ORIGINAL PAPER



Removal of HSS from industrial amine solution by anionic resin (case study: llam gas refinery)

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Received: 9 July 2018 / Accepted: 14 September 2018 / Published online: 24 September 2018 © Institute of Chemistry, Slovak Academy of Sciences 2018

Abstract

In this research, the removal of heat stable salts was considered as one of the most effective factors in the process of amine degradation. To remove this type of salts, ion-exchange method was used. A resin purification system was investigated to separate the heat stable salt ions of acetate, formaldehyde, chloride, oxalate, thiosulphate, sulphate, and sulphite from alkanolamine solution flowing in the Ilam gas refinery sweetening units. To remove the existing ions in the lean amine solution, a strong anionic resin designated as INDION GS 300 was tested. Ion-exchange systems operated in batch and continuous mode (fixed-bed column) were applied to remove these salts. The effects of different operating variables such as contact time, temperature, and amount of resin were examined. The optimum values of amount of resin and temperature found for both systems were 5 g and 25 °C, respectively. Furthermore, the optimum times for batch and continuous systems were 30 and 10 min, respectively. Results of experiments revealed that around 95.5 and 97% of salts were removed using batch and column operations, respectively. Moreover, the amine solution pH increased from 10 to 11, indicating a corrosion rate reduction in the amine system of the Ilam gas refinery.

Keywords Heat stable salts · Amine solution · Ion-exchange method · Anionic resin

Introduction

Recently, the process of gas sweetening using amine solutions has been applied as a main process to sweeten the gas in the world gas industries (Gupta et al. 2016; Jaafari et al. 2018; Keewan et al. 2018; Muhammad and GadelHak 2014). Regarding the numerous advantages of using amines, in comparison with other processes, it can be understood that this trend will continue in the next coming years (Banat et al. 2014; Panahi et al. 2017). However, based on the literature, we have seen the changes in the quality of amine solution

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over time which can be attributed to its destruction (Cummings et al. 2007; Davoudi et al. 2014). This phenomenon causes problems in process units such as metal corrosion, foaming in absorption towers, and reducing the capacity of towers (Garcia-Arriaga et al. 2010; Nielsen 1997; Maddox 1985).

Amine degradation (decomposition of the amine solution) may be included the thermal and chemical decomposition (Nielsen 1997). In general, the thermal decomposition phenomenon occurs because of the high temperature of the wall surfaces in the boiler pipes (Campbell et al. 1999; Nielsen 1997; Maddox 1985). Chemical decomposition of amine solvent is a complex phenomenon that depends on various factors such as pressure, temperature, initial amine concentration, input gas ingredients, solution pH, and the presence of metal ions. This problem can be caused by the irreversible reactions of gas impurities such as oxygen, CO₂, CS₂, and COS, with amine, in addition to destroying and decomposing the amine solvent, which produces highly corrosive products which are, themselves, the important factors in the intensification of chemical decomposition (Abry and DuPart 1995; Haws 2001; Singh et al. 2016; Stewart and Lanning 1994).

One of the most important factors in reducing the quality of in circulation amine is the accumulation of heat-resistant salts (HSS) caused by prolonged application of amine solutions (Niazmehr et al. 2016). These amine ionic compounds not only cannot be removed with common amine regeneration methods, but also cannot be separated from the amine solution by common filters (Nielsen 1997; Maddox 1985).

There are various methods for controlling the amount of HSS in the amine solution cycle of gas refineries, such as neutralization, purification neutralization, purging, filtration, and rebuilding. Amine rebuilding carries out in three ways, namely, thermal regeneration, electrolysis, and ion exchange (Alnaimat et al. 2018; Mohammadi et al. 2004). Among the above-mentioned methods, amine ion exchange represented a fruitful performance. This method is very simple and cost-effective for factories and can reduce HSS in the amine cycle to a very low level of 0.5% by weight (Nielsen 1997; Maddox 1985). HSS compounds are in salt type and have a strong tendency to deposit and cause the reduction of the amount of free amine and the capacity of the acid gas sweetening by the amine solution (Nielsen 1997; Maddox 1985; Verma and Verma 2009). Up to now, many researchers have used anionic resins. Among the common types of HSS salts in amine systems, sulphate (Dron and Dodi 2011; Haghsheno et al. 2009; Samatya et al. 2006), chloride, nitrate (Kadnar and Rieder 1995), acetate, formate, oxalate, sulphite, thiosulphate, and thiocyanate can be mentioned (Matulionyte et al. 2007; Song et al. 2012; Vaaramaa and Lehto 2003; Xu et al. 2011).

The first industrial application of ion-exchange resins was the recovery of amine solutions reported by Morgan and Cler in 1977, in which a side stream of circulating amine solution infected with sodium chloride was percolated through a bed containing a strong anionic exchange resin and the chloride ion of the solution was replaced by hydroxide ion (Morgan and Klare 1977).

Oxygen is one of the most important agents for the formation of thermal stable acids in the systems. The amine solution reacts with oxygen under high operational temperature conditions and decomposes into carboxylic acids (organic acids). Then, carboxylic acids react with amine solution and create heat stable amine salts. Acetate, formate, and oxalate are heat-resistant amine salts that are formed in the process of amine destruction by oxygen (Nielsen 1997; Maddox 1985). Pal et al. (2013) used ion-exchange resins in the process of treating thermal stable salts to remove sulphur bivalence oxygenated anions.

Chloride, phosphate, and nitrate ions can be considered among the most important heat-resistant salt anions which are introduced into the gas processing systems through impure make up water and sour water along with gas, as well as corrosion inhibitors and anti-foam. Thiosulphate, sulphate, and sulphide are the other HSS salts in solution that are the products of the oxidation reaction of various sulphur compounds in gas with oxygen, which can also be introduced into system through impure make up distilled water. In general, an enhancement in the concentration of anions of heat stable salts in amine solution and system temperature increases the corrosion rate (Nielsen 1997; Maddox 1985). Atash Jameh (2010) used ion-exchange beds to remove and control the amount of thermal stable salts in the ethanolamine solution to less than 3% by weight. However, according to the literature, there is no indication of either nature or composition in the application of ion-exchange resins (Morgan and Klare 1977).

The ion-exchange method and the application of commercial resins have been recognized as the most appropriate complete recovery approaches to eliminate these harmful compounds in amine solutions. Ion-exchange resins contain cationic and anionic charges, so that they are electrically neutral, in which only one of the two ions is mobile and replaceable. Due to the presence of anions of thermal stable salts in the methyl di-ethanolamine (MDEA) solution of the gas processing unit, there is a serious requirement for application of anionic replacement resin, in which, by replacing the movable OH or Cl anion in its structure with the anion in the solution, an improvement will be observed in solution quality and process performance.

A typical research in this field was conducted in 2013 by Pal and co-workers (Pal et al. 2013) at the Abu Dhabi Gas Engineering Institute, the main purpose of which was to test four common types of ion-exchange resins to remove anions of organic acids from industrial MDEA solution. According to this study, among all the thermal stable salts present in the industrial amine solution, organic acids are ones that exhibit the highest amount. The tested solution was methyl di-ethanol amine 45% and the studied resins were D203, D303, ZGA351MB, and ZGA351 manufactured in China. To select the best resin, 1 g of each pre-prepared resin types were added to 50 ml of lean amine solution, and stirred for 24 h to reach equilibrium conditions. The results of the four tested resins showed that ZGA351MB resin had the best potential for removing organic acids along with mineral ions like sulphate and nitrate from the solution (Pal et al. 2013). To the best of our knowledge, there is no relevant literature about the removal of HSS from industrial amine stream using ion-exchange resin.

In this study, the removal of HSS ions mixture from lean amine of Ilam gas refinery using ion-exchange resins in two batch and continuous systems was investigated. The effect of process parameters including, resin regeneration, temperature, resin to solution ratio, and time was studied. Kinetic and thermodynamic parameters for the ion-exchange process were assessed. The ion-exchange priority was also determined for HSS ion mixture.

Materials and methods

Materials

Regarding the separation factors that are anions of thermal stable salts in the amine solution, strong anionic resins for anion exchange in aqueous solutions were considered. INDION GS 300 resin was selected as a most appropriate resin. The specifications of used resin are presented in Table 1.

In the ion-exchange process, sodium hydroxide solution was used to remove chloride anion from resin structure causing its neutralization, so that the resin can adsorb the anions in the amine solution. The removal of chloride from the fresh resin (R–Cl) structure and HSS ions (X^-) transfer from the amine aqueous solution and interaction with the resin solid phase can be described as follows.

$$R - Cl + NaOH \rightarrow ROH + NaCl$$
(1)

 $MDEAH^+X^- + ROH \rightarrow MDEA + RX + H_2O.$ (2)

The sodium hydroxide 10% solution was used to reduce the chloride ions in the resin structure. The sodium hydroxide was purchased from Merck Co, Germany, and also from an Iranian company-producing chemical products. Methyl di-ethanol amine solutions from lean amine of Ilam gas refinery were used to reduce the amount of heat stable salts in the amine solution and prepare them for reuse. The concentration of ions in the amine solution was analyzed using a Metrosep A SUPP 5-250 ion chromatography instrument and is presented in Table 2.

A column was used for the direct contact of the resin with the amine solution in the continuous system and is illustrated in Fig. 1. The amine solution enters from the bottom of the column, which is the amine input, and after passing through the column, exits from the top of the

Table 1Physical and chemical characteristics of the resin INDIONGS 300

| Anion-exchange resin | INDION GS 300 |
|---------------------------|-----------------------------------|
| Matrix | Styrene divinylbenzene copolymer |
| Functional group | Benzyl trimethyl amine |
| Ionic form as supplied | Chloride |
| Total exchange capacity | 1.2 meq/ml |
| Moisture holding capacity | 48–54% |
| Max operating temperature | 60 °C in OH form 80 °C in Cl form |
| Operating pH range | 0–14 |

Table 2Concentration of HSSions in the lean amine solution

| Ion | Lean amine (mg/l) |
|--------------|-------------------------|
| Acetate | 2335 |
| Formate | 2354 |
| Chloride | 49 |
| Oxalate | 574 |
| Thiosulphate | 1843 |
| Sulphate | 544 |
| Sulphite | 176 |

column. The column is made of Pyrex glass and its dimensions are 1.574 inches in diameter and 30 cm in length.

Methods

Batch experiments

In this study, two systems (e.g., batch and continuous) were used to remove the heat sable salts from methyl di-ethanolamine solution. In the batch system, the influence of different parameters such as contact time (in 30, 180 and 300 min),



Fig. 1 Continuous ion-exchange packed-bed set-up

amount of resin (at 2, 3.5 and 5 g), and temperature (at 25, 35, and 45 $^{\circ}$ C) was investigated. Batch operations were performed in four stages to achieve the optimal conditions of the highest removal rates of salts. After each step of amine recovery, the resin was regenerated with the 10% sodium hydroxide to be placed again in the system for recovery operation.

In the first stage, 50 ml of amine solution with the known HSS dosage was mixed with 5 g of resin in a flask with stirring rate of 600 rpm for 30 min, and then, the remaining solution was analyzed to measure the residual amount of heat stable salts. The next stages were carried out similarly, with the difference that the resin is regenerated with the 10% sodium hydroxide solution and reused.

Continuous experiments

In continuous system, 2 l dirty amine was continuously analyzed for the removal of heat stable salts. A glass ionexchange column with an input at the bottom and an outlet on top of it was applied. The packed-bed column was made of Pyrex glass tube of 4 cm diameter and 30 cm height. In this column, 100 g resin was first placed inside yarn filters that the resin was not able to pass through, and then placed on the top and bottom of the column. For continuous flowing of dirty amine, a pump with a flow rate of 432 ml/min was used, using a return flow to reduce dirty amine flow rate to 222 ml/min.

Results and discussion

Batch studies

Effect of regeneration on the efficiency of resin

Due to the high chloride content of INDION GS 300, it is difficult to remove this anion from its structure. The process of regeneration in the batch system was carried out by two stages of washing with sodium hydroxide and distilled water during a few steps. To ensure the complete removal of chloride ions, these steps were performed in 24 h (although resin was recovered in 30 min) until the resin was completely free of chloride ions. Based on Fig. 2, the removal amount of stable salts using resins regenerated with solutions containing different concentrations of sodium hydroxide is presented. It is observed that the concentration of all ions in amine solution was reduced by increasing the concentration of regeneration solution. Furthermore, the conditions are different for chloride ions. The chlorine concentration in the amine solution was increased and then followed by a decrease. This is because of the existence of a large amount of chlorine ions in the structure of the anionic resin, which,



Fig. 2 Effect of reduction solution concentration on HSS removal from amine solution: a acetate, formate, and thiosulphate; b sulphate and oxalate; c chloride and sulphite

if not well regenerated, enter into the amine solution and increase the concentration of chlorine ions. However, results showed that thiosulphate, sulphate, and oxalate ions were reduced sufficiently with one regeneration cycle by 10% sodium hydroxide solution. However, acetate, formate, and chloride ions did not significantly decrease, which may be due to the polarity of ions.

Figure 3 shows the effect of the number of resin regeneration cycles on HSS removal. According to the figure, due to the presence of chloride in the resin structure, the fresh anionic resin should be regenerated with 10 wt%



Fig. 3 Effect of regeneration on removal of HSS from amine solution: a acetate, formate, and thiosulphate; b sulphate and oxalate; c sulfite and chloride

sodium hydroxide solution, prior to the ion-exchange process. Therefore, it is observed that the resin did not remove the chloride from the amine solution, due to the high chloride contents in its structure, after recovery. Thus, we continued the resin recovery operation until the complete removal of the chloride ions from the resin structure was obtained. It can be seen that, after three



Fig.4 Effect of contact time on removal of HSS ions from amine solution

regenerations, the resin was approximately became free of chloride ions, and the amount of stable salts in the amine solution was significantly reduced.

Effect of time

The contact time is a critical parameter in the performance of resin for ion-exchange operations to remove anions from amine solution. In fact, the optimum time should be found, so that the resin can maximize the exchange and also the reduction in the concentration of stable salts to the required amounts. Therefore, a suitable analysis of this parameter is very important. For the batch system, these experiments were carried out at during a period time between 0 and 35 min, to analyze the effect of time on the uptake kinetics of the different salts. As shown in Fig. 4, the appropriate time for removal of salts was obtained as 30 min. After about 30 min, the salt concentration achieves the equilibrium state. The initial ion-exchange rate values confirm the higher number of active sites at the surface of resin particles.

The variation in the solute uptake with time is explained by the sorption kinetics and its parameters give essential information for modeling and design purposes. Among the various existing kinetic models, the pseudo-second-order and pseudo-first-order models are the most widely used to describe the sorption process. The pseudo-first-order kinetic model is presented by the following form (Abd El-Magied et al. 2017):

$$\ln(q_{\rm e} - q_t) = \ln q_{\rm e} - k_1 t, \tag{3}$$

where q_t and q_e are the amounts of adsorbed HSS ions at time t (min) and equilibrium in mg/g, and k_1 is the rate constant of the equation in min⁻¹. The ion-exchange rate constant (k_1) can be determined by plotting $\ln(q_e - q_t)$ versus time (t). The pseudo-second-order kinetic model is given by Eq. (4) (Abd El-Magied et al. 2017):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$
(4)

Table 3 Parameters of the kinetic model for ion exchange

| $\frac{\overline{k_1 \text{ (min}^{-1)}}}{0.0362} \frac{q_e \text{ (mg g}^{-1)}}{3.06} \frac{R^2}{0.973} \frac{\overline{k_2}}{0.01338} \frac{q_e \text{ (mg g}^{-1)^a}}{37.878} \frac{R^2}{0.999}$ | Pseudo-first-order kinetic model | | с | Pseudo-second-order kinetic model | | | |
|--|----------------------------------|-------------------------------|-----------------------|--|---|-----------------------|--|
| 0.0362 3.06 0.973 0.01338 37.878 0.99 | $k_1 ({\rm min}^{-1})$ | $q_{\rm e} ({\rm mg~g^{-1}})$ | <i>R</i> ² | $\frac{k_2}{(\text{g mg}^{-1} \min^{-1})}$ | $q_{\rm e} ({\rm mg}~{\rm g}^{-1})^{\rm a}$ | <i>R</i> ² | |
| | 0.0362 | 3.06 | 0.973 | 0.01338 | 37.878 | 0.997 | |

 ${}^{a}q_{e}$ (experimental) = 35.3 mg g⁻¹

where q_t is the sorption capacity at time t, k_2 is the rate constant of the second-order equation, and q_e is the sorption capacity at equilibrium.

The calculated kinetic parameters for the ion-exchange process are given in Table 3. The results shows that the ion-exchange kinetics of HSS with resin is better described by the pseudo-second-order kinetic model (R^2 =0.9973). Thus, the pseudo-second-order model can be applicable to all the ion-exchange data. The calculated ion-exchange capacities using the second-order model showed good agreement with exchange capacities determined experimentally which is near to 35.5 mg/g. Moreover, it can be concluded that the sorption mechanism is the rate-controlling step and it occurs due to electrostatic attraction.

Effect of temperature

In processes that deal with resins, temperature variations are very sensitive, due to this fact that the structure of the resins can easily collapse because of a sudden increase in temperature or even at high temperatures, and the resin will not be able to carry out the ion-exchange process (Clifford 1990; Harland 2007). In addition, the thermodynamic analysis of the equilibrium data explained the dependence of the ion-exchange process with temperature. In this sense, the removal of HSS from amine solution was carried out at different temperatures. As shown in Fig. 5, the ion exchange was decreased with increasing temperature. This trend was far higher for ions with a charge of -2.

Thermodynamic behavior of the HSS ion exchange was substantiated by the calculation of thermodynamic parameters including free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°).

The free energy change was calculated using Eq. (5) (Abd El-Magied et al. 2018a):

$$\Delta G^{\rm o} = -RT \ln K_{\rm d},\tag{5}$$

where, R (8.314 J.mol⁻¹.K⁻¹) is gas constant and T(K) is temperature. The distribution coefficient K_d was calculated by the following equation:

$$K_{\rm d} = \frac{(C^{\rm o} - C^{\rm e})}{C^{\rm o}} \times \frac{V}{W},\tag{6}$$



Fig. 5 Effect of temperature on removal of HSS from amine solution: a acetate, formate, and thiosulphate; b sulphate and oxalate; c sulfite and chloride

where C^{o} and C^{e} are the initial and equilibrium concentrations of ions in solution (mg/l), respectively. *V* is the volume of solution (l) and *W* is the mass of resin (g).

On the other hand, free energy change with enthalpy and entropy is related to the Gibbs–Helmholtz equation (Abd El-Magied et al. 2018b):

$$\Delta G^{\rm o} = \Delta H^{\rm o} - T \Delta S^{\rm o}. \tag{7}$$

By combining Eqs. (5) and (7), Eq. (8), which indicates the temperature dependence of the distribution coefficient, is obtained (Abd El-Magied et al. 2018b):

$$\ln K_{\rm d} = \Delta S^{\rm o}/R - \Delta H^{\rm o}/RT.$$
(8)

The ΔH° and ΔS° values were calculated by the slope and intercept of linear plot of ln $K_{\rm d}$ versus 1/*T*. The thermodynamic parameters which are calculated based on total ions removal are shown in Table 4.

The negative values of free energy change (ΔG) at the temperatures of 298–316 K show that the ion exchange of the HSS by the resin is thermodynamically spontaneous and feasible, and the ion-exchange process is physical in nature. The negative value of enthalpy shows that the exchange of HSS is exothermic.

Effect of amount of resin

To attain the optimum dosage of resin, desalination of the constant amount of amine solution was investigated. The influence of amount of resin on the elimination of acetate and formate salts is presented in Fig. 6, considering a contact time of 30 min and after four-step regeneration at ambient temperature. In this test, the amounts of resin were of 2, 3.5, and 5 g and the highest removal was attained at 5 g. However, higher dosage of resin caused more removal efficiency, but, due to economic costs and to find the optimal amount of resin, the dosage of resin should be proportional to the amount of exchanged amine (Clifford 1990; Harland 2007). In the batch system, the best proportional of resin to amine was achieved to 1:10. Consequently, the optimum amount of resin is 5 g for 50 ml of amine solution, and based on this amine dosage, further experiments were performed and the highest efficiency removal for heat thermal salts was obtained. It is also observed that the removal of ions with -2 charge is far higher than ion with -1 charge.

The removal efficiency of heat stable salts in the applied amine solution was investigated under the experimental conditions: contact time 30 min, temperature 25 °C, and amount of resin 5 g. The resin was reacted with amine and filtrated after 30 min and followed by regeneration using NaOH solution 10 wt%. This process was repeated for four times. Results of this analysis are presented in Fig. 7 and Table 5. Accordingly, oxalate, thiosulphate, sulphate, and sulphite ions were extremely reduced in the primary stages, but this trend for acetate and formate ions was observed after the third step. This observation can be

Table 4 Thermodynamic parameters of HSS ion exchange

| $\Delta G^{\circ} (\text{kJ mol}^{-1})$ | | $\Delta H^{\circ} (\text{kJ mol}^{-1})$ | $\Delta S^{\circ} (\mathrm{J} \mathrm{mol}^{-1}.\mathrm{K}^{-1})$ | |
|---|---------|---|---|---------|
| 296 (K) | 306 (K) | 316 (K) | -72.73 | - 19.84 |
| - 66.86 | - 66.66 | -66.46 | | |



Fig. 6 Effect of amount of resin on removal of HSS from amine solution: **a** acetate and formate; **b** sulphate, oxalate, sulphite, and thiosulphate

due to atomic charge of -2 for these ions, whereas the formate, chloride, and acetate ions have atomic charge of -1.

FTIR analyses

FTIR spectra were acquired using a VERTEX70-Bruker at room temperature for the prototype, OH⁻ form, ion exchanged with sulphate and acetate ions. The FTIR spectra of samples are shown in Figs. 8. Data acquisition was done



Fig. 7 Change of lean amine color with HSS ions removal

Table 5 Stage removal of HSS ions in degraded amine solution

| Ion | Lean amine mg/l | Step 1 mg/l | Step 2 mg/l | Step 3 mg/l | Step 4 mg/l |
|--------------|--------------------|----------------|----------------|----------------|----------------|
| Acetate | 2335 | 2151 | 686 | 257 | 96 |
| Formate | 2354 | 1976 | 423 | 65 | 82 |
| Chloride | 49 | 96 | 23 | 23 | 26 |
| Oxalate | 574 | 100 | 0 | 0 | 0 |
| Thiosulphate | 1843 | 142 | 0 | 0 | 0 |
| Sulphate | 544 | 117 | 4 | 3.8 | 2.6 |
| Sulphite | 176 | 40 | 0 | 0 | 0 |
| | | | | | |



Fig.8 FT-IR spectra of ion-exchange resins: a prototype, b OH-form, c ion exchanged with sulphate, and d acetate ions

from 4000 to 400 cm⁻¹. The large peak has been detected at around 3400 cm⁻¹ due to the presence of (O–H) stretching of moisture which is not the structural part of the resin. There are two peaks at 540 and 775 cm⁻¹ for prototype resin which can be assigned to the presence of C_1 vibrations. There are no two chlorine quarks in the OH⁻ form resin spectrum, and in general, the vibrations of hydroxide in the form of stretching and bending in the region of 2400–3400 cm⁻¹ and the bending of 1600 cm⁻¹ appear. The presence of a medium–strong band at 1600 cm⁻¹ is due to C=C-stretching vibration of benzene rings and deformation vibration of –CH2– N⁺(CH3)3...OH⁻. For sulphate-exchange resins, the vibrations in 440, 564, 502, and 618 cm⁻¹ regions belong to the sulphate group, and the SO group appears in the 1050 cm⁻¹ region. For spectrum of resin exchanged with acetone, the carbonyl acetate group appears in the normal state at 1735 cm⁻¹, but, in this spectrum, a sharp peak at 1625 cm⁻¹ has appeared. The reason for its shift from the 1625–1735 cm⁻¹ is the formation of a hydrogen bond.

Continuous system

In the continuous system, the resin bed regeneration was also carried out in a multi-stage process, where the continuous recovery processes were performed. Therefore, after the exiting amine solution from the inside of the column, the process of washing resin was carried out initially by a reverse water flow (backwash) with flow rate of 432 ml/min for 5–15 min. Then, a NaOH solution 10 wt% with a flow rate of 432 ml/min was passed through the resin bed for 30 min in the form of counter current. In the third step, a slow flow of water at 432 ml/min was percolated through the bed for 30 min to transfer the reducing agent to all points of resin. Finally, in the last stage, a flow of water with a flow rate of 432 ml/min was through over the resin bed for 10 min to remove the remaining NaOH solution and anionic ions (Coberly et al. 1998; Harland 2007).

Results of continuous ion-exchange system are presented in Fig. 9. It can be concluded that the resin initially adsorbs high amount of heat stable salts and depletes the amine solution from salts, but the resin became saturated after 20 min from the start of process and could not efficiently adsorb anions. It is not worthy to say that the amine which used in this study was completely depreciated and has a high amount of HSS ions. However, in the case of the fresh amine entering the process, the rate of HSS ions production was low and their concentration could be controlled with this resin. Therefore, the resin bed was saturated much later.

Thus, the optimum time for the complete removal of salts was chosen as 10 min. After the saturation of resin, the amine reduction stopped and the bed regeneration was conducted using NaOH solution 10 wt% for the continuation of the amine recovery process. The removal of the heat-resistant salts contained in the methyl di-ethanolamine solution of the Ilam gas refinery can be marked by increasing pH and changing the color of the amine solution. After the process of ion exchange between resin and amine, the pH of the amine solution increased to 11, indicating an increase in the alkalinity of the amine solution and reducing the salts. In addition, the high color change of the amine solution from dark green to light yellow reveals the essential changes in the structure of amine.

Analyzing results from Table 5, which shows the amount of heat stable salts in the initial and after fourth stages for batch process and from the continuous system for a time



Fig. 9 Breakthrough curves of HSS ions at the exit of the column: a acetate and formate; b oxalate and sulphate; c chloride, thiosulphate, and sulphite

of 10 min, it can be concluded that both systems have high ability of removing the heat stable salts.

The anion reduction efficiencies of batch and continues processes were of 95.5 and 97%, respectively. Furthermore, more volume of amine can be desalinated in the continuous process, but this process required more material and apparatus. HSS was removed from MDEA solution used in the Ilam gas refining company by INDION GS 300 Resin. Since this resin has a high content of chloride in its structure, any contact between resin and amine solution led to increasing chloride concentration. Therefore, the regeneration was done for the complete removal of structural chloride using 10% NaOH solution in a three-step process. The removal of heat stable salts in a batch system was investigated and the results indicated that 95.5% ions were removed from amine solution after four steps. In the first step, the concentrations of oxalate, thiosulphate, sulphate, and sulphite ions were extremely decreased, whereas acetate and formate ions concentrations decreased significantly, after third step. The removal efficiency of salts using continuous system increased to 97%, in which the resin system could remove all the salt ions and became slowly saturated after about 20 min of operation.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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