Process optimization of industrial waste salts separated into acid/base for the realization of resource utilization by bipolar membrane electrodialysis

Jiachao Yao, Lu Yang, Zhiping Ye, Jiade Wang*, Yiren Li, Xinyi Tong

College of Environment, Zhejiang University of Technology, Hangzhou 310014 China, Tel. +86 057188320915; Fax: +86-571-88320882; email: jdwang@zjut.edu.cn (J.D. Wang), Tel. +86 18768003028; email: 372605692@qq.com (J.C. Yao), Tel. +86 15957106270; email: 1162349774@qq.com (L. Yang), Tel. +86 057188320914; email: 632845473@qq.com (Z.P. Ye), Tel. +86 057188320937; email: yirenli@zjut.edu.cn (Y.R. Li), Tel. +86 057188320945; email: xinyitong@zjut.edu.cn (X.Y. Tong)

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ABSTRACT

In this study, the process optimization of industrial waste salts separated into acid/base for the realization of resource utilization was evaluated using bipolar membrane electrodialysis. Initial salt concentration and current density were believed to be the main factors for recycling performance, and then central composite design (CCD) of response surface methodology (RSM) was conducted to optimize the operating parameters regarding the generation of acid/base. The analyses of RSM revealed that the influencing degree of initial salt concentration on the acid/base generation was more significant than that of current density. Initial salt concentration of 240 g/L and current density of 36.54 mA/cm² were obtained as optimized conditions by RSM. Under optimum conditions, acid concentration of 1.89 mol/L and base concentration of 2.28 mol/L were predicted which had good agreement with experimental results, the corresponding current efficiencies were 66.73% for acid, and 71.28% for base, respectively. Meanwhile, the energy consumptions were calculated as 6.21 kWh/kg for acid and 5.03 kWh/kg for base. Furthermore, the effects of total organic carbon (TOC) concentration of using and energy consumption were also investigated. The results revealed that the TOC concentration of 0.68 g/L was benefited for the generation of acid/base and reduction of energy consumption.

Keywords: Bipolar membrane electrodialysis; Acid; Base; Waste salt; Process optimization

1. Introduction

Saline wastewater is produced in many industries including textile, mining, olive, pharmaceutical, chemistry, metallurgy, and petrochemistry [1,2]. Moreover, membrane technology in environmental applications produces a large amount of membrane brine which contain lots of waste salts [3,4]. The residual salts are one of the main pollutants in these wastewater, which pose great challenge in terms of environmental safety and public health [5]. Stricter reuse or discharge standards for saline wastewater treatment are being introduced and oblige industrial factories to upgrade their

existing waste treatment systems. Advanced oxidation methods are usually adopted for wastewater treatment: organic compounds and color can be efficiently removed; however, they are powerless for desalination. Several other methods, such as reverse osmosis, ion exchange, and activated carbon adsorption, are also used for the treatment of saline wastewater; however, these techniques may result in secondary pollution, which must be treated later and therefore increase the overall cost of the process [6]. The salt problem is one of the most core environmental problems which needs to be solved. It is also a problem for reuse of wastewater. Thus, a more sustainable solution may be to advocate considering the waste salts as renewable resource, and make the salts and the

^{*} Corresponding author.

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treated wastewater to be reused or recovered for economic reasons and environmental protection.

Electrodialysis (ED) is an electro-membrane separation process, in which ions migrate through ion permeable membranes from one solution to another. The ED process is considered as a promising alternative for saline wastewater treatment (i.e., desalination) due to its advantages of high efficiency, easy operation, and environmental compatibility; however, it cannot achieve resource utilization in a high level [7]. Remarkably, bipolar membrane electrodialysis (BMED), a technology of combining conventional ED and water dissociation of bipolar membrane, provides an attractive salts recovery method with environmental benignity [8,9]. It can not only migrate ions through ion exchange membranes from one solution to another but also split water into H⁺ and OH⁻ under a reverse bias of direct current field [10]; thus, it can be used to recycle valuable components from wastes by generating acid or base sources in situ [11,12]. Nowadays, owing to its technical advance, economic competence and environmental benignity, BMED has been widely used to produce, separate, and convert chemicals in the industrial field [13]. For example, Shen et al. [14] successfully fractionated glyphosate and NaCl from glyphosate neutralization liquor (1.28% glyphosate and 16.8% NaCl) by BMED; it served a double target: glyphosate recovery and a closed loop for the recycling of NaOH and HCl from NaCl conversion in glyphosate production. Li et al. [15] also investigated the BMED process for the treatment of simulated ammonium chloride wastewater, indicating that 57.67 g/L HCl and 45.85 g/L NH₃·H₂O could be obtained under optimum conditions. In this paper, it seems feasible to dissolve industrial waste salts into liquid phase, and then treated by BMED to produce acid/ base for the realization of resource utilization. Additionally, the treated wastewater may also be reused.

The performance of BMED process is affected by many factors, such as membrane materials (including bipolar membrane and ion exchange membrane), wastewater characteristics, and operating parameters [16,17]. Once the membrane materials are determined, the influences of wastewater characteristics and operation parameters seem to be crucial for the efficiency of BMED process. Tran et al. [18] investigated simultaneous regeneration of inorganic acid and base from a metal washing step wastewater by BMED, 1.76 N acid and 2.41 N base were produced in a long-term experiment at current density of 60 mA/cm² and initial acid/base concentration of 0.2 N. Xue et al. [19] reported the treatment of sodium acetate waste residue by coupling of diffusion dialysis or electrodialysis with bipolar membrane electrodialysis, indicating that the products purities and acid/base concentration decreased with an increase of total organic carbon (TOC) concentration due to the transport competition between organic matter and salt ions. Actually, many studies reported that current density, initial acid/base concentration, electrolyte concentration, flow rate, etc. were the main factors which could affect acid/ base generation and energy consumption in BMED [20-22]. Furthermore, the interactions between these factors also play important roles in generation of acid/base and energy cost. Zhang et al. [23] reported the effects of operating parameters (i.e., current density, flow rate, and initial acid concentration) and their interactions on the performance of BMED process

for treatment of glutamic acid fermentation wastewater. The analysis of variance indicated that current density was the most significant factor that influenced average current efficiency, followed by the interactions between current density and flow rate. Therefore, except for the investigation of the effects of main factors on BMED process, it is necessary to select an appropriate experimental method to investigate the influences of interactions among the factors.

Response surface methodology (RSM) is an effective technique for analyzing the interactions among operating factors, exploring the relationships between the response and the independent variables, and optimizing the processes or products [24]. The main advantage of RSM is less experimental quantity needed to evaluate multiple experimental parameters, which makes the entire optimization process more facile and cost-effective [25].

In sum, the purpose of this study is to investigate the process optimization of industrial waste salts separated into acid/base for the realization of resource utilization by BMED. Main factors (i.e., salt concentration and current density) were selected to evaluate the effects on generation of acid/base and energy consumption. Central composite design (CCD), as a method of RSM, was employed to reveal the interactions among main factors, and further obtain the optimum conditions for BMED process. Besides, the effect of organic impurity (i.e., TOC concentration) was also investigated on the generation of acid/base and the corresponding energy consumption.

2. Experimental

2.1. Characteristics of industrial waste salts

The industrial waste salts were selected from a pharmaceutical factory located in the region of Taizhou, Zhejiang province, China. In the pharmaceutical companies, the waste salts were mainly derived from two pathways. One pathway is through the chemical reactions in the pharmaceutical process which would produce waste salts, such as ammonium salt. The other was that, lots of salts were added in the separation phase to demulsify or dehydrate, such as sodium chloride and sodium sulfate; thus a large number of waste salts would be produced. In this study, the waste salt mainly contained NH⁺, Na⁺, Mg²⁺, Cl⁻, SO²⁻, and TOC (contributed by the residual organics during the pharmaceutical process), as shown in Table S1. In order to separate industrial waste salts into acid/base for the realization of resource utilization, the solid salts were dissolved into ultrapure water to obtain different concentrations of waste salts solutions, and then electro-oxidation process with Ti/PbO, anode and Ti cathode under current density of 15 mA/cm² was used as pretreatment before BMED process to remove color and a part of TOC from waste salts solution. The main characteristics of waste salt solutions for BMED process are summarized in Table 1.

2.2. BMED process

The schematic model and lab-scale BMED cell used in this study are shown in Fig. S1. Each membrane had an effective membrane area of 189 cm². The properties of cation exchange

Table 1	
Characteristics of waste salt solutions for BMED process	

Waste salt solutions (g/L)	80	120	160	200	240
TOC (g/L)	1.74	2.41	3.22	3.68	4.32
Conductivity (mS/cm)	96.32	138.43	174.13	217.71	248.38
pH	3.79	3.36	3.04	2.76	2.24

Table 2 Variables and experimental design levels for response surface

Independent factors	-α	Low level –1	0	High level +1	+α
Initial salt concentration (g/L)	47	80	160	240	273
Current density (mA/cm ²)	21	25	35	45	49

Alpha (α) value used was 1.414.

membranes (FKB, Germany), anion exchange membranes (FAB, Germany), and bipolar membranes (BMP) used in the experiments are listed in Table S2. Electrodes were made of titanium coated with ruthenium, and the two electrode compartments were rinsed with electrolyte solution. Compartments were separated by spacers with a thickness of 0.70 mm, and each compartment was connected to a submersible pump. The current applied in BMED was provided by a constant voltage/current-controlled DC power source (MPS 1005, Tradex, China).

For each experiment, the electrode compartment was filled with 0.2 mol/L Na₂SO₄ solution, the acid and base compartments were filled with 0.05 mol/L HCl and 0.05 mol/L NH₄OH, respectively. The flow rate was controlled at 20 L/h. The waste salt solution was pumped into the salt compartment. To ensure the same osmotic pressure, each compartment was filled with 500 mL solution. Before an electric current was applied, the solution in each compartment was circulated for half an hour to eliminate the visible gas bubbles in the stack which would increase the resistance of the stack [26].

In the process, initial salt concentration and current density were selected as two main parameters to observe the effect of single-factor on generation of acid/base and energy consumption. The concentrations of salt solution from 80 to 240 g/L, and current density from 25 to 45 mA/ cm² were selected in the experiments. Pre-experiments indicated that when the conductivity within the effluent was less than 10 mS/cm, it was no longer suitable to be treated by BMED, because the low salt concentration in salt compartment could lead to high energy consumption; thus, conductivity of 10 mS/cm was determined as the signal point for the end of experiment. Then, CCD of RSM was employed for the process optimization of industrial waste salts separated into acid/base for the realization of resource utilization. Meanwhile, the main effects and interactions between the operating parameters were also analyzed. In addition, two second-order polynomial models were established to describe the relationships between response and variables.

2.3. Response surface methodology

Owing to the significance of two effects on acid and base yield could be compared after they were coded, two variables X_i (X_1 X_2) were coded as x_i (x_1 x_2) according to Eq. (1):

$$x_i = \frac{X_i - X_0}{\Delta X} \tag{1}$$

where X_i is the uncoded value of the independent variable, X_0 is the center point of the investigated area, ΔX is the step change of variation. The initial salt concentration (X_1) and the current density (X_2) are selected as initial variables with five levels of -1.41 (α), -1, 0, +1, +1.41 (α) base on the single experimental results. Their range and level are shown in Table 2.

The second-order polynomial model was used to describe the relationship between response and variables that consists of linear, quadratic, and interactive components as follows [27]:

$$Y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ij} X_i^2 + \sum_{i_{i< j}}^k \sum_j^k b_i X_i X_j + e$$
(2)

where *Y* is response factor (acid/base concentration, mol/L), *i* and *j* denote linear and quadratic coefficients, respectively; b_0 is the intercept, b_i is the first order model coefficient, *k* is the number of factors, and *e* is a random number. After single factor experimental, the CCD with 13 runs was applied by Design-Expert 8.0.6.1 trial software.

2.4. Analysis methods

The concentrations of generated acid and base from BMED were determined by titrating with a standard sodium hydroxide and hydrochloric acid solution. Phenolphthalein and methyl orange were used as the indicator of titration end-points, respectively. Conductivity and pH value of waste salt solution were monitored by a conductivity meter and pH meter, respectively. The TOC was measured by TOC Analyzer (TOC-V CPN, Shimadzu, Japan) based on the combustion-infrared method.

The current efficiency CE (%) was calculated in Eq. (3) [27]:

$$CE = \frac{n(C_t - C_0)VF}{NIt} \times 100\%$$
(3)

where *n* is the ion's absolute valence, C_0 and C_t are the acid/ base concentration (mol/L) at time 0 and *t*, respectively. *V* (L) is the recirculated volume of solution in the acid/base compartment, *F* is the Faraday constant (96,485 C/mol), *N* is the number of operating units (*N* = 5), *I* (A) is the current.

The energy consumption E (kWh/kg), defined as the practical electric energy needed for producing 1 kg acid/base, was calculated using Eq. (4) [28]:

$$E = \int \frac{UIdt}{(C_t - C_0)VM} \tag{4}$$

where U (V) is the voltage drop across the BMED stack, M is the molar mass of acid/base.

All the experimental data were averaged from three independent experiments. The error was calculated to be approximately $\pm 5\%$.

3. Results and discussion

3.1. Influence of initial salt concentration

Fig. 1a shows the effect of initial salt concentration on the voltage drop across the membrane stack. The results indicated that the voltage drop decreased with the increase of the initial salt concentration. It was logically true that higher the salt concentration was, lower the electrical resistance would be. For each curve, the voltage drop decreased sharply in the beginning, manifesting that H⁺ and OH⁻ produced by water dissociation in the intermediate layer of bipolar membrane under application of the electric field and then the electrical resistance decreased. Afterwards, the voltage drop changed slightly with time, suggesting that the system was stable and reliable. Finally, the voltage drop bounced back, indicating that the ions depleted in the salt compartment.

The influence of initial salt concentration on acid/base yield is shown in Fig. 1b. It was exhibited that both acid and base yield rose as initial salt concentration increased. It was believed that at higher initial salt concentration, more ions would be migrated from salt compartment into acid/base compartment to produce acid/base. When it came to each curve, the acid/base concentration increased obviously with operation time at first, and then increased slightly. This was related to the decrease of ion concentration in salt compartment with operation time. Meanwhile, it was also observed that the generated base concentration was always higher than the acid concentration. It could be explained that the phenomenon of ion leakage occurred in the ion exchange membrane, and the leakage of the hydrogen ion was easier than hydroxide ion [29,30].

As shown in Fig. 1c, the energy consumption increased with the increase of initial salt concentration. Actually, as seen from Eq. (4), the influence factors of energy consumption not only include voltage drop, current, and generated acid/base concentration but also include operation time. Among them, the operation time was mainly related to the conductivity of salt solution as mentioned in Section 2.2: conductivity of 10 mS/cm was determined as the signal point for the end of experiment. The operation time was proportional to the initial salt concentration in this section which resulted in the variation of energy consumption. Another reason was that more organic impurities were contained with the increase of initial salt concentration, which might lead to the competition of ions migration, reducing acid/base generation [31].



Fig. 1. Influences of initial salt concentration on voltage drop (a), acid/base yield (b), and energy consumption (c).

3.2. Influence of current density

Fig. 2 displays the variations of voltage drop, acid/base yield, and energy consumption in function of current density. As shown in Fig. 2a, the voltage drop across BMED stack increased with an increase of current density. For each curve, the voltage drop at different current densities had a similar variation trend. It could be explained in the same way as that in Fig. 1a.

Fig. 2b shows the effect of current density on the acid/ base yield. The concentrations of generated acid and base rose as current density increased, reason being that more water was dissociated in the intermediate layer of bipolar membrane at higher current density [32,33]. At the end of the experiments, the concentration of generated acid increased from 1.56 to 1.79 mol/L, and the concentration of generated base increased from 1.82 to 2.13 mol/L as current density rose from 25 to 45 mA/cm², respectively. Meanwhile, increase of current density could also shorten the operation time effectively.

As shown in Fig. 2c, when the current density increased from 25 to 45 mA/cm², the current efficiency of acid decreased from 66.21% to 49.60% and the corresponding energy consumption increased from 6.43 to 8.14 kWh/kg; meanwhile, the current efficiency of base decreased from 71.30% to 62.40% and the corresponding energy consumption increased from 5.14 to 7.38 kWh/kg, respectively. This phenomenon could be explained by the following reason [14]: the concentration of generated acid/base increased with current density increased, which meant the osmotic pressure in acid/base compartment also increased. The higher pressure could accelerate the leak of ions, and thus resulted in a decrease of current efficiency and an increase of energy consumption.

3.3. Model fitting and process optimization

The levels of factors (i.e., initial salt concentration and current density) and their interactions on acid/base yield were analyzed by the CCD of RSM. The variations of acid/ base concentrations of experimental results and predicted values by CCD design are shown in Table 3. According to these two models, two linear (X_1, X_2) and squared $(X_1^2$ and $X_2^2)$ model items were significant for acid/base yield in BMED. The predicted responses $(Y_1 \text{ and } Y_2)$ could be expressed by second-order polynomial models in terms of coded factors, as:

$$Y_1 = 1.64 + 0.39X_1 + 0.078X_2 - 0.053X_1X_2 - 0.14X_1^2 - 0.079X_2^2$$
(5)

$$Y_2 = 2.00 + 0.41X_1 + 0.11X_2 - 0.043X_1X_2 - 0.14X_1^2 - 0.11X_2^2$$
 (6)

The results of the second-order response surface model fitting in the form of analysis of variance (ANOVA) are shown in Table 4. According to the data, the significance of each model was evaluated based on the R^2 of p value, Prob. (P) > F and adjusted R^2 [34]. The results revealed that the model values of Prob. (P) > F were less than 0.001 and the values of lack of fit were higher than 0.05, indicating that two models were statistically significant which could provide a good prediction with the experimental data. In addition, the

adjusted R^2 value of acid concentration model was 0.9847, and the adjusted R^2 value of base concentration model was 0.9619, suggesting that the model could explain 98.47% and 96.19% of the response changes, respectively [35,36]. Table 4 also shows that, for single-factor experiments, the *p* values of acid concentration on initial salt concentration and current density were <0.0001 and 0.0014 respectively; meanwhile, the p values of base concentration were <0.0001 and 0.0016, respectively. These results indicated that the effect of initial salt concentration on acid/base yield was more significant than that of current density.



Fig. 2. Influences of current density on voltage drop (a), acid/ base yield (b), and energy consumption (c).

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Significance of the coefficients in the regression model for acid and base concentrations

Table 4

Fig. 3 shows the influence of initial salt concentration and current density on the generated acid/base concentration by 3D plots. The acid/base concentration increased as current density increased from 25 to 38 mA/cm², and then showed a slight change with further increase of current density. Meanwhile, the acid/base concentration increased considerably with the increase of initial salt concentration. The results indicated that the influencing degree of initial salt concentration on the acid/base generation was more obvious than that of current density, which was consistent with the results in Table 4. Fig. 3 also shows that the interactions between initial salt concentration and current density affected the response obviously. The coefficients of interaction constant of these two variables in quadratic polynomial equation were less than 0.05 which also confirmed this observation. The optimum conditions for generation of acid/base could be determined by the analysis of response surface and the regression equations (Eqs. (5) and (6)): initial salt concentration of 240 g/L and current density of 36.54 mA/cm² were obtained. The results of three parallel experiments and model predictions under optimum conditions are listed in Table 5, suggesting that the model had high prediction accuracy and could overall reflect the changing regulation factually. Under the optimal operation conditions by the response surface design, the final generated acid and base concentration were 1.89 and 2.28 mol/L, the corresponding current efficiencies were 66.73% for the acid, and 71.28% for the base, respectively. Meanwhile, the energy consumptions were 6.21 kWh/ kg for acid and 5.03 kWh/kg for base.

3.4. Transport behavior of organic matter

Fig. 4a shows the distributions of TOC concentration in salt, acid, and base compartments with different initial TOC concentrations in salt compartment during BMED

Table 3 Experimental results and predicted values of the CCD design

			conc	Acid entration nol/L)	conc	Base entration mol/L)
Run	X_1	X_2	Actual	Predicted	Actual	Predicted
1	0	0	1.68	1.64	1.98	2.01
2	-1	-1	0.95	0.90	1.23	1.20
3	0	0	1.61	1.64	1.95	2.00
4	0	-1.41	1.34	1.37	1.64	1.56
5	0	0	1.65	1.64	2.04	2.02
6	0	0	1.64	1.64	1.97	1.99
7	-1	1	1.16	1.16	1.53	1.55
8	0	0	1.63	1.64	2.06	2.03
9	0	1.41	1.63	1.59	1.97	2.00
10	-1.41	0	0.77	0.80	1.07	1.06
11	1.41	0	1.94	1.90	2.41	2.31
12	1	-1	1.78	1.78	2.01	2.12
13	1	1	1.78	1.83	2.14	2.19

X₁: initial salt concentration; X₂: current density.

			Regression mo	odel for acid c	oncentration			F	kegression mod	lel for base c	oncentration	
	Sum of		Mean		<i>p</i> -value		Sum of		Mean		<i>p</i> -value	
Source	squares	df	square	F value	$\operatorname{Prob} > F$	Significant	squares	df	square	F value	$\operatorname{Prob} > F$	Significant
X	1.20		1.20	652.13	<0.0001	**	1.56		1.56	238.06	<0.0001	**
X,	0.048	1	0.048	26.02	0.0014	*	0.16	1	0.16	25.05	0.0016	*
X_1X_2	0.011	1	0.011	5.97	0.0446	*	0.044	1	0.044	6.72	0.0358	*
X_1^2	0.14	1	0.14	78.21	<0.0001	**	0.17	1	0.17	26.09	0.0014	*
X_2^2	0.044	1	0.044	23.57	0.0018	*	0.11	1	0.11	16.40	0.0049	*
Model	1.43	Ŋ	0.29	155.25	<0.0001	**	2.02	ŋ	0.40	61.51	<0.0001	**
Residual	0.013	~	1.848E-3				0.046	4	6.562E-3			
Lack of fit	0.010	ю	3.418E-3	5.10	0.0747		0.037	ю	0.012	5.47	0.0671	
Pure Error	2.680E-3	4	6.700E-4				9.000E-3	4	2.250E-3			
Cor total	1.45	12					2.06	12				
For acid: R-Squ For base: R-Squ	ared = 0.9467; ared = 0.8660;	Adj R-Sc Adj R-Sc	q = 0.9847; Adec q = 0.9619; Adec	A precision = 37 A precision = 25	7.589; * Significa 3.307; * Significa	nt ($p < 0.05$); ** Hi unt ($p < 0.05$); ** Hi	ghly significan ghly significar	it $(p < 0.0)$ it $(p < 0.0)$	01). 01).			

process under optimal operation conditions. The results indicated that the TOC could migrate from salt compartment to acid/base compartment: higher the initial TOC concentration in salt compartment, more the TOC would diffuse into acid/base compartment. Meanwhile, the TOC concentration of acid compartment was lower than that of base compartment, because the anion exchange membrane had a stronger inhibitory effect on organic impurities [19,37].

Fig. 4b shows the effect of TOC concentration on the acid/base yield. It indicated that both acid and base concentrations decreased with TOC concentration increased. The main reason was that a competition existed between ions and TOC migration: high TOC concentration could restrain the migration of ions from salt compartment to acid/base compartment. After 120 min treatment, with TOC concentrations increased from 0.68 to 4.33 g/L, the acid concentrations decreased from 2.24 to 1.88 mol/L, and the base concentrations decreased from 2.81 to 2.25 mol/L, respectively. Correspondingly, the energy consumptions for acid increased from 4.32 to 6.74 kWh/kg, and the energy consumptions for base increased from 3.52 to 5.63 kWh/kg, as shown in Fig. 4c. These results demonstrated that reduction of TOC concentration in feed liquid was beneficial to increase acid/base yield and reduce energy consumption.



Fig. 3. 3D surface plot of interaction between the parameters and acid (a) / base (b) yield.



Fig. 4. Influences of initial TOC concentration in salt compartment on TOC distribution in three compartments (i.e., acid, base and salt compartments) (a), acid/base yield (b); energy consumption (c) after 120 min treatment.

Table 5

Comparisons of experimental results and optimized values under optimal operation conditions

	Experimental 1	Experimental 2	Experimental 3	Predicted value
Acid concentration (mol/L)	1.85	1.88	1.86	1.89
Base concentration (mol/L)	2.27	2.25	2.24	2.28

4. Conclusion

In this study, it was environmentally and technically feasible to generate acid and base from industrial waste salts for the realization of resource utilization using BMED process. The operation parameters, such as initial salt concentration and current density, were investigated as the main factors for recycling performance. Based on single-factor experiments, CCD design of RSM was chosen to optimize the BMED process to produce acid and base, and thus regression models were established. Initial salt concentration of 240 g/L and current density of 36.54 mA/cm² were obtained as operation conditions by RSM. Under optimum conditions, acid concentration of 1.89 mol/L and base concentration of 2.28 mol/L were predicted which had good agreement with experimental results. Furthermore, the effects of TOC on the acid/base yield and energy consumption were investigated. With the TOC concentration of 0.68 g/L, acid concentration of 2.24 mol/L and base concentration of 2.81 mol/L were achieved, the corresponding energy consumptions were 4.32 kWh/kg for acid and 3.52 kWh/kg for base. In conclusion, BMED process is an attractive technology that has significant economic and social benefits in reclamation of industrial waste salts. After BMED process, the generated acid/base and treated wastewater could be reused for economic reasons and environmental protection.

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Supplementary information

Table S1

Main ion contents of the industrial waste salts

Ions	NH_4^+	Na⁺	Mg ²⁺	Al ³⁺	Ca ²⁺	Cl-	SO ₄ ²⁻	TOC
Content (%)	47.13	1.37	0.31	0.14	0.12	40.28	4.10	1.97

Table S2

Main characteristics of the membranes used in BMED experiments

Membrane	Thickness (mm)	IEC (meq/g)	Area resistance (Ω cm ²)	Transport number
BMP	0.16-0.23	-	_	-
FKB	0.11-0.13	1.2–1.3	<5	>0.98
FAB	0.11-0.13	>1.1	<3	0.95





Fig. S1. Schematic model (a) and lab-scale (b) BMED (BPM: bipolar membrane; AEM: anion exchange membrane; CEM: cation exchange membranes; (1) electrolyte tank; (2) feed tank; (3) acid tank; (4) base tank; (5) BMED stack; (6) flow meter).