



Removal of heat stable salts from *N*-methyldiethanolamine wastewater using electro dialysis: a pilot-scale study

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ABSTRACT

Heat stable salts (HSS) are well-known degradation products of gas desulfurization using *N*-methyldiethanolamine (MDEA) solvents. Their formation in MDEA solution causes significant problems in gas processing industrial systems. In this study, a pilot-scale electro dialysis (ED) stack was assembled for the removal of the HSS from spent MDEA solution. Results show that the optimum voltage and dilute MDEA solution flow rate were determined of 80 V and 4 m³/h based on the HSS removal efficiency and the loss of MDEA during continuous operation. During batch experiments, the effect of initial pH in the spent MDEA solution was investigated. By adding NaOH to adjust the initial pH = 10.5 of the MDEA solution, the HSS removal efficiency is 77%, which is 26.09% higher than that without NaOH addition, the loss of MDEA is 5.73%, which is 12.65% lower than that without NaOH addition. The total process cost of ED method is calculated to be 748.68 \$/(T HSS).

Keywords: Desalination; Electro dialysis; Heat stable salts; *N*-methyldiethanolamine

1. Introduction

Integrated gasification combined cycle (IGCC) power generation system is an emerging high-efficiency coal fired power generation technology. The main system components include air separation, coal gasification, synthesis gas purification, and gas/steam combined cycle power generation. Coal synthesis gas generated in coal gasification systems includes H₂, CO, CO₂, H₂S, and other acidic gases, the acidic component of the gas must be purified prior to release, to avoid serious air pollution and greenhouse effects. In synthesis gas purification systems, the use of *N*-methyldiethanolamine (MDEA) solvents shows

promise as an effective desulfurizing absorbent, for the highly selective removal of acidic gases [1,2].

However, chemical degradation, thermal degradation, and oxidative degradation gradually occur during the long-term desulfurization, the formation of so-called heat stable salts (HSS) caused by the chemically irreversible reactions between these degradation products and other impurities gases in the feed gas stream [3]. HSS have a very complex composition but are commonly composed of formates, acetates, glycolates, and oxalates, such as Cl⁻, SO₄²⁻, SCN⁻, HCOO⁻, CH₃COO⁻, and CH₃CH₂COO⁻, in addition to other compounds. Because HSS cannot be regenerated in the regenerated stripper under high temperatures, with

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the increase of desulfurization time, HSS will accumulate in the MDEA solution [4,5]. The accumulation of HSS in the MDEA solution has a detrimental impact on the process of gas absorption in gas purification systems, by reducing the effective capacity of MDEA absorption systems and potentially reducing the life-span of equipment due to corrosion and fouling [6,7]. Therefore, the removal of HSS from MDEA solutions is urgently required for practical industrial application [8].

Traditionally, most production facilities in China have adopted intermittent methods to reduce the HSS content of MDEA solutions. For example, the removal of unwanted impurities generally rely upon neutralization of MDEA with sodium or potassium hydroxides, or replacement of part of the MDEA content with fresh MDEA solution [9]. However, although neutralization can reduce the loss of MDEA, it also adds new impurities to the MDEA solution, such as Na^+ , K^+ , in addition, it only resolves the HSS from the binding amine ($\text{MDEAH}^+\text{HSS}^-$) into the MDEA solution, but does not remove the HSS out of the solution. Under high temperatures, few sodium and potassium salts will pass through to the gas turbine, causing corrosion of the turbine blades. Or worse, the amount of sodium ions introduced will affect the absorption of H_2S by MDEA solution [10]. Replacement of MDEA solutions results in a high level of waste, as well as creating a large economic burden and a negative environmental impact. The method of distillation can also be used for removal of HSS in lean MDEA wastewater, but it is highly energy intensive and can cause degradation of MDEA, limiting its practical application [5].

Anion exchange resin method is an effective way to separate HSS from MDEA solutions in industrial systems, although the relatively high cost of resin and the frequent regeneration of resins methods limits their practical applicability [11]. In addition, the frequent regeneration of saturated resins results in a high requirement for acid and alkaline solutions, as well as causing serious secondary pollution due to the acid and alkaline wastewater produced. Reports also show that the desalination procedure of exchange resin method was not successive and the quality of resins decreased, resulting in a potential reduction in water quality due to the frequent need for regeneration [12].

Electrodialysis (ED) is gaining increasing attention in the field of water resource management, with evidence suggesting it may hold promising for high salt water desalination, valuable resources recycling and power generation systems [13–15]. ED utilizes an electrical current to drive ions from one solution to another, allowing salt water solutions to be desalted using electricity, while little additional energy inputs are required [14,16]. Compared to other desalination techniques, ED can avoid some major problems

such as high volume waste production, high operational costs and the need for discontinuous desalination. Due to these advantages, several studies have investigated the removal of HSS from MDEA wastewater using ED [8,9,17].

However, in a majority of current research, experiments were conducted with simulated MDEA solutions or in lab-scale experimental set-ups, with effective industrial ED applications scarcely reported in the literature. Furthermore, in most literatures, processing costs are calculated as the cost of processing each T of MDEA solution [18,19]. In fact, due to the HSS contents in different MDEA wastewater are different, the degree, and amount of HSS removal are also different. This calculation method is difficult to reflect the actual treatment cost. In addition, researchers considered adjusting the pH of MDEA solution to promote HSS removal efficiency, but they did not consider the effect of other ions introduced after adjusting the pH, such as Na^+ , K^+ , on the MDEA solution itself and the desulfurization system.

Therefore, the main objective of this study was to assess the removal of HSS from MDEA solutions using an ED method in pilot-scale. The aims of this research were to (1) investigate the HSS removal efficiency, the loss of MDEA and the water transfer at optimal operation voltage and dilute MDEA solution flow rate circular flow rate in continuous experiments, (2) investigate the effect of NaOH addition in intermittent experiments, (3) estimate the daily HSS removal capacity and calculate the actual economic cost of the ED process by removing per ton of HSS.

2. Experimental

2.1. Materials

This pilot-scale experiment completed the entire pilot-scale experiment in an IGCC power plant in Tianjin, China, with the spent MDEA solution collected from the H_2S desulfurization stripper at this facility. The feed solution contained 23.0 wt.% MDEA and 8.5 wt.% HSS. The conductivity and pH of the spent MDEA solution were 24.12 mS/cm and 9.26, respectively. The specific water quality of spent MDEA solution is shown in Table 1. AMX (ASTOM Corporation, Japan) and CMX (ASTOM Corporation, Japan) membranes were used for ED experiments, with their properties listed in Table 2.

2.2. ED set-up

A flow-process diagram of the pilot-scale ED system is provided in Fig. 1. The processing capacity of this ED system is 1–4 T/h. The system was composed of (1) a cathode and an anode are fixed on the cathode and anode plates, respectively, made of platinum-coated titanium and

Table 1
Content of HSS components in the spent MDEA solution

Cation	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Concentration (mg/L)	547.4	776.6	429.4	23.73	63.6
Anion	Cl^-	COOH^-	SO_4^{2-}	SO_3^{2-}	CH_3COO^-
Concentration (mg/L)	2,672.3	1,576.2	1,753.3	2,532.6	2,630.2

$$E = \frac{\int_0^t U I d_t}{V(C_{d,0} - C_{d,t})} (\text{kW h} / (\text{kg HSS})) \quad (3)$$

where U is the voltage drop across ED stack (V), I is the current across ED stack (A), V is the volume of the dilute MDEA solution (L), $C_{d,0}$ is the initial HSS concentration of the dilute solution, wt.%, $C_{d,t}$ is the HSS concentration of the dilute solution at t -time, wt.%.

2.4. Analytical methods

The conductivity and pH of the spent MDEA solution were real-time monitored using a conductivity meter (COND 8300, Guangdong Minghong Instrument Co., Ltd., China) and a portable pH meter (DDB-303A, Leici, China), respectively. The data stored in an intelligent control system, along with electrical current and voltage data. The ion concentration was measured by ion chromatography (ICS1100, DIONEX, USA). To detect the HSS concentration, a strong H-form cation exchange resin was placed in the spent MDEA solution, with the obtained solution titrated against 0.1 mol/L NaOH using phenolphthalein as an indicator [18]. The total MDEA concentration was determined according to the Analytical method of chemical composition for activated MDEA decarbonization desulfurization agent (GB/T 31589–2015).

3. Results and discussion

3.1. Effect of applied voltage during continuous operation

In this study, the potentiostatic voltage mode was selected due to the constant voltage is safer than a constant current [20]. It is mainly due to that when the ED system was operated at a constant current, ion concentrations decrease in compartments, and strong hydrolytic separation occurs on the surface of the ion exchange membrane, to maintain a constant current [21]. In constant voltage mode, the current can change according to the solution resistance, reducing the effect of concentration polarization [22]. The applied voltage is a critical operating condition in ED desalination systems, as the voltage determines the current and hence the separation efficiency of HSS as well as energy consumption [9].

Here, nine voltages between 55 and 95 V were selected to investigate the effect of voltage on the removal efficiency of HSS and the loss of MDEA, while the dilute MDEA solution flow rate constant at 4 m³/h. After the ED system had fully stabilized for half an hour, experimental data collection was initiated. As shown in Fig. 2, the HSS removal efficiency is proportional to the applied voltage. It is mainly due to a higher voltage can bring out a stronger mass transfer driving force for ions, to increase the mobility of ions further [23]. A higher applied voltage is beneficial for HSS removal, resulting in shorter treatment durations. Therefore, a relatively high applied voltage is required. However, Fig. 2 also shows that the loss of MDEA increases with the increase of voltage. It is mainly due to the hydrolysis of MDEA occurs in aqueous solution and the hydrolysis MDEAH⁺ migrates to the concentrate solution under the action of

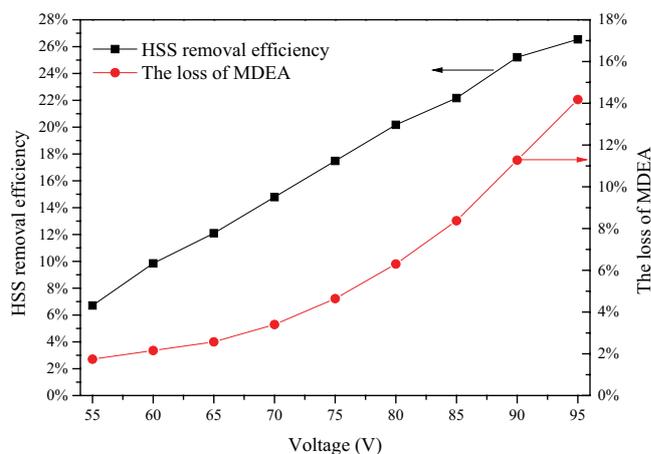


Fig. 2. Variations in HSS removal efficiency and the loss of MDEA under different applied voltages.

electric field. The migration speed of MDEAH⁺ increased with the increasing voltage, resulting in the increase of the loss of MDEA with the same running time. In addition, a high voltage will lead to a decrease in the life-span of membranes by accelerating membrane fouling and concentration polarization [18]. Therefore, consideration of both HSS removal efficiency and the loss of MDEA, 80 V was selected as the appropriate voltage for subsequent experiments.

3.2. Effect of dilute MDEA solution flow rate during continuous operation

The dilute MDEA solution flow rate is one of the important factors that affects the ions transfer rate [24]. Different dilute MDEA solution flow rate change the flow of solution in the ED stack, which is closely related to the solution viscosity and geometrical parameters of the membrane [25].

In this work, experiments were conducted at dilute MDEA solution flow rate: 2, 4, and 6 m³/h. In these cases, all the operations were carried out at the voltage of 80 V and the experimental results are shown in Fig. 3. It can be obviously seen that the higher the dilute MDEA solution flow rate, the higher the HSS removal efficiency.

It is mainly due to during the ED process, the ion migration is closely related to the adsorption of ions on the membrane surface. When the dilute MDEA solution flow rate increases, the turbulence of the solution increases, cause a thinner diffusion boundary layer on the membrane surface and a smaller internal resistance of the membrane. Therefore, the ion migration rate increases [26]. Though a higher dilute MDEA solution flow rate will cause a shorter retention time of ions on the membrane surface. The ions concentration remain a relatively high level during the continuous experiment, cause the dilute MDEA solution with high ions concentration has little influence on the probability of ions adsorbing and binding to the membrane surface.

Fig. 3 also shows that the loss of MDEA has a relatively stable level for the dilute MDEA solution flow rate of 2 and 4 m³/h, but a sharp increase from 5.41% to 9.43% for the dilute MDEA solution flow rate of 4 and 6 m³/h. It is mainly due to the radius of MDEAH⁺ hydrated ion is obviously

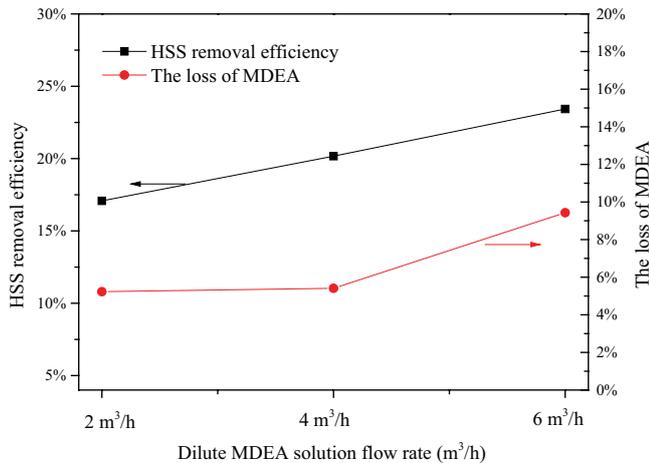


Fig. 3. Effect of dilute MDEA solution flow rate.

larger than other cations, such as Na^+ , K^+ , in the spent MDEA solution. The effect of dilute MDEA solution flow rate on MDEAH^+ is much lower than that of other cations [19]. Therefore, as Fig. 3 shown, the loss of MDEA is similar when the flow rate of dilute MDEA solution are 2 and 4 m^3/h . When the dilute MDEA solution flow rate increases to 6 m^3/h , the pressure of the dilute compartment becomes larger, which is higher than the pressure of the concentrate compartment, so that the MDEA molecules and water molecules in the dilute compartment have the power to move to the concentrate compartment, thus increasing the loss of MDEA. Therefore, the optimal dilute MDEA solution flow rate were determined to be 4 m^3/h .

3.3. Operating at the optimal voltage and dilute MDEA solution flow rate during continuous operation

3.3.1. HSS concentration in dilute and concentrate MDEA solution

Fig. 4 shows the variation of the HSS concentration in the dilute and concentrate MDEA solution over time. The change of HSS concentration in the concentrate MDEA solution over time follows DoseResp equation, and the correlation coefficient $R^2 > 0.99$. The HSS concentration rapidly increased from 8.50% to 20.16% in the first 3 h. As the time continued to increase, HSS concentration continued to slightly increase and tended to be stable. The HSS concentration in dilute MDEA solution decreased from 8.5% to 6.36% in the first hour, then gradually increased to 6.87% and then fluctuated around this point for the rest of the experimental period.

As we know that, in the ED process, salt flux is affected by two processes. Firstly, diffusion flux occurred due to the chemical potential gradient, caused by the difference in solute concentrations across the membrane. Secondly, migration flux occurs due to the electrical potential gradient, caused by the electrical current [27]. At the beginning of the experiment, the HSS concentration in dilute compartment and concentrate MDEA solution are almost the same, resulting in a small chemical potential gradient. As a result, the electrical potential gradient plays a dominant

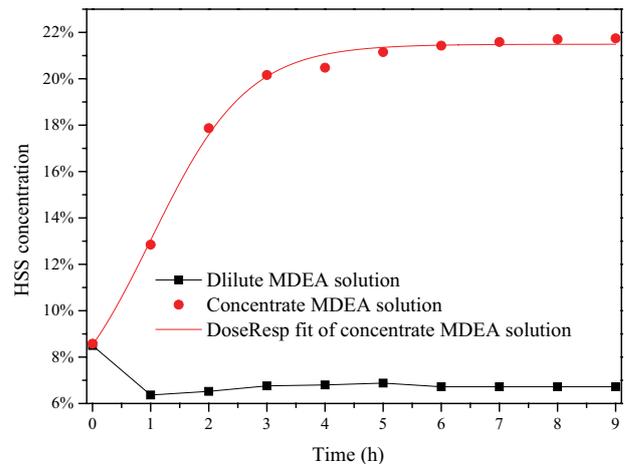


Fig. 4. Variation in current and HSS concentration of dilute, concentrate compartment over time.

role in the salt migration process. As the HSS concentration in the concentrate MDEA solution gradually increases, the chemical potential gradient between dilute MDEA solution and concentrate MDEA solution increase with time, driving the ions in the concentrate MDEA solution to migration to the dilute MDEA solution. The HSS migration in dilute MDEA solution into the concentrate MDEA solution gradually becomes slower. Therefore, the increase rate of HSS concentration in concentrate MDEA solution reduces, while the HSS concentration in dilute MDEA solution increases. When the electrical potential gradient and the chemical potential gradient gradually reach equilibrium, the concentrations of both the concentrate compartment and the dilute compartment stabilize and the current no longer changes.

3.3.2. Water transfer from dilute compartment to concentrate compartment

The water transfer from dilute compartment to concentrate compartment is a key indicator of the effectiveness of the ED process performance, as it affects the processing capacity and the energy consumption of the follow-up treatment process, such as the mechanical vapor recompression system. As shown in Fig. 5, in the ED process, there are two forms of water molecules in MDEA solution, one is free water, and the other is hydrated water which is adsorbed by ion hydration shell. The two main possible sources of water transfer were osmosis and electroosmosis. Osmotic flux occurs due to the chemical potential gradient across the membrane, while electroosmotic flux occurs due to water transfer caused by ion migration through the membrane [27]. As shown in Fig. 6, the observed water transfer sharply increased in the first hour, then increased steadily until finally stabilizing at about 22 L/h.

Due to the initially similar ion concentrations of the dilute MDEA and concentrate MDEA solution, the osmotic pressure between the concentrate compartment and the dilute compartment was negligible and electroosmosis played a dominant role in the solution migration process. Therefore, the water transfer in the concentrate compartment gradually increased and ions migrate to the concentrate

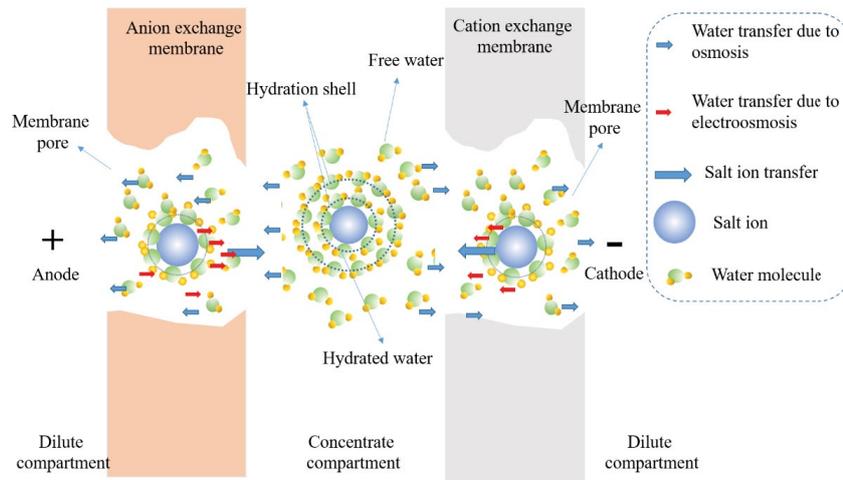


Fig. 5. Water transfer through a pore in ion-exchange membrane.

compartment, causing the concentration of ions to gradually increase. The osmotic pressure of the concentrate and dilute MDEA solutions gradually increased, resulting in the migration of water in the dilute compartment toward the concentrate compartment. Under the osmotic pressure present in the system, a slow rate of increase of concentrate liquid was observed in the concentrate MDEA solution tank. Therefore, the growth rate of water transfer was highest in the first few hours, then gradually become stabilized when osmosis and electroosmosis gradually reach equilibrium. Furthermore, the water transfer remained constant, in the region of ~22 L/h.

3.3.3. Loss of MDEA during the ED process

During the ED process, it was observed that MDEA concentrations in the dilute compartment showed an average reduction of 6.52%, as compared to the initial MDEA concentrations as shown in Fig. 7. This effect is mainly caused by both the electric-migration of MDEA according to ionic status and the migration of HSS with binding MDEA molecule. MDEA can be hydrolyzed in the aqueous phase, according to the reaction shown in Eq. (4):



When MDEAH^+ in dilute MDEA solution pass through the cation exchange membranes and migrate into the concentrate MDEA solution under the electric field. Causing the hydrolysis equilibrium of MDEA in Eq. (4) to proceed a right direction and therefore, a reduction in MDEA concentrations in dilute MDEA solution. Considering the high financial cost of MDEA (more than 3,000 \$/T), methods should be required to reduce MDEA loss during ED process.

3.4. Effect of initial pH in the spent MDEA solution during batch experiments

To reduce the loss of MDEA, the recommended method is adding NaOH into the spent MDEA to neutralize the acidic HSS and regenerate MDEA. Thus, batch experiments were performed to investigate the effect of initial

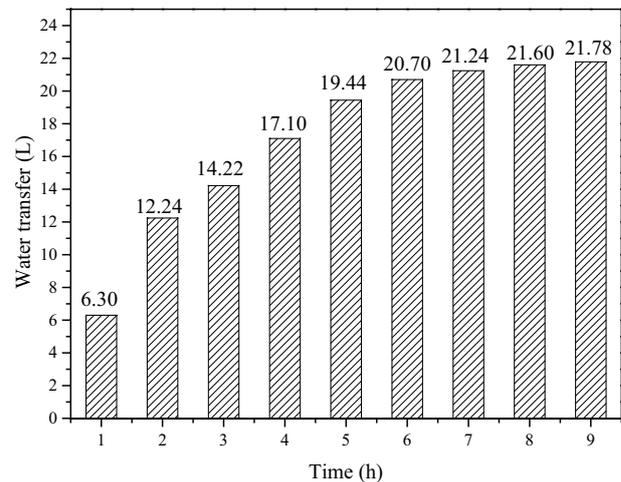


Fig. 6. Variation in water transfer over time.

pH on HSS removal efficiency and MDEA loss. 1 T of spent MDEA solution circulated in each batch. The concentrate and dilute compartment were initially filled with deionized effluent and spent MDEA solution, respectively. The addition of NaOH into the spent MDEA solution to neutralize the MDEA, is an effective method to alleviate HSS buildup and allow regeneration of MDEA. The initial solution pH values were chosen to be in the range of 9.5–12.5. Higher pH values were avoided as most anion exchange membranes contain quaternary ammonium groups, which are not stable in a strongly basic conditions [28]. Furthermore, it is not economically viable to add high volumes of NaOH solution.

3.4.1. Effect to HSS removal efficiency

Fig. 8 show the effects of initial pH of the spent MDEA solution on conductivity, in both the dilute and concentrate compartment of the ED stack. A higher pH got a higher initial conductivity but a faster rate of conductivity decline. Because a higher pH means a higher ion concentration, thus a stronger ability to transmit current and a faster ion

migration. Fig. 9 shows the effects of initial pH of the spent MDEA solution on HSS removal efficiency after 60 min operation time. The change of HSS removal efficiency of the initial pH with time follows DoseResp equation, and the correlation coefficient $R^2 > 0.99$. HSS removal efficiency rapidly increased from 51.14% to 77.23% when the pH value increased from 9.26 (without adding NaOH) to 10.5. As the pH value continued to increase, HSS removal efficiency continued to slightly increase and tended to be stable. A higher pH caused a faster HSS removal efficiency, as the addition of NaOH increased the concentration of ions in the spent MDEA solution, thus increased the ability to transmit current and enhance the ion migration rate

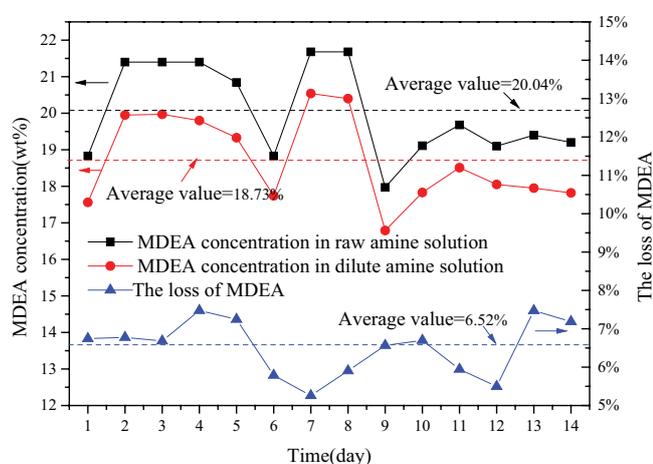


Fig. 7. MDEA concentrations (wt.%) and the loss of MDEA in the ED stack over a 14 d period.

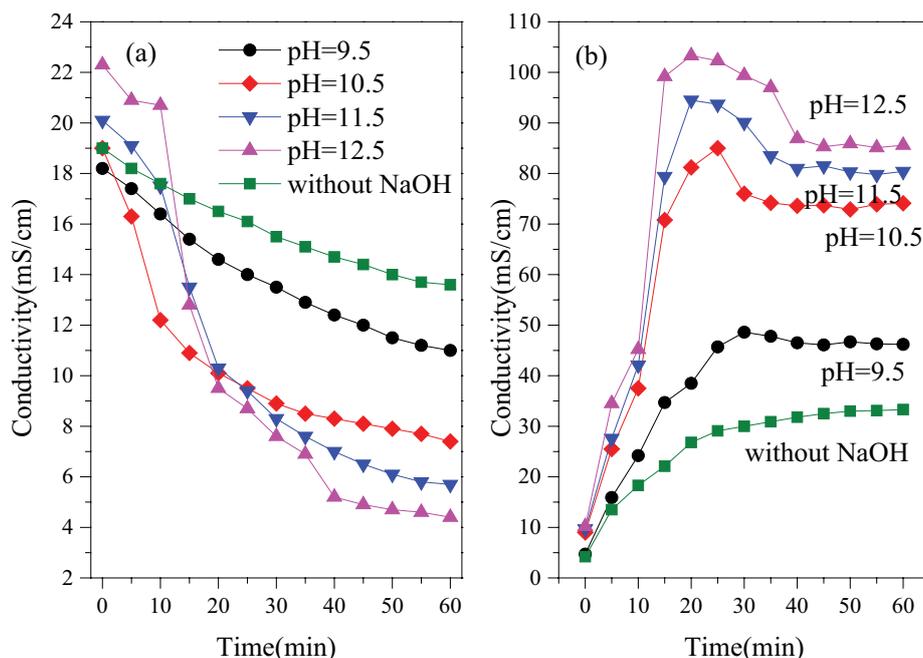


Fig. 8. (a) Conductivity in the dilute compartment of the ED stack, under varying initial pH conditions and (b) conductivity in the concentrate compartment of the ED stack, under varying initial pH conditions.

from solution to the membrane was significantly. However, excessive pH is also unattractive due to an excessive pH also means an excessive Na^+ and OH^- concentration in spent MDEA solution. The role of OH^- is to react with acidic substances and binding amine ($\text{MDEAH}^+\text{HSS}^-$) in spent MDEA solution. There would be a large amount of OH^- remained in the dilute compartment after the reaction is completed due to the excess NaOH concentration. The remaining OH^- would migrate from dilute compartment to the concentrate compartment under the action of electric field. Therefore, remaining OH^- would form a competitive relationship with HSS in the dilute compartment and affect the migration of HSS. Therefore, pH = 10.5 is an optimum choice by considering both HSS removal efficiency and chemical consumption.

3.4.2. Effect to the loss of MDEA

As previously discussed, the loss of MDEA is inevitable but should be avoided as much as possible. After the addition of NaOH, ions in solution react according to Eqs. (5) and (6):



where A^- denotes impurity anions such as Cl^- , SO_4^{2-} , SCN^- , HCOO^- , H_3CCOO^- , and $\text{CH}_3\text{CH}_2\text{COO}^-$. When NaOH is added to the spent MDEA solution, the OH^- will react with binding amine (MDEAH^+A^-) to regenerate MDEA as defined in Eq. (5). Meanwhile, the addition of NaOH will cause the hydrolysis equilibrium of MDEA in Eq. (4) to proceed a left direction as shown in Eq. (6). Both Eqs. (5) and (6) can help reduce the loss of MDEA.

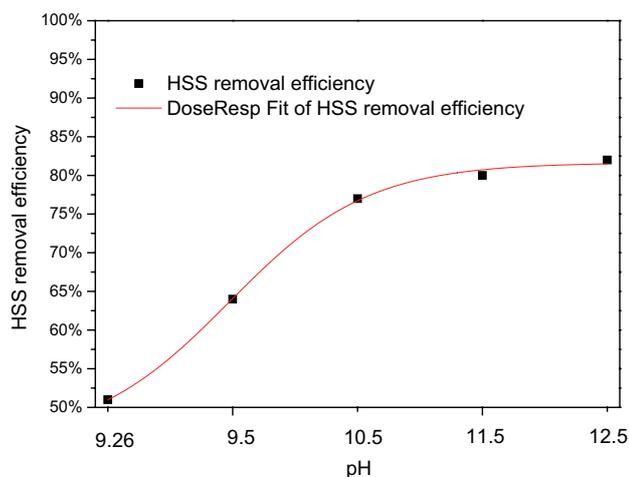


Fig. 9. Effect of initial pH of the spent MDEA solution on HSS removal efficiency after 60 min operation time.

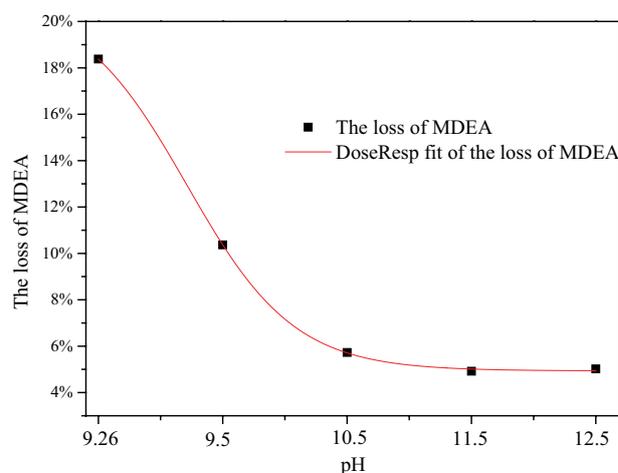


Fig. 10. Effect of initial pH of the spent MDEA solution on the loss of MDEA after 60 min operation time.

Fig. 10 shows the effect of initial pH of the spent MDEA solution on the loss of MDEA after 60 min operation time. The change of HSS the loss of MDEA of the initial pH with time follows DoseResp equation, and the correlation coefficient $R^2 > 0.99$. The loss of MDEA rapidly decreased from 18.38% to 5.73% when the pH increased from 9.26 (without adding NaOH) to 10.5. As the pH continued to increase, the loss of MDEA continued to slightly decrease and tended to be stable. A relatively high pH is needed due to more OH^- can participate in the reaction of Eqs. (5) and (6) to regenerate more MDEA. However, the amount of MDEA that can be regenerated is limited. When OH^- completed the reaction of MDEA regeneration, the remaining OH^- will not play the role of MDEA regeneration, but affect the HSS removal efficiency. Therefore, excessive NaOH concentration is also not unattractive. Therefore, pH = 10.5 is an optimum choice by considering both MDEA loss and chemical consumption.

3.4.3. Effect to Na^+ concentration

Although the addition of NaOH solution is beneficial for the regeneration of MDEA and the improvement of HSS removal efficiency, secondary pollution by Na^+ is introduced. The large amount of Na^+ will affect the absorption of H_2S by MDEA solution, which will cause the excess of H_2S in purified gas. The absorption principle of H_2S by MDEA is as shown in Eq. (7):



The formed weak-acid weak-base salt ($\text{MDEAH}^+\text{HS}^-$) has poor thermal stability. It can be decomposed under heating conditions to produce corresponding MDEA molecules and H_2S . MDEA is regenerated and H_2S is released at the same time. The introduced Na^+ binds with HS^- to form strong base-weak acid salt (NaHS), which is difficult to decompose by heating [10]. Therefore, NaHS can exist stably under the condition of MDEA regeneration. Due to the same ion effect, the HS^- bound by Na^+ shifts the equilibrium

of reversible reaction (5) to the left, and keeps a high equilibrium concentration of H_2S in the gas phase during the absorption of H_2S by MDEA solution. Furthermore, in the IGCC power generation plants, turbine blades in the gas and steam combined cycle power generation system were found to suffer from serious corrosion, which was mainly caused by Na^+ and other anions. When the regenerated MDEA solution is subjected to gas purification, steam is generated due to the high temperature of the gas. If excessive Na^+ is present in the MDEA solution, then Na^+ impurities are carried in the steam flow and enter the gas and steam combined cycle power generation system with the purified gas (H_2 and CO), which causes corrosion to the turbine blades.

Therefore, the concentration of Na^+ impurities in the dilute solution is critical to the stability of the whole IGCC system. The relationship between the concentration of Na^+ and pH is shown in Table 3, with higher pH conditions causing higher Na^+ impurity concentrations. However, there are currently no definitive standard methods for limiting the concentration of sodium ions in the MDEA solution and there is no current information available on the concentration of sodium ions required to cause corrosion to the system. Therefore, excessive pH condition is not recommended as a method to increase the HSS removal efficiency.

3.5. Process economy

Calculating the operating costs for spent MDEA solution treatment is essential to determining whether it is economically feasible to apply ED processes. The economic cost of pilot-scale ED is very close to the cost of practical engineering. In most of the literature, processing costs are calculated as the cost of processing each ton of MDEA solution [18,19]. In fact, due to the HSS content in the MDEA solution is different, the degree and amount of HSS removal are different. This calculation method is difficult to reflect the actual treatment cost. Therefore, we calculate the actual economic cost of the ED by removing per T of HSS. The result is listed in Table 4.

Table 3
Na⁺ content under different initial pH conditions

	Inlet Na ⁺ content (mg/L)	Na ⁺ in concentrate compartment (mg/L)	Na ⁺ in dilute compartment (mg/L)
pH = 12.5	13,607.0	47,120.1	1,902.1
pH = 11.5	10,125.8	38,092.3	1,507.2
pH = 10.5	8,652.3	29,825.9	1,021.6
pH = 9.5	617.9	3,330.1	36.2
pH = 9.26 (without adding NaOH)	547.5	3,127.6	34.1

Table 4
Calculation of the process cost

	Parameters	ED process
Energy cost	Stack energy consumption (kW h/m ³)	4.27
	Peripheral equipment consumption (kW h/m ³)	1.62
	The quantity of HSS removed (T/m ³)	0.0122
	Electricity charge (\$/kW h)	0.2
	Total energy cost (\$/(T HSS))	96.50
Chemical cost	Parameters	ED process
	Na ₂ SO ₄ (\$ 200/T)	0.04
	HCl (\$180/T)	0.27
	Total chemical cost (\$/(T HSS))	0.31
Investment cost	Parameters	ED process
	Membrane cost (\$ 250/m ²)	124.76
	Stack cost (\$/(T HSS))	187.14
	Peripheral equipment cost (\$/(T HSS))	280.71
	Maintenance (\$/(T HSS))	59.26
	Total investment cost (\$/(T HSS))	651.87
Total process cost		748.68\$/(T HSS)

In general, the process cost is sum of energy consumption and chemical consumption for ED process, the investment cost. The energy consumption of ED process was calculated to be 4.27 kW h/m³ spent MDEA solution at the applied voltage of 80 V and dilute MDEA solution flow rate of 4 m³/h. Other equipment power consumption includes pump, monitoring, control panel, resulting in a total requirement of 1.62 kW h/m³. The quantity of HSS removed was about 12.2 kg/m³ spent MDEA solution. Therefore, the energy cost is calculated to be 96.50 \$/(T HSS). The chemical consumption mainly includes Na₂SO₄ and HCl. Since the MDEA solution is weakly alkaline, the anion exchange membrane will degrade immerse in the alkaline environment for a long time. To prolong the service life of the anion exchange membrane, after the end of the daily experiment, the membrane stack is washed with a hydrochloric acid solution of pH = 2. At the same time, in order to prevent the MDEA solution from entering the cathode compartment and the anode compartment to corrode the plates, we replace the electrolyte rinse with a 5% Na₂SO₄ solution every week. The chemical cost is 0.31 \$/(T HSS) in total. The investment cost is 651.87 \$/(T HSS), is the sum of the stack cost and peripheral equipment cost. The total process cost

is calculated to be 748.68 \$/(T HSS), it is similar with previous lab-scale experimental study, 14.6 \$/(T wastewater) (equal with 752.58 \$/T HSS) [18]. Compare with distillation method, ED method is more cost effectively, because the energy consumption of ED process is 5.89 kW h/m³ (equal with 0.48 kW h/kg HSS), much less than that of distillation method (12 kW h/kg HSS) [29]. Compare with ion exchange resin method, ED method is more environmentally friendly, because ED method has no secondary pollution but ion exchange resin will produce much alkaline wastewater [6]. Therefore, ED is an economical and environmentally friendly method to removal HSS and regenerate MDEA from MDEA wastewater.

4. Conclusions

A pilot-scale ED system was used to remove HSS from spent MDEA solution. In continuous experiments, the optimal voltage and dilute MDEA solution flow rate are 80 V and 4 m³/h, respectively. Under these operating conditions, the HSS removal efficiency, the loss of MDEA and water transfer of ED method are 20.17%, 5.41% and 22 L/h, respectively. In batch experiments, a relatively high is beneficial to

ED system, by adding NaOH to adjust the initial pH = 10.5 of the MDEA solution, the HSS removal efficiency is 77%, which is 26.09% higher than that without NaOH addition, the loss of MDEA is 5.73%, which is 12.65% lower than that without NaOH addition. However, excessive pH increase the Na⁺ concentration in dilute MDEA solution, which will possibly affect the absorption of H₂S by MDEA solution. The total process cost is calculated to be 748.68 \$(/T HSS) with the energy consumption of 96.23 \$(/T HSS). Overall, these findings show that ED is an effective method to remove HSS from spent MDEA solution. This pilot-scale study provides a useful baseline for the effective application of ED in practical engineering scenarios.

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