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## A win-win strategy for the reclamation of waste acid and conversion of organic acid by a modified electrodialysis



Yu-xiang Jia, Xiang Chen, Meng Wang\*, Bei-bei Wang

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, China College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

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#### ABSTRACT

In view of some inherent problems, such as the high mobility of protons and low dissociation degrees of organic acid, the conventional electrodialysis technology must be improved before being applied widely in the related fields. In this work, a win-win strategy for simultaneously reclaiming industrial waste acid and producing organic acid by ion substitution electrodialysis (ISED) was put forward. Above all, the ISED technology was further investigated, including its universality and work performance influenced by the membrane selection. Subsequently, a modified ISED was developed and applied in the conversion of acetic acid using the simulated waste acid effluent as proton source. The experiments indicated that a much better work performance, including improved current efficiency and conversion rate and reduced energy consumption, can be achieved when compared to the conventional technology. Especially, it was observed that the content of electro-migrated metal ions in the produced organic acid was so low that a high purity organic acid product can be easily obtained after a simple post-treatment.

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#### 1. Introduction

It is well known that the metal finishing industries, such as electroplating and acid pickling, have played important roles in the consumption of various acids including hydrochloric acid, sulfuric acid and nitric acid. Accordingly, excess quantities of waste acid are produced, for example, more than 25 million tons per year relevant waste acid in China according to a roughly estimation [1]. In general, the waste acid embraces some characteristics, such as being enriched with heavy metals (e.g. iron, nickel, zinc, chromium and many others), relatively low acid concentration (e.g. below 5%) and huge effluent volume. Nowadays, it has been widely accepted that the direct discharge of the waste acid solution is not only a serious threat to environment but also a huge resource waste.

Many techniques have been put forward to reduce its negative impact on the receiving environment or recover valuable resources from it, e.g. heavy metals, acid and water [2,3]. Among them, ion-exchange-membrane-based techniques have attracted much attention, including conventional electrodialysis [4–6], bipolar membrane electrodialysis (BMED) [7], electro-electrodialysis (EED) [8], neutralization dialysis [9], diffusion dialysis [10–16], and so on. However, some practical work performances have

E-mail address: wangmeng@ouc.edu.cn (M. Wang).

indicated there still exist some unresolved problems to limit their applications in the reclamation of the waste acid. For example, the proton leakage of anion exchange membrane (AEM) usually seriously deteriorates current efficiency of electrodialysis process for acid concentration and even results in failure to recovering acid with a relatively high concentration [17]. Besides, as a separation process driven by concentration gradient, the diffusion dialysis generally becomes little efficient at low acid concentration [2].

On the other hand, large amounts of researches have indicated that the ion-exchange-membrane-based techniques can play important roles in the conversion of organic acids from their corresponding organic acid salts [18]. Roughly speaking, two categories can be divided according to the utilized proton sources, including the in situ production of protons and extra input of inorganic acids. The typical representatives of the former case are EED technology [19–21] and BMED technology [22–27], in which the protons are generated by means of electrode reactions and solvent split. respectively. For the latter case, represented by electrometathesis (EMT) [28], the weak organic acid can be produced from its corresponding organic salt via double composition reaction with the additional strong inorganic acid. However, EMT technology usually suffers from high energy consumption and low producing capacity due to the low dissociation degree of organic acid and the migration of organic acid anions through membranes and then needs some additional matches for the process intensification [29]. For

<sup>\*</sup> Corresponding author at: College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China.

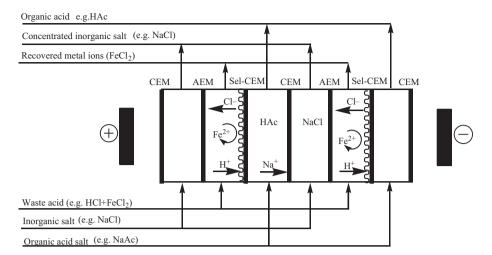


Fig. 1. Schematic diagram of the modified ISED membrane stack. (CEM: cation exchange membrane; Sel-CEM: monovalent selective cation exchange membrane; AEM: anion exchange membrane.)

instance, Choi et al. put forward so-called ion substitution electrodialysis (ISED) technology in which only cation exchange membranes (CEMs) were employed and successfully recovered lactic acid from sodium lactate [30]. Although a relatively low potential drop was observed when compared to the conventional electrodialysis, the process efficiency was reduced significantly because the back transport of the organic acid cation became more and more serious along with its accumulation in the inorganic acid feed.

In this report, a modified ISED technology is developed for further improving its work performance and attempted to simultaneously reclaim the industrial waste acid and convert the organic acid salt into the corresponding organic acid. Just as demonstrated in Fig. 1, the repeating unit of the so-called modified ISED membrane stack consists of two adjacent CEMs and one AEM. Different from the previous technology, the salt produced by the ion substitution will be isolated from the acid feed and then its back transport can be effectively avoided. Besides, the monovalent selective CEM is inserted between waste acid compartment and organic acid salt compartment for an effective separation between protons and heavy metals. Hopefully, a Win-Win strategy for the reclamation of waste acid and production of value-added organic acid by a modified ISED can be carried out efficiently.

#### 2. Experimental section

#### 2.1. Materials

All the chemicals purchased from Sinopharm Chemical Reagents CO. Ltd., such as sodium formate, sodium acetate, sodium malonate, sodium hydroxide, sodium sulfate and ferrous chloride, were analytically pure and used as received. Deionized water supplied by Qing-dao Xin-da Ltd. was used throughout the study.

#### 2.2. Setup

The electrodialysis setup comprises the following sections, such as DC power supply (DF1731SD2A, Ningbo Zhongce Electronics Co. Ltd.), peristaltic pump (Baoding Longer Precision Pump Co., Ltd., China) to regulate the flow rate (300 ml/min) and a lab-made membrane stack. The membrane stack contains two electrode compartments in which 0.2 M  $\rm Na_2SO_4$  solution are fed as electrode solution. Besides, two titanium electrodes coated with ruthenium are inserted for supplying the constant current. CEMs and AEMs

(effective area, 4 cm × 4 cm) are separated by plexiglas spacers (8 mm in thickness). In order to eliminate the effects of electrode reactions as much as possible, three repeating units were employed during the electrodialysis experiments. Series of constant-current electrodialysis experiments were conducted in a batch mode by the ISED membrane stack in which only CEMs were assembled and the modified ISED membrane stack, respectively, and compared. Therein, three kinds of typical CEMs which embrace different proton transport behaviors, including Fumasep FKB (Fuma), CIMS (ASTOM) and NAFION 117(DuPont), were employed. Besides, the JAM-II-05 AEMs (Beijing Ting-run) were adopted for the construction of the modified ISED membrane stack. The main characteristics of all the used membranes were listed in Table 1.

#### 2.3. Composition analysis

Samples were taken every thirty minutes. The acid concentrations were determined by acid-base titration using phenolphthalein as indicator. The concentrations of metal ions were determined by Atomic Absorption Spectroscopy (Perkin Elmer, 9700T). The volume variations of the remaining fluid in the reservoirs were recorded in real time according to the changes of the liquid level of tanks. In addition, conductivity meter (DDSJ-308A, Lei-ci) and pH meter (pHS-3G, Lei-ci) were daily calibrated for the online measurements.

**Table 1**The main characteristics of the membranes used in this study [31].

Properties	Grade			
	Fumasep FKB	NAFION-117	NEOSEPTA CIMS	JAM-II-05 <sup>a</sup>
Characteristics	CEM for BPED	Proton exchange membrane	Monovalent selective CEM	AEM for ED and BPED
Thickness (mm)	0.08- 0.10	0.18	0.14-0.17	0.16-0.23
Ion exchange capacity (meq/g)	0.9-1.0	0.89	2.0-2.5	1.8-2.2
Area resistance $(\Omega \text{ cm}^2)$	<4	1.5	1.8	4-8
Permselectivity	>0.96			0.90-0.95

<sup>&</sup>lt;sup>a</sup> Supplied by the manufacturer.

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