollution. Thus, it is a popular and environmental friendly method to produce acid and base [9–15], recover inorganic salt [16,17] and separate organic acid [18,19]. However, the component of saline wastewater is normally so complex that it is difficult to recover different compounds by one method. Thus, different treating processes are combined [20]. Peng et al. [21] used coupling of electrodialysis-electrolysis to treat copper-containing wastewater. They recovered almost 99.5% of copper and 100% of water with low energy consumption. Jiang et al. [22] used a lab-scale electro-electrodialysis with conventional electrodialysis stack to produce LiOH. They reported that low energy consumption would be obtained with this combination after scaling up. Xue et al. [23] used a coupling of ED and BMED processes to treat sodium acetate waste solution.

Since ED and BMED use electrical field as driving force to move ions, energy consumption increases when wastewater contains high salt and acid concentration. Thus, the recovery process needs to be optimized to reduce the energy consumption. Diffusion dialysis (DD) is a spontaneous membrane separation process driven by concentration gradient without addition of electrical field. Thus, if DD is applied before ED and BMED process to recover the majority of acid from saline wastewater, the total energy consumption can be reduced.

In this study, different combinations of DD, ED and BMED were applied to recover sulfuric acid (H_2SO_4) and tetrabutylammonium (TBA) cations from industrial organic wastewater. The energy consumption, acid and TBA^+ recovery, and operation time were compared. All results indicate that DD/ED/BMED combination is the most efficient and economical method to recover sulfuric acid and TBAOH from the wastewater. TBAOH can be used as basic organic chemical, electronics cleanser, and the ion pair of mobile phase in chromatography. It is also often used as phase transfer catalyst to promote alkylation, hydrocarbylation and deprotonation reactions. Thus, it is significant to produce TBAOH from TBA waste salt. This is one of the key points to treat this type of wastewater in this study.

2. Experimental details

2.1. Chemicals, materials and apparatus

T-0C diffusion dialysis equipment and CH-0T electrodialysis equipment were supplied by Shanghai Tsingross Environmental Technology Co., Ltd. (Shanghai, P.R. China). TRPB3010-I BM electrodialysis equipment was from Asahi Glass Co., Ltd. (Tokyo 100-8405, Japan). Following membranes were purchased from Asahi Glass Co., Ltd.: the DSV (standard) anion exchange membrane for DD process, AMV (standard) anion exchange membrane and CMV (standard) CEM for ED process, as well as BM-I bipolar membrane and JAM-II AEM for BMED process. The JCM-II CEM for BMED process was supplied by Beijing Tingrun Membrane Technology Development Co. Ltd. (Beijing, P.R. China).

Adjustable constant voltage and constant current DC power supply HY5003D and TPR-3030D were purchased from Hangzhou Huayi Electronic Industry Co., Ltd. (Zhejiang, P.R. China) and Longwei Instruments (HK) Co., Ltd., (Hongkong, P.R. China) respectively. DDSJ-308A conductivity meter was purchased from Shanghai INESA Scientific Instrument Co., Ltd. (Shanghai, P.R. China) HL-2S constant-flow pump was from Shanghai Jiapeng Technology Co., Ltd. (Shanghai, P.R. China).

The wastewater was directly provided by Xinxiang Chemical Fiber Factory, Henan. It contained 230 g/L sulfuric acid (H_2SO_4), 80 g/L dimethyl sulfoxide (DMSO) and 40 g/L tetrabutylammonium hydrogen sulfate ($TBAHSO_4$) (Table 1). Sodium hydroxide (NaOH) and concentrated H_2SO_4 with analytical grade were purchased from Shanghai Titan Scientific Co., Ltd. (Shanghai, P.R. China) 0.01 mol/L tetrabutylammonium hydroxide (TBAOH) and DI water (7.52 μS/cm) were prepared in our lab.

2.2. Membrane stack

2.2.1. Diffusion dialysis membrane stack

The diffusion dialysis membrane stack was partitioned into 20 compartments by 19 pieces of membranes with a valid area of 0.018 m^2/piece. Two neighboring membranes were separated by a spacer with thickness of 1.9 mm. The schematic is shown in Fig. 1(a). "A" is the AEM. Wastewater and DI water were peristaltic pumped into retentate compartments and the diffusate compartments, respectively, with an opposite feeding direction.

2.2.2. Electrodialysis membrane stack

Electrodialysis (ED) membrane stack, as illustrated in Fig. 1(b), was comprised of membranes, spacers and electrodes. "A" and "C" indicate the AEM and CEM, respectively. Membranes were packed between two electrodes with an arrangement of AEM-spacer-CEM-spacer in series. Wastewater was pumped into dilute compartments and circulated in the system with volume flow of 200 L/h. 0.05 M of H_2SO_4 was fed into concentrate compartments and circulated. 5% H_2SO_4

Table 1
Composition of wastewater

Components	Content (g/L)
H_2SO_4	230
DMSO	80
$TBAHSO_4$	40

solution was circulated in the electrode compartments. The whole ED process took certain time until H^+ concentration in concentrate compartment did not change any more.

2.2.3. Bipolar membrane electrodialysis membrane stack

Three-compartment BMED can produce pure acid and pure base at the same time. Thus, it was chosen as the membrane configuration to treat $TBAHSO_4$ waste residue. In Fig. 1(c), the numerals "1", "2" and "3" indicate the acid compartment, salt compartment and base compartment, respectively. This BMED membrane stack contains ion exchange membranes (IEMs) and BMs. "A" is the AEM or the anion side of the BM, while "C" is the CEM or the cation side of the BM. Pretreated solution was fed into salt compartments and circulated in the system with volume flow of 100 L/h. 0.01 M of TBAOH, 0.05 M H_2SO_4 solution, and 5% NaOH solution were also circulated in base compartments, acid compartments and electrode compartments, respectively.

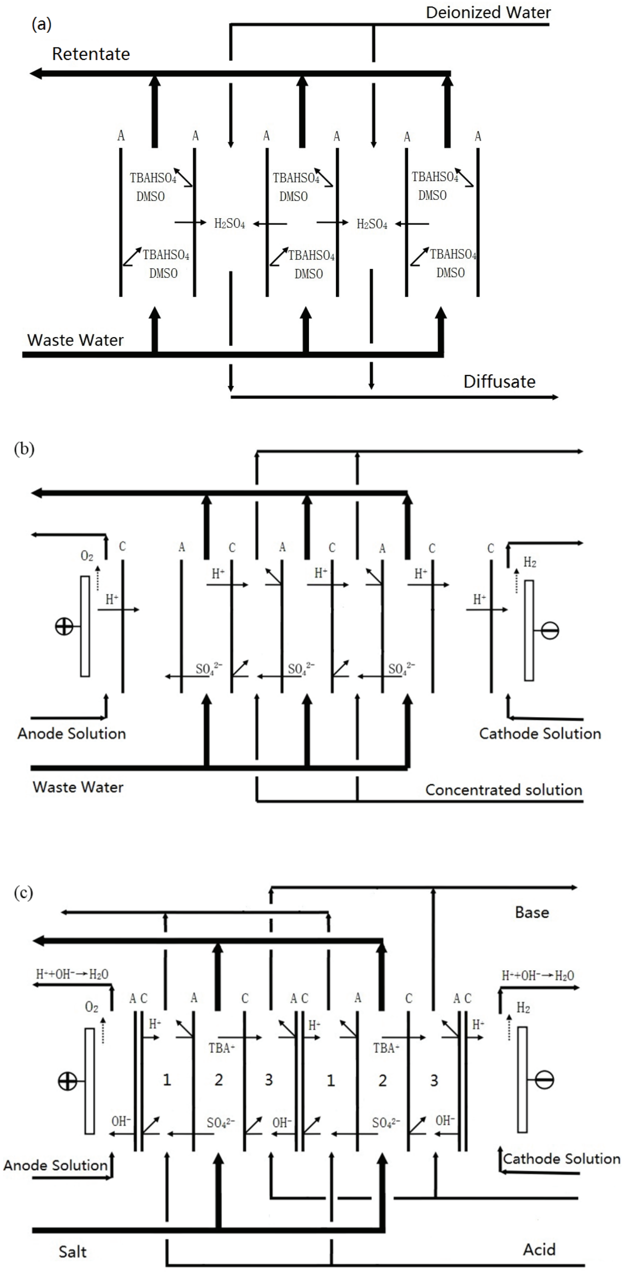

Fig. 1. Scheme of membrane stacks for (a) diffusion dialysis, (b) electrodialysis and (c) bipolar membrane electrodialysis.

2.3. Experimental process

2.3.1. Diffusion dialysis process

For experiments started with DD process, wastewater was first stored in No. 4 graduated cylinder and pumped into the membrane stack by No. 5 constant-flow pump (shown in Fig. 2). Meanwhile, DI water was pumped into the membrane stack from No. 7 graduated cylinder. The retentate solution and diffusate coming out of the membrane stack were collected in No. 6 and No. 9 graduated cylinder, respectively. The volumes of solutions collected in No. 6 and No. 9 graduated cylinder and consumed in No. 4 and No. 7 graduated cylinder were measured during experiment. The temperature was kept at 35°C by a constant temperature water bath and a circulating pump during the whole process. A degas membrane stack and a vacuum pump were used to remove any gas in the system to obtain stable data.

2.3.2. Electrodialysis process

The ED process was composed of a membrane stack, tanks, circulating pumps, a DC power supply and conductivity meters. The feed solution was either the retentate solution obtained from DD process or the original wastewater. As illustrated in Fig. 3, feed solution, 0.05 mol/L sulfuric acid and 5% sulfuric acid were stored in tanks to supply dilute, concentrate and electrode compartment, respectively.

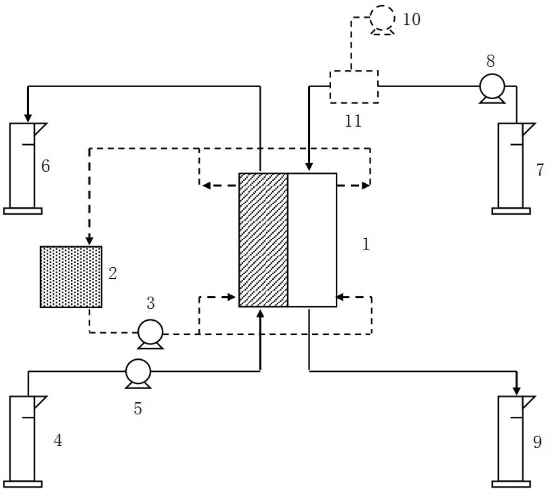

Fig. 2 Scheme of diffusion dialysis process. (1) Diffusion dialysis membrane stack, (2) constant temperature water bath, (3) circulating pump, (4) graduated cylinder for wastewater, (5) constant flow pump for wastewater, (6) graduated cylinder for retentate solution, (7) graduate cylinder for DI water, (8) constant flow pump for DI water, (9) graduated cylinder for recycled acid (diffusate), (10) vacuum pump, (11) degas membrane stack.

Solutions were pumped into corresponding compartments with a flow rate of 200 L/h. The membrane stack was powered by a constant current and constant potential DC power supply.

2.3.3. Bipolar membrane electrodialysis process

BMED process setup is illustrated in Fig. 4. The feed solution was the acid-removed wastewater obtained from either ED or DD-ED process. The initial solutions for base and acid tanks were 0.01 mol/L TBAOH and 0.05 mol/L sulfuric acid, respectively. 5% sodium hydroxide (NaOH) was initially stored in the electrode tank. All the solutions were circulated in the whole system for certain time with the same flow rate of 200 L/h. A constant current and constant potential DC power was applied to the BMED membrane stack.

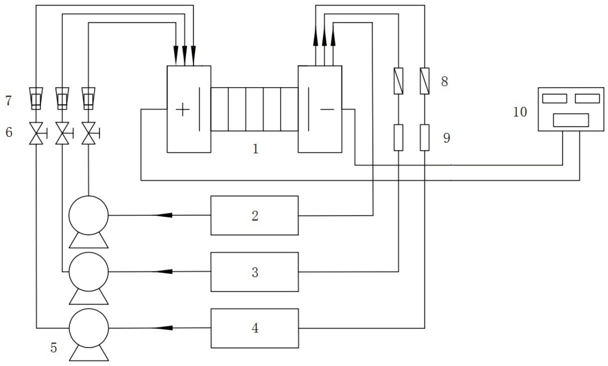

Fig. 3. Scheme of electrodialysis process. (1) Electrodialysis membrane stack, (2) tank for electrode compartment, (3) tank for dilute compartment, (4) tank for concentrate compartment, (5) circulating pumps, (6) valves, (7) flow meters, (8) conductivity meters, (9) pH meters, (10) DC power supply.

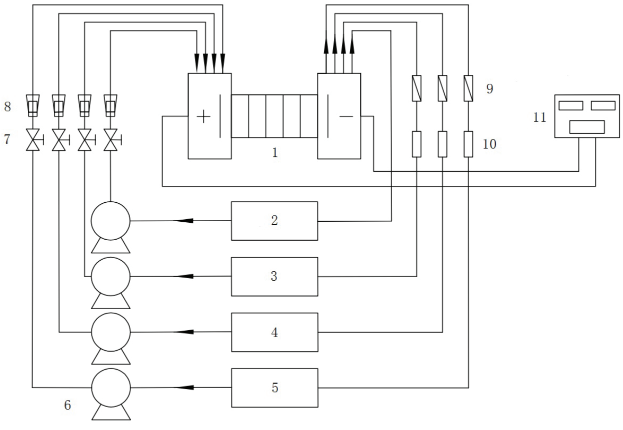

Fig. 4. Scheme of bipolar membrane electrodialysis process. (1) Bipolar membrane electrodialysis membrane stack, (2) tank for electrode compartment, (3) tank for base compartment, (4) tank for salt compartment, (5) tank for acid compartment, (6) circulating pumps, (7) valves, (8) flow meters, (9) conductivity meters, (10) pH meters, (11) DC power supply.

2.4. Analyzing methods and data analysis

Samples were collected every 0.5 h during the whole experiment. H^+ concentration in all the recovered acid solutions was determined by a titration method with 0.1 M NaOH solution (standard) and phenolphthalein (phph) as the indicator. TBAOH concentration from BMED process was titrated with 0.005 M HCl solution (standard) and methyl red as the indicator. The concentration of SO_4^{2-} was determined by a volumetric procedure. The conductivity meter was used to measure the solution conductivity. Impurity content in final TBAOH solutions was analyzed by FTIR. In addition, the voltage and current applied for ED and BMED process were recorded, as well as the solution volume in all the tanks.

The DD performance could be assessed by acid recovery (*R*), which was calculated from the concentrations of recovered acid solutions (Eq. (1)). Energy consumption *W* (kW·h) (Eq. (2)) and current efficiency η (%) (Eqs. (3) and (4)) were used to evaluate ED and BMED performance.

$$R = \frac{c_2 V_2}{c_1 \left(V_1 - V_r\right)} \times 100\% \tag{1}$$

In which, c_1 and c_2 (M) are the H^+ concentrations of wastewater and recovered acid, respectively. V_1 and V_2 (L) are the volumes of original wastewater and recovered acid, respectively. V_r (L) is the volume of the untreated wastewater left in DD process.

$$W = \int_0^t \frac{UI\mathrm{d}t}{3600 \times 10^3} \tag{2}$$

In which, *U* (V) is the applied voltage. *I* (A) is the current applied to the membrane stack. *t* (s) is the operation time.

$$\eta_{\text{acid}} = \frac{Fz(c_t V_t - c_0 V_0)}{n^* It} \times 100\% \tag{3}$$

$$\eta_{\text{base}} = \frac{Fz(c_t V_t - c_{t'} V_{t'})}{n^* I \Delta t} \times 100\% \tag{4}$$

where *F* is the Faraday constant, 96,485 C/mol. *z* is the number of electrons needed to transfer ions. c_0 (M) is the concentration of recovered acid at the beginning of either ED or BMED process, while c_t is the concentration of acid or base detected during experiment for corresponding process. c_t is the concentration of base solution detected at half an hour before c_t. V_0 and V_t (L) are the volumes of recovered acid solutions before and during either ED or BMED process, respectively. V_t is the volume of base solution detected at half an hour before V_t. n^* is the number of membranes packed in a stack. ED process was assembled with 10 membranes while that for BMED process was five pieces. *I* and *t* are the same as those used in Eq. (2). Δ*t* is the operation time between *t* and *t*′, that is, 30 min, for base solution.

3. Results and discussions

3.1. Operation processes

DD, ED and BMED processes were combined in three different ways. Operation time, energy consumption and recoverability were compared selecting the most efficient and economic method. In Method 1, DD was coupled with BMED process. Wastewater was first treated by DD to recover the acid, and then the retentate was fed into BMED to obtain TBAOH. For Method 2, ED was used as the pretreatment for acid recovery and then combined with BMED process. However, for Method 3, a combination of three processes was used. Wastewater was fed into DD process to remove the majority of acid. The retentate from DD process was further treated by ED process to collect acid-free solution for subsequent BMED process. Finally, solution from dilute compartments of ED process was fed into the BMED process to produce TBAOH and conjugate acid. All of these three methods started with 2 L of wastewater. Detailed operating information and results for each process are discussed in this section.

3.1.1. Method 1: coupling of DD and BMED process

Wastewater was first treated by DD process. Ion diffusion through membranes in DD process is driven by concentration gradient. It also depends on the membrane type. AEM was used in this study, so that SO_4^{2-} in the wastewater can penetrate through the membranes to diffusate sides. To maintain electrical neutrality in diffusate sides, H^+ or TBA^+ ions need to diffuse through the membrane as well. It is known that diffusion in DD process is highly related to the ions size. Since the size of TBA^+ is larger than that of H^+, TBA^+ ions are blocked at the retentate side, while H^+ ions penetrate to the diffusate side. Furthermore, DMSO is a large organic molecule without charge, so DMSO molecules also remain in retentate sides. Therefore, the majority of sulfuric acid could be separated and recovered from the wastewater. The flow rate was set to 0.1641 L/h for both wastewater and DI water. At the end of experiment, about 12.2 h operation, the concentration of sulfuric acid in retentate was 0.917 M. 77.1% of sulfuric acid was recovered. Sulfuric acid cannot be totally recovered by DD process. This is because that H^+ can diffuse back to retentate as the concentration of H^+ in diffusate is higher than that of retentate. Detailed discussion of flow rate effect is illustrated in section 3.2.

The retentate from DD was then fed into the salt compartments of BMED. The initial current density was set as 144 A/m^2. As Fig. 5(a) shows, sulfuric acid concentration in the acid compartments increases consistently. The increase in rate slows down after 4 h of operation. Oppositely, the TBAOH concentration in base compartments does not change for the first 4 h (Fig. 5(a)) until the pH of the solution in salt compartment reaches 3. This can be ascribed to the relatively high acid concentration in salt compartments. Since the size of H^+ ions are smaller than that of TBA^+ ions, H^+ ions are easier to permeate through the CEM to the base compartments. The migration rate of H^+ ions is higher than that of TBA^+ ions for the first 4 h. Permeated H^+ ions react with dissociated OH^- ions to form water, which can be regarded as an acid removal process for salt compartments. The H^+ concentration in salt compartment decreases with further treatment until it is lower than 0.001 M (pH > 3, 4 h indicated in Fig. 5(a)). At this time, TBA^+ ions are the main component in salt compartment and migrate through the membrane to produce TBAOH in base compartment. Since averaged total current efficiency for TBAOH is generally low in this research, the current efficiency is averaged every half an hour by Eq. (4) and plotted in Figs. 5(b) and 7(c). The current efficiency of base compartment is zero for first 4 h (Fig. 5(b)), this is because no TBAOH is formed during this period. Even though more TBA^+ ions move to base compartment than H^+ ions after 4 h, the current efficiency does not increase dramatically as expected. This is because the size of TBA^+ ions is so large that they are difficult to migrate through the CEM. As a result, TBAOH concentration increases slowly in base compartments. In addition, OH^- ions in the base compartments can also diffuse to the salt compartments to slow down the TBAOH concentration rise rate and reduce the current efficiency. To keep the salt compartments electrically neutral, H^+ ions also immigrate to salt compartments from acid compartments. Moreover, since the concentration of H^+ ions in acid compartments is higher than salt compartment, H^+ ions also diffuse back to salt compartments. These result in a slow-down of H_2SO_4 concentration increase rate in acid compartments after 4 h operation. After 8.5 h operation, the sulfuric acid concentration in acid compartments is 0.535 M. TBAOH concentration in base compartments

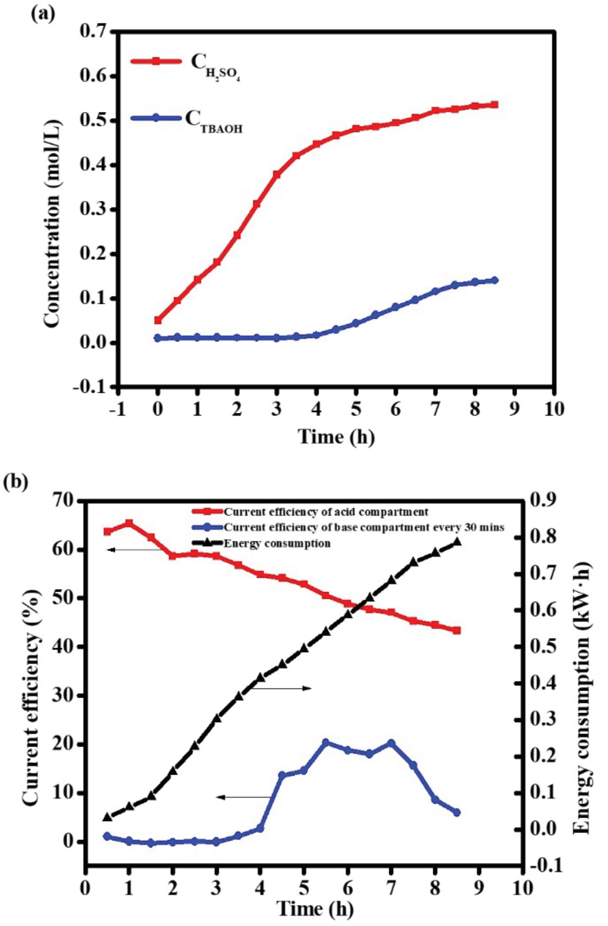

Fig. 5. BMED performance within DD-BMED (Method 1) including: (a) H_2SO_4 and TBAOH concentration; and (b) energy consumption and current efficiency for H_2SO_4 and TBAOH.

is 0.140 M. Thus, the TBAOH recovery is 99.6%. There is 1.87% impurity in TBAOH solution. The energy consumed in BMED process is 0.786 kW·h.

3.1.2. Method 2: coupling of ED and BMED process

In Method 2, wastewater was first treated with ED at a constant current of 166 A/m^2. The H$^+$ concentration in concentrate compartments reaches maximum of 3.226 M after 12 h (Fig. 6), while that for dilute compartments are 1.462 M. The acid recovery from ED process is 69.6% with an energy consumption of 0.247 kW·h. The H$^+$ concentration starts to decrease slowly after 12 h and eventually attains stable state. This result indicates that ED process reaches its limit and cannot recover more H$^+$ ions. This is because near the end of the ED treatment, the H$^+$ concentration in concentrate compartments are much higher than that in dilute compartments. Back migration of H$^+$ ions becomes significant and it equilibrates slowly with forward migration. The H$^+$ recovery reaches maximum at 12 h with a current efficiency of only 48.2%. On the other hand, the calculated current density based on H$^+$ concentration in concentrate compartment is much higher than 100% for first 1 h (as shown in Fig. 6). This attributes to higher H$^+$ concentration in dilute compartments than that in concentrate compartments. H$^+$ ions transfer from dilute compartments to concentrate compartments not only driven by the electrical field force but also the concentration gradient. As a result, H$^+$ ions spontaneously diffuse through the membranes and the initial current efficiency is higher than 100%. However, the H$^+$ concentration in dilute compartments after ED process (1.462 M) is much higher than that in the retentate after DD process (0.917 M). The acid recovery is only 69.9%. Thus, using ED to recover H_2SO_4 from wastewater is not as efficient as DD process. BMED process part of this method is not going to be discussed.

3.1.3. Method 3: combination of DD-ED-BMED process

To be comparable with method 1, DD process flow rate of Method 3 was set the same as that for method 1. The final H$^+$ concentration in the retentate is 0.979 M, which is close to 0.917 M from Method 1. The acid recovery is about 76.9% for DD process. This solution is fed into ED process for further acid recovery. A constant current was set as 166 A/m^2. After 3 h of operation, the final H$^+$ concentration in concentrate compartments is 0.837 M (Fig. 7(a)) and that for dilute compartments decreases to 0.023 M. Most of the sulfuric acid is removed and the acid recovery reaches 98.1%. Current

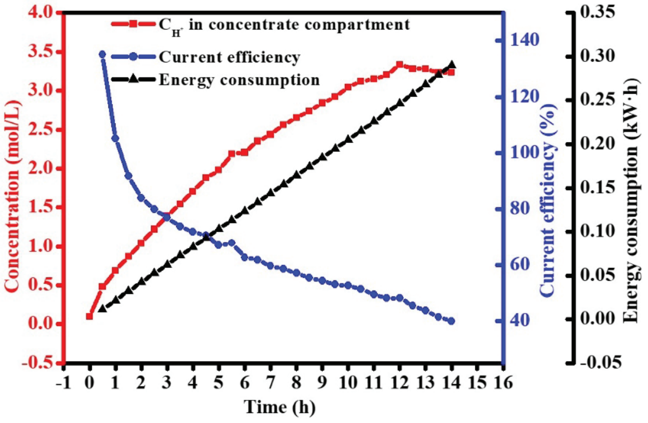

Fig. 6. ED performance within ED-BMED process (Method 2) including: H$^+$ concentration in concentrate compartment (i.e., concentrate compartment), energy consumption and current efficiency.

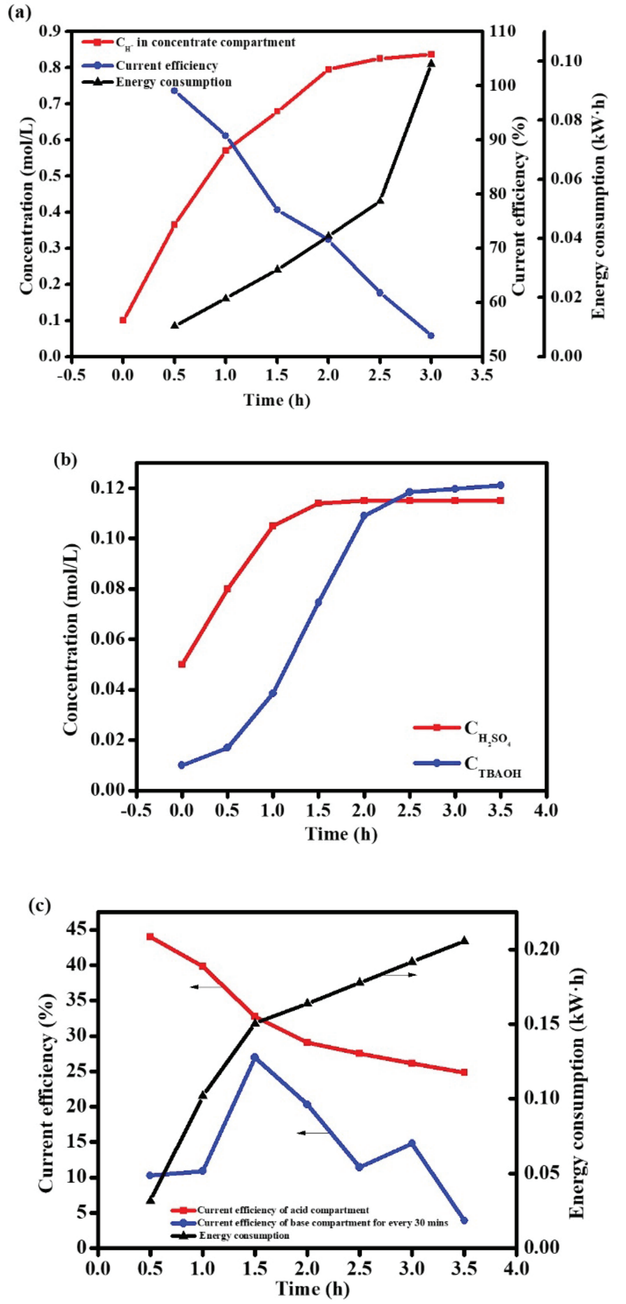

Fig. 7. ED and BMED performance within DD-ED-BMED process (Method 3) including: (a) H$^+$ concentration in concentrate compartment, energy consumption and current efficiency for ED process; (b) H_2SO_4 and TBAOH concentration in BMED; (c) energy consumption and current efficiency for H_2SO_4 and TBAOH.

efficiency is 53.9%, and energy consumption for ED process is 0.099 kW·h. Following this, the solution from dilute compartments of ED process is used as feed for BMED. The initial current density was set to 144 A/m^2. Since the initial H$^+$ concentration is only 0.023 M, it takes much shorter time than Method 1 to remove H$^+$ ions from salt compartments. The concentration of H_2SO_4 in acid compartments and TBAOH in base compartments increases at the beginning of BMED process, which is different from Method 1. Since the feed solution contains little amount of SO_4^{2-}, the H_2SO_4 concentration in acid compartment reaches maximum (0.115 M) very fast, that is, only 1.5 h, and remains plateau after that (shown in Fig. 7(b)). This is because most of SO_4^{2-} in salt compartment are immigrated to the acid compartment. With further operation, H$^+$ ions produced by BM diffuse to salt and base compartments. Similarly, Fig. 7(c) also shows that the current efficiency for acid compartment decreases dramatically for first 1.5 h. The initial current efficiency in acid compartment is only 44.0% (shown in Fig. 7(c)). This is because there are almost no H$^+$ ions in salt compartment, similar to the 4th hour in Fig. 5(b). This 3-h treatment in BMED process of method 3 (data shown in Fig. 7(c)) can be regarded as 4th to 8th hour in the BMED process of method 1 (shown in Fig. 5(b)). After 3.5-h treatment with BMED process in Method 3, the TBAOH concentration in base compartment reaches maximum, 0.121 M, with 1.74% impurity. The TBAOH recovery is 93.1% for Method 3. The current efficiency for every half hour maintains at around 10%–20%. The energy consumption for BMED process is 0.206 kW·h.

3.1.4. Comparison of three methods

Operation time, acid recovery before BMED process, TBAOH recovery and energy consumption of these three methods are compared and listed in Table 2.

According to Table 2, even though Method 3 has one more procedure, it takes shorter time than both Method 1 and Method 2. Acid recovery before BMED indicates the removal ability of the processes before BMED. The higher value indicates the lower acid concentration in the feed solution for BMED. The acid recovery of Method 3 is 99.6%, which is much higher than that of Method 1 (77.1%) and Method 2 (69.6%). The lower acid concentration in BMED feed solution, the shorter time is needed to further remove H$^+$. Consequently, energy consumption is lower. Thus, the total energy consumption for Method 3 is only 0.305 kW·h, which is much lower than that of Method 1 (0.786 kW·h). However, since Method 3 has one more procedure, more material could be lost during the operation. This explains why the TBAOH recovery from Method 3 is lower than that of Method 1. The TBAOH recovery and energy consumption are not compared for Method 2, since the BMED process is not discussed above. Nevertheless, 93.1% recovery still meets the industry requirement. Overall, Method 3 should be the best combination to recover acid and salt from this type of wastewater.

3.2. Economic evaluation

As discussed above, a combination of DD, ED and BMED process is the best process to recover acid and salt from wastewater. Thus, this method is evaluated and economically optimized for industry scale application. Assuming that 150 L/h is the treating capacity in industry. The total treatment economy (*M*) is calculated based on equipment investment (*I*) and electricity (*E*), shown as (Eq. (5)).

$$M = I + E \tag{5}$$

where

$$I = I(\mathrm{DD}) + I(\mathrm{ED}) + I(\mathrm{BMED}) \tag{6}$$

$$E = E(\mathrm{ED}) + E(\mathrm{BMED}) \tag{7}$$

Since IEMs cost more for equipment investment, the *I* can be simplified to the membrane cost, as Eq. (8) shows. According to the membrane stack used in this study, one membrane group used in DD process is one piece of AEM. One piece of AEM and one piece of CEM (AEM-CEM) is regarded as one membrane group in ED process. For BMED process, one membrane group contains two pieces of AEMs and CEMs (AEMs-CEMs), as well as one piece of BM.

$$\begin{aligned} I = {} & k_{\mathrm{IEM}}S(\mathrm{DD}) + k_{\mathrm{IEM}}S(\mathrm{ED}) + k_{\mathrm{IEM}}S_{\mathrm{IEM}}(\mathrm{BMED}) \\ & + k_{\mathrm{BM}}S_{\mathrm{BM}}(\mathrm{BMED}) \end{aligned} \tag{8}$$

Table 2
Parameters comparison between three methods

Experimental method	Operation process	Time (h)		Acid recovery (%)		TBAOH recovery (%)	Energy consumption[a] (kW·h)	
Method 1	DD	12.2	20.7	77.1		99.6	0	0.786
	BMED	8.5		–			0.786	
Method 2	ED	12	–	69.6		–	0.247	–
	BMED	–		–			–	
Method 3	DD	12.2	18.7	76.9	99.6	93.1	0	0.305
	ED	3.0		98.1			0.099	
	BMED	3.5					0.206	

[a] Energy consumption is calculated based on the energy consumed by applied DC power. The energy consumed by circulating pump and constant flow pump is not included.

In which, S (m^2) is the required total area of IEMs to treat 150 L/h wastewater for corresponding process. k_{IEM} (\$/m^2) is the market price for AEM or CEM used in each process. k_{BM} is the bipolar membrane price used in BMED.

The electricity is calculated based on energy consumption, shown as following:

$$E = k_e\left[W(\mathrm{ED}) + W(\mathrm{BMED})\right] \tag{9}$$

where k_e (\$/(kW h)) is the averaged industrial electricity price.

For the experiments discussed above, in DD process, 19 pieces of membranes are used and each membrane has a valid area of 0.018 m^2. Thus, the total valid area is 0.3420 m^2 for DD. Ten pieces of IEM with valid area 0.01817 m^2/piece are assembled in the ED membrane stack. The total valid membrane area for ED process is 0.1817 m^2. Five membranes with 0.0209 m^2 are used in BMED process. The total valid membrane area for BMED process is 0.1045 m^2.

Since there is almost no acid in the feed solution for BMED process, treating time and energy consumption are mainly related to original solution volume of salt compartment. Acid concentration effect can be ignored. According to Table 2, treating time and energy consumption of BMED process are 3.5 h and 0.206 kW·h, respectively, to treat 2 L of this wastewater. Thus, to treat 150 L/h wastewater, the BMED equipment needs to be scaled up. The total AEM-CEM area and BM area needed in BMED process are calculated and shown in Eqs. (10) and (11), respectively. The energy consumption is shown in Eq. (12) as follows:

$$S_{\mathrm{IEM}}(\mathrm{BMED}) = \frac{150 \times 3.5}{2} \times 0.1045 \times 2\ \mathrm{m}^2 = 54.86\ \mathrm{m}^2 \tag{10}$$

$$S_{\mathrm{BM}}(\mathrm{BMED}) = \frac{150 \times 3.5}{2} \times 0.1045\ \mathrm{m}^2 = 27.43\ \mathrm{m}^2 \tag{11}$$

$$W(\mathrm{BMED}) = \frac{150 \times 3.5}{2} \times 0.206\ \mathrm{kW\ h} = 54.08\ \mathrm{kW\ h} \tag{12}$$

Treating time and energy consumption of ED process is not only related to total solution volume in dilute compartments, but also related to the initial H$^+$ concentration of dilute compartments. For the lab-scale test, that is, with a fixed treating volume of 2 L, the treating time and energy consumption for ED process are shown as following:

$$t' = \mathrm{f}\left(C_{H^+}\right) \tag{13}$$

$$W = g\left(C_{H^+}\right) \tag{14}$$

Data were collected during the experiment and plotted in Fig. 8(a). The experiments finished when the resistance of the system suddenly changed. As Fig. 8(a) shows, both the treating time and energy consumption for ED process are linearly related to C_{H+}. Thus, Eqs. (13) and (14) are fitted linearly to get Eqs. (15) and (16), respectively.

$$t' = 2.856C_{H^+} - 0.1833, R^2 = 0.9834 \tag{15}$$

$$W = 0.072C_{H^+} + 0.0463, R^2 = 0.9075 \tag{16}$$

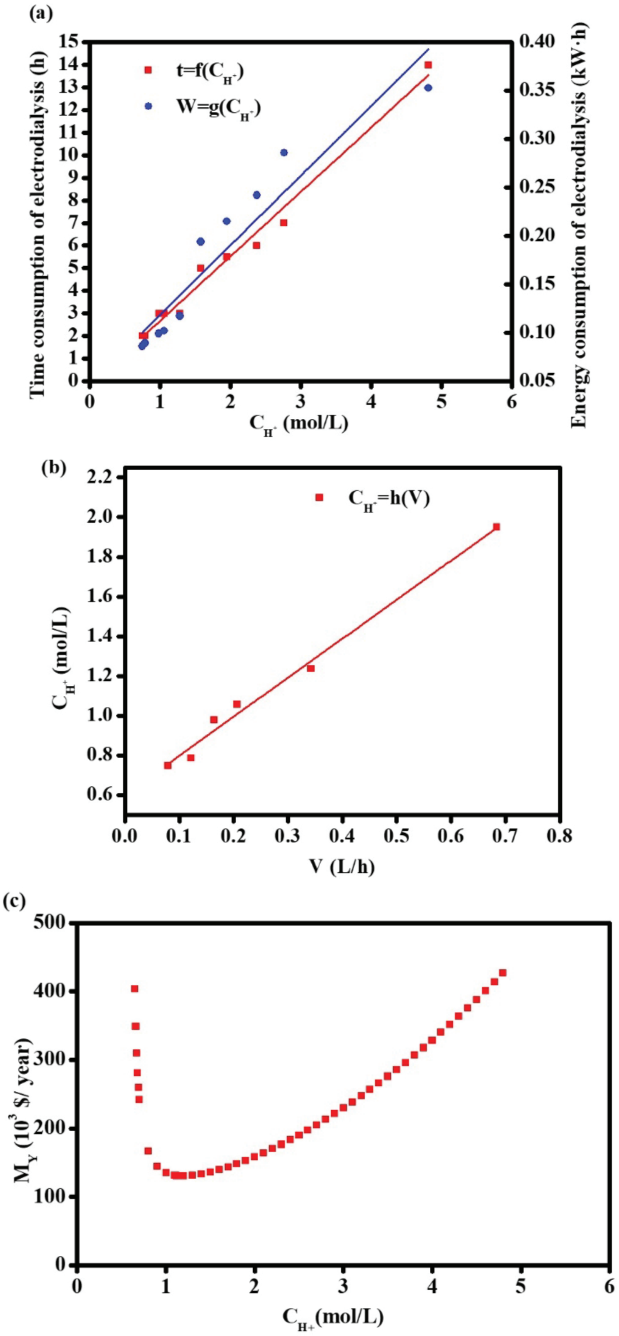

Fig. 8. Economical evaluation for wastewater treatment with Method 3 after scale up. (a) Time and energy consumption of ED; (b) relationship between H$^+$ concentration of retentate and flow rate for DD process and (c) relationship between the total cost and H$^+$ concentration of retentate of DD process.

When the wastewater treating amount increases to 150 L, the needed membrane area and energy consumption can be calculated by the following equations:

$$S(\mathrm{ED}) = \frac{150\times\left(2.856C_{H^+} - 0.1833\right)}{2}\times 0.1817\times 2 = 77.84C_{H^+} - 4.996\ \left(\mathrm{m}^2\right) \tag{17}$$

$$W(\mathrm{ED}) = \frac{150\times(2.856C_{H^+} - 0.1833)}{2}\times\left(0.072C_{H^+} + 0.0463\right) = 15.42{C_{H^+}}^2 + 8.928C_{H^+} - 0.6365\left(\mathrm{kW{\cdot}h}\right) \tag{18}$$

Thus, as Eqs. (17) and (18) show, the smaller C_{H+} value, the less ED membrane area and energy consumption required. However, since the feed solution of ED process is from DD process, C_{H+} is the H^+ concentration of the retentate after DD process. Smaller C_{H+} indicates bigger valid membrane area needed for DD process, which increases the investment for DD equipment. The C_{H+} from DD process is a function of operational volume rate, shown in Eq. (19) as follows:

$$C_{H^+} = h\left(V\right) \tag{19}$$

Fig. 8(b) shows a plot of collected data during DD process. It indicates that the C_{H+} in retentate is linearly related to the operating volume rate. To fit the plot by a linear equation, the result is shown as Eq. (20):

$$C_{H^+} = 1.965V + 0.6022, R^2 = 0.9898 \tag{20}$$

To treat 150 L/h wastewater, the membrane area needed for DD process is illustrated as follows:

$$S\left(\mathrm{DD}\right) = \frac{150\times 1.965}{\left(C_{H^+} - 0.6022\right)}\times 0.3420 = \frac{100.8}{C_{H^+} - 0.6022}\left(\mathrm{m}^2\right) \tag{21}$$

According to Eq. (21), C_{H+} should be larger than 0.6022 M. When C_{H+} is smaller than 0.6022 M, S(DD) is below 0, which is unreasonable. One possible explanation is that it is out of DD process operation ability to left less than 0.6022 M of C_{H+} in retentate when the flow ratio of wastewater and DI water is 1:1. Since the H^+ concentration in original wastewater is about 4.800 M, C_{H+} is restricted between 0.6022 and 4.800 M. Eq. (21) indicates that as C_{H+} increases, the membrane area is smaller, meaning that less equipment investment is required for DD.

To calculate the total economy, equipment depreciation is calculated based on 3 years. Energy consumption is calculated based on working for 330 d per year and 24 h/d. The equipment investment for 1 year is shown as following:

$$I_Y = \frac{1}{3}\left[\begin{array}{c} k_{\mathrm{IEM}}\dfrac{100.8}{C_{H^+} - 0.6022} + k_{\mathrm{IEM}}\left(77.84C_{H^+} - 4.996\right) \\ +k_{\mathrm{IEM}}\times 54.86 + k_{\mathrm{BPM}}\times 27.43 \end{array}\right](\$) \tag{22}$$

Electricity for 1 year is:

$$E_Y = 330\times 24\times k_e\left(15.42{C_{H^+}}^2 + 8.928C_{H^+} - 0.6365 + 54.08\right)(\$) \tag{23}$$

Thus, total cost for 1 year is calculated based on a sum of I_Y and E_Y shown in Eq. (24) as follows:

$$M_Y = I_Y + E_Y \tag{24}$$

where

$k_{\mathrm{IEM}} = 468$

$k_{\mathrm{BM}} = 2340$

$k_e = 0.1061$

So

$$M_Y = \frac{15725}{C_{H^+} - 0.6022} + 12956{C_{H^+}}^2 + 19640C_{H^+} + 74069 \tag{25}$$

Take derivation of Eq. (25) and get:

$$\frac{\mathrm{d}M_Y}{\mathrm{d}C_{H^+}} = -\frac{15725}{(C_{H^+} - 0.6022)^2} + 25912C_{H^+} + 19640 \tag{26}$$

Set

$$\frac{\mathrm{d}M_Y}{\mathrm{d}C_{H^+}} = 0 \tag{27}$$

And get

$C_{H+} = 1.164$ (mol/L)

Thus, when H^+ concentration of retentate from DD process is 1.164 M, M_Y has the smallest value (142,474 \$/year), which is the least averaged cost to recover H_2SO_4 and TBA^+ ions from the wastewater. Such result is also indicated as the lowest point in Fig. 8(c).

Since 99.6% acid and 93.1% TBAOH are recovered from Method 3, the recovery of total acid and TBAOH each year with 150 L/h treatment is 315.5 ton/year and 37.40 ton/year, respectively.

All the economical parameters calculated after the scale up is shown in Table 3.

To meet the industrial treatment requirement, that is, 150 L/h, and minimize the total cost, the membrane area for DD process should be 179.4 m^2 to obtain 1.164 M of H^+ ions remained in the retentate. Meanwhile, ED process requires 85.61 m^2 of AEM and CEM in total. BMED process needs 27.43 m^2 of BM and 54.86 m^2 of AEM and CEM in total. Under this circumstance, the energy consumption for ED and BMED

Table 3
Economical evaluation

Process	Membrane area (m^2)	Investment ($/year)	Energy consumption (10^3 kW·h/year)	Electricity ($/year)
DD	179.4	27,986	0	0
ED	85.61	13,354	242.7	25,746
BMED	54.86 + 27.43	29,952	428.3	45,436
Total	347.3	71,292	671.0	71,182

process is 242.7×10^3 kW·h/year and 428.3×10^3 kW·h/year, respectively. The total cost is the lowest (142,474 $/year), among which the equipment investment is 71,292 $/year and electricity is 71,182 $/year. The total recovery of sulfuric acid and TBAOH from the wastewater is 315.1 ton/year and 37.40 ton/year, respectively.

4. Conclusions

In this research, three methods were studied and compared with treat a type of wastewater containing 230 g/L of H_2SO_4, 80 g/L of DMSO and 40 g/L of $TBAHSO_4$. By comparing the operation time, acid recovery before BMED process, TBAOH recovery and energy consumption, a process combination of DD/ED/BMED is selected as the best recovery method for wastewater. This combination takes shortest time, least energy consumption and recovers the most acid and TBA salt with high percentage: 99.6% for sulfuric acid and 93.1% for TBA^+ ions.

Based on this combination, to meet the 150 L/h treating requirement in industrial scale with least cost, the membrane area used in DD process should be 179.4 m^2 and left 1.164 M of H^+ in retentate. The total membrane area used in ED process is 85.61 m^2. BMED process needs 54.86 m^2 of total AEM and CEM and 27.43 m^2 of BM. With these parameters, the energy consumption for ED and BMED processes are 242.7×10^3 kW·h/year and $428.3\ ′\ 10^3$ kW·h/year, respectively. The lowest total cost is 142,474 $/year, in which the equipment investment is 71,292 $/year and electricity is 71,182 $/year. The total recovery of sulfuric acid and TBAOH from the wastewater is 315.1 ton/year and 37.40 ton/year, respectively. This study is meaningful for recovering acid and salt from organic saline wastewater containing acid.

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Symbols

R — Acid recovery, %
c_1 — H^+ concentrations of wastewater, M
c_2 — H^+ concentrations of recovered acid, M
V_1 — Volumes of original wastewater, L
V_2 — Volumes of original recovered acid, L
V_r — Volume of the untreated wastewater left in DD process, L
W — Energy consumption, kW·h
U — Applied voltage, V
I — Applied current, A
t — Operation time, s
η — Current efficiency, %
F — Faraday constant; 96,485 C/mol
z — Number of electrons needed to transfer ions
c_0 — Concentration of recovered acid or base at the beginning of either ED or BMED process, M
c_t — Acid or base concentration detected during experiment, M
$c_{t'}$ — Base concentration detected 30 min before t in BMED process, M
V_0 — Volume of recovered acid solutions before either ED or BMED process, L
V_t — Volume of recovered acid or base solutions during either ED or BMED process, L
$V_{t'}$ — Volume of recovered base solutions 30 min before t in BMED process, L
n^* — Number of membranes packed in a stack
M — Total treatment economy, $
I — Equipment investment, $
E — Electricity, $
I(DD) — Equipment investment for DD process, $
I(ED) — Equipment investment for ED process, $
I(BMED) — Equipment investment for BMED process, $
E(ED) — Electricity used for ED process, $
E(BMED) — Electricity used for BMED process, $
k_{IEM} — Market prices for AEM or CEM, $/$m^2$
k_{BM} — Market prices for BM, $/$m^2$
S(DD) — Required total membrane area for DD process, m^2
S(ED) — Required total membrane area for ED process, m^2
S_{IEM}(BMED) — Required total AEM and CEM area for BMED process, m^2
S_{BM}(BMED) — Required total BM membrane area for BMED process, m^2
k_e — Averaged industrial electricity price, $/kW·h
W(ED) — Energy consumption for ED process, kW·h
W(BMED) — Energy consumption for BMED process, kW·h
t' — Treating time for ED process
C_{H+} — H^+ concentration from retentate of DD process
I_Y — Equipment investment for 1 year
E_Y — Electricity for 1 year
M_Y — Total cost for 1 year

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