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Removal of heat stable salts (HSS) from spent alkanolamine wastewater using electrodialysis

Yaoming Wang[a], Wei Li[b], Haiyang Yan[b], Tongwen Xu[a,*]

[a] *CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*
[b] *Hefei ChemJoy Polymer Materials, Co., Ltd., Hefei, Anhui 230601, People's Republic of China*

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ABSTRACT

The formation of heat stable salts (HSS) is a tough problem for aqueous alkanolamines solution in gas processing industry. In this study, a self-made electrodialysis stack was assembled to remove the HSS from spent amine wastewater. Results indicated that the optimum current density is 15 mA/cm^2. An increase in pH is beneficial for amine recovery but is harmful to the lifespan of membranes. The ED process cost is estimated to be 14.6 $/t with the energy consumption of 39.4 kWh/T. Comparison with the conventional neutralization or replacement methods, ED is not only energy-saving but also environmentally friendly for the removal of HSS from the spent amine wastewater.

Introduction

Aqueous alkanolamines are promising desulfurizing absorbents in gas processing industry to remove acidic gases [1,2]. These amines are considered as one of the most economical and widely used absorbents to effectively remove H_2S, CO_2, and other acidic components. But the degradation of the amine absorbents during gas desufurization causes increasing operational costs and maintenance. In commercial plants, the contamination and degradation of amines is unavoidably happened. It is caused by the oxidation and thermal degradation of the amines themselves, the entrance of some trace compounds produced during normal refining activities, or by the reaction between oxygen and H_2S and CO_2. As a consequence, HSS which cannot be regenerated in the stripper, are formed in a variety of operations especially in refineries and gas-treating industries. HSS are the products of reaction between the degraded organic acids and alkanolamines, containing formates, acetates, glycolates, oxalates, etc. Hence, the composition of HSS is very complex. It includes inorganic HSS with the anions impurities such as Cl^-, SO_4^{2-}, and SCN^- as well as the organic HSS with the anions impurities such as $HCOO^-$, CH_3COO^-, $CH_3CH_2COO^-$, and etc. The accumulation of HSS has a detrimental impact on amine system operations. The formation of HSS will reduce the effective capacity of the amine solution, will cause corrosion, will aggravate operational problems such as foaming, amine loss and change in the vapor liquid equilibrium, as well as will increase amine replacement and make-up [3–6]. To address these problems, various options and processes for removal of HSS from amine gas treating solutions are proposed such as neutralization of amine with sodium or potassium caustic and replacement of part amine with fresh one for a certain period of time. However, neutralization can solve the amine loss but the other problems such as foaming, corrosion, etc. cannot be overcome [7]. The replacement with fresh amine leads to the discharging of a large number of wastewater and places a heavy burden on the environment. The other options include distillation of the free amine away from the salt and regeneration of amine with ion exchange resin [8,9]. But the energy consumption of distillation is a practical shortcoming. In case of ion exchange method, a frequent regeneration of exhausted exchange resin not only requires a high consumption of chemicals but also causes severe secondary pollution for the disposal of salty sewage water. Moreover, it is preferable to recycle rather than discharging the amine by considering the low biodegradability of the spent alkanolamine spent wastewater.

Electrodialysis (ED), as a well proven separation technology, has found more and more applications in water desalination, clean production or separation, resources recycling, and power generation [10–12]. As opposed to other separation techniques, ED does not suffer from major drawbacks, such as generation of large

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* Corresponding author.
E-mail address: twxu@ustc.edu.cn (T. Xu).

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amounts of waste, use of hazardous solvents, short lifetimes of adsorbents, etc. [13,14]. For these reasons, ED has been attempted to remove HSS from amine solution [15–18]. These studies have proved the feasibility of ED for the removal of HSS from the amine solution. But most of these studies were conducted with a simulated amine solution. The basicity property of amine in wastewater is harmful to most common quaternary anion exchange membranes [19,20]. But the long stability of the membranes for the recovery of amine from spent wastewater was never studied. Besides, the effect of applied current density, one of the most important parameters affecting the performance of ED process is still lacking in the literature. To industrialize the ED technology for spent amine recycling, the process cost as well as the stability of the membranes must be investigated. These issues are scarcely reported in the literature. Therefore, the main objective of this study is to (1) investigate the effect of current and initial pH on the removal of HSS and the amine recovery; (2) evaluate the stability of ion exchange membranes; (3) estimate the cost of ED process.

Experimental

Materials

The spent amine wastewater was collected from the H_2S desulfurization stripper in a thermoelectric factory. The feed solution contains 20.38 wt% *N*-methyldiethanolamine and 2.54 wt % HSS. The conductivity and pH value of the feed solution were 13.96 mS/cm and 10.55, respectively. The membranes used for the ED experiments were CJ-MA-1 (Hefei ChemJoy Polymers Co., Ltd., China) and CJ-MC-1 (Hefei ChemJoy Polymers Co., Ltd., China), and their properties were listed in Table 1. All the chemicals were of analytical grade.

ED set-up

A schematic diagram of bench-scale ED was illustrated in Fig. 1. It was composed of (1) a cathode and an anode were respectively fixed on two organic glasses plate each with a rectangular notch; the electrodes were made of iridium–tantalum with a thickness of 1.5 mm. The electrodes were fixed into the notch with epoxy glue to make an even surface on the organic glasses. A direct current power supply (WYL1703, Hangzhou Siling Electrical Instrument Ltd.) was connected on the electrodes. The voltage drop across the stack was directly read from indicators on the power supply. (2) Ten pieces of cation exchange membranes and ten pieces of anion exchange membranes were alternatively arranged. The effective area of each membrane was ~200 cm^2. (3) Sealing spacers made from PE with a thickness of 0.75 mm was used to separate the membranes; (4) beakers to store the feed. Each beaker was connected with a submersible pump (AP1000, Zhongshan Zhenghua Electronics Co. Ltd., China, flow rate of 22 L/h) to form a circulating loop. In our experiments, three circulating loops, namely, electrode compartment, concentrate compartment, and diluate compartment were established in this ED stack. A 400 mL Na_2SO_4 solution (0.3 mol/L) was fed into the electrode chambers as the rinse electrolyte. A 400 mL aqueous alkanolamine solution was fed into the diluate compartment and the same volume of tap water was fed in the concentrate compartment. Before the experiment, each chamber was circulated for 30 min to eliminate the visible bubbles. All the experiments were run at room temperature.

Table 1
The main characteristics of the membranes used in the experiments.

Properties	CJ-MC-1	CJ-MA-1
Thickness (mm)	0.200	0.145
Ion exchange capacity (mmol/g)	1.50	1.25
Water uptake (%)	35	32
Resistance ($\Omega\,cm^2$)	2.0–3.5	2.0–3.5
Transfer number (%)	98	99
Break stress (MPa)	>3.5	>3.5

Energy consumption

The energy consumption (E, kWh L^{-1}) of the ED process was calculated as Eq. (1),

$$E = \int_0^t \frac{UIdt}{C_t VM} \tag{1}$$

$U(V)$ is the voltage drop across ED stack; $I(A)$ is the current applied; V is the volume of feed compartment;

Membrane stability evaluation

To evaluate the stability of the ion exchange membranes, two pieces of anion and cation membrane with each size of 10 cm × 30 cm were tailored to dozen small pieces. Each piece was marked and the dry membrane weight was determined. These small piece membranes were immersed in the spent amine wastewater. One piece of membrane was picked out from the wastewater solution after the setting time period. The immersed membranes were measured from ion exchange capacity (mmol/g dry membrane), area resistance (R_m, $\Omega\,cm^2$), and dry weight (g). The variation rate (λ) of the membrane after immersing in the spent amine solution was defined in following Eq. (2).

$$\lambda = \frac{W_{final} - W_{initial}}{W_{initial}} \tag{2}$$

where W_{final} (g) and $W_{initial}$ (g) denote the dry weight of membrane after and before immersing in the spent amine wastewater, respectively.

Analytical methods

The conductivity of the spent amine solution (dilute chamber) was monitored by a conductivity meter (DDS 307, Shanghai INESA Scientific Instrument Co., Ltd., China). To determine the HSS concentration, the spent amine solution was exchanged with a strong H-form cation exchange resin and pretreated with 50 mesh size filter, and the obtained supernatant solution was titrated against 0.05 mol/L NaOH using phenolphthalein as indicator. The total amine concentration was determined by titration with 0.05 mol/L H_2SO_4 using bromocresol green/methyl red as indicator.

Results and discussion

Effect of current density

The applied current density is one of the most important parameters affecting the performance of ED process. In ED process, less membrane area will be needed for a certain size of installation at a higher current density. Therefore, a high current density saves the capital cost but leads to a decrease in the life-span of the membranes. A low current density is beneficial for current utilization and energy consumption; but a low current density is not favorable to the capital cost. Fig. 2 shows the effect of current density on the voltage drop in the ED stack and conductivity in the spent amine solution during the experiment. The starting voltage is linearly increased with an increase in current density. This is consistent with the Ohm's law. Meanwhile, the voltage drops first

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