Iran. J. Environ. Health. Sci. Eng., 2010, Vol. 7, No. 4, pp. 345-352

REMOVAL OF UROTROPINE FROM INDUSTRIAL WASTEWATER BY ACIDIC CATION EXCHANGE RESINS

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Received 6 January 2010; revised 31 Jully 2010; accepted 20 August 2010

ABSTRACT

The industrial wastewater produced by urotropine plants is considered as a major environmental polluting factor and hence its treatment is required. In this work, strongly acidic cation exchange resins including C100H (Purolite), Amberlite IR120 and Amberlyst 15W were used for removing of urotropine from wastewater. Optimum conditions for the three resins and regeneration were studied. The required amounts of resins for efficient exchange of urotropine and amount of acid for regenerating process of exhausted resins were determined and the potential of these resins in removing of urotropine and ammonia from the wastewater were compared. It was found that C100H resin has a higher capability in removing of urotropine in comparison with tow other resins. This capability of C100H was 2 and 7 times greater than Amberlite IR120 and Amberlyst 15W, respectively. The comparison of results with other methods indicates that this method reduces urotropine concentration more effectively. The simple and fast conductometric method has been developed for determination of urotropine in wastewater in the presence of formaldehyde and ammonia without any interference.

Key words: Urotropine; Cation exchange resin; Industrial wastewater treatment

INTRODUCTION

Water is an important natural resource of the earth and essential for the existence of all living organisms. On the other hand, shortage of water resources and the occurrence of water pollution have occurred as the result of the increase in population, the concentration of population in big cities and the development of industries (Silbert, 1999).

The most important contaminants of water are organic compounds, microorganisms and heavy metals which cause many problems for the environment. Consequently, treatment of water for industrial and potable uses is necessary.

One of the polluted industrial effluents is the urotropine wastewater. Urotropine or hexamethylenetetramine or hexamine, $(CH_2)_6N_4$, is a colourless, crystalline compound with amine odor and its experimental solubility in water is 45.00% (w/w) at 20°C (Aladko *et al.*, 2007). It is quite stable in the alkaline medium. Urotropine is used in pharmaceutical industries as a primary feed material, and in chemical industries as an intermediate material. The most common production method of urotropine in industrial scale is the reaction of formaldehyde with ammonia or ammonium salts. This reaction (equation 1) in aqueous solution at room temperature is very fast and produces the considerable amount of heat and water (Alamdari and Tabkhi, 2004).

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$6CH_2O + 4NH_3 \rightarrow C_6H_{12}N_4 + 6\ H_2O$ (1)

Urotropine wastewater that is formed in the production of urotropine usually contains residual amounts of urotropine, ammonia, formaldehyde, formic acid and methanol. Urotropine must be considered as a real wastewater pollutant and should not be allowed to enter water resources and soils because its molecule has a cyclic symmetric structure (Fig. 1) and is very stable. On the other hand, these specifications create the significant problems in the treatment of wastewater containing urotropine (Chou *et al.*, 1999).

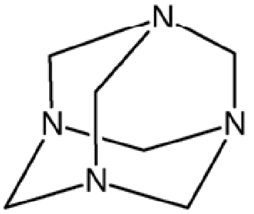

Fig. 1: The structure of urotropine

Biological treatment of industrial wastewater containing urotropine is ineffective (Kaszycki and Koloczek, 2002) because urotropine is resistant to biodegradation, even when sludge has been acclimated for a long period (Hutnan *et al.*, 2005; Middelhoven and Doesburg, 2007). The physicochemical separation and chemical reaction methods have been investigated for treatment of urotropine wastewater. For example, reverse osmosis has been applied to separate urotropine from wastewater (Bangxiao and Zhijun, 1986; Golovashin *et al.*, 2001).

The traditional Fenton process, one of the advanced oxidation processes (AOPs), is widely used as a suitable treatment method for highly concentrated wastewaters due to its effectiveness in producing hydroxyl radicals (Farrokhi *et al.*, 2004; Khavanin *et al.*, 2005). One of the drawbacks for Fenton method is the production of a significant amount of ferric hydroxide sludge that needs further separation and disposal. Previously reported results have indicated that application of only Fenton process is not adequate to treat the urotropine wastewater (Chou *et al.*, 1999; Ting *et al.*, 2007). Electro-Fenton method, applied H_2O_2 and electrogenerated ferrous ion, have been investigated for treating the urotropine containing wastewater (Chou *et al.*, 1999; Ting *et al.*, 2007). It has proven that this method is more effective than conventional Fenton's reagent, but it needs more complicated equipments.

One of the separation methods that can be applied for wastewater treatment is the use of ion exchanger resins (Karcher *et al.*, 2002; Jorgensen and Weatherley, 2003; Rahmani *et al.*, 2009).

In this work, suitable conditions in treating urotropine wastewater by three strongly acidic cation exchange resins and also regenerating of the resins have been studied. Furthermore, a conductometric method has been developed for the direct quantitative analysis of urotropine in wastewater in the presence of formaldehyde and ammonia without any interference.

MATERIALS AND METHODS

Apparatus

A Metrohm type 712 conductometer was used for conductivity measurements. For pH measurements, a Metrohm type 691 pH meter with resolution (ΔpH) of 0.01 was used. A Shimadzu spectrophotometer type 120-01 was used for spectrophotometric measurement of formaldehyde.

Chemicals

Silicotungstic acid (STA, >99%), ammonia 25% and sulfuric acid 95-97% with high purity were purchased from Merck company. The urotropine used for standard solution preparation, was urotropine powder (99.5%) (Merck Co.), dried at 60°C to constant weight. $HgSO_4$ (98%), $K_2Cr_2O_7$ (99.5%) and sulfuric acid, all from Merck Co. and with high purity, were used for COD measurements. Chromotropic acid (98.5%) reagent (Merck Co.) was used for determination of formaldehyde (Fagnani *et al.*, 2003). The strongly acidic cation exchange resins including, C100H (Purolite), Amberlite IR120 (Merck) and Amberlyst 15W (Merck) were used and were all in hydrogen form. Wastewater samples were obtained from a chemical industrial plant of urotropine production located in Iran.

Procedures

Determination of urotropine in wastewater

For the measurement of urotropine in the wastewater before and after treatment with the resin, the conductometric titration method was used. In conductometric determination of urotropine, the sample solutions (50 mL) containing urotropine were placed in a vessel and were titrated with the addition of concentrated silicotungstic acid (STA) solution using a calibrated micropipette. For high amounts of urotropine, 0.05 M STA and for little amounts, 0.0025 or 0.0015 M STA was used. The conductance of the solution was measured after each addition. Determinations were carried out at room temperature. The end point of titration was determined from the conductometric curve and the quantity of urotropine was reported. Each mL of 0.05 M solution of STA corresponded to 28.039 mg urotropine.

Because of the presence of ammonia in urotropine wastewater and its interference in determining the urotropine concentration by conductometric method, the conditions for this measurement were also optimized. For this purpose, determination of urotropine was conducted in the presence of ammonia at various pH values and the optimum pH was evaluated.

Treatment of wastewater in laboratory and pilot scales

For treatment of wastewater by cation exchange resins, the wastewater was passed through a column (25 cm high and 4 cm ID) packed with dry resin. Determination of the suitable flow rate was done by the measurement of urotropine in the effluent wastewater in different flow rates. The pH of this solution was also determined each time. According to these examinations, a proper pH range was achieved for the effluent wastewater so that in higher pH, the resin needed to be regenerated.

Studies on C100H resin were performed in the pilot scale. The column used in this scale was a cylindrical column, 80 cm high and 15 cm ID. 5000 mL of C100H resin was poured in the column and was then washed with water, which increased the resin volume. The flow rate of the wastewater in this case was evaluated based on the suitable flow rate obtained from previous experiment in laboratory scale and was 400 mL/min.

Regeneration of resins

For the regeneration of the hydrogen form of the cation exchange resin, 10% solution of sulfuric acid was used. The normality of influent acid was 3.62. The flow rate for acid through the resin was similar to the rate of the wastewater. Acid was added in definite amounts to the resin column and each time the efficiency of acid in regenerating of the resin was studied. For this purpose, the normality of acid was measured before and after passing through the resin. The addition of acid to the column was continued until the normality of effluent acid became equal to its initial normality. At this point, the resin was considered to be regenerated completely and could be reused for the next cycle.

RESULTS

The conductometric curve obtained for measurement of 10 mg urotropine in the presence of 200 mg/L ammonia is shown in Fig. 2.

Fig. 3 shows the results of optimum pH for determination of various amounts of urotropine in the presence of ammonia by STA as titrant with conductometric method, which was obtained as 6.00 ± 0.05. Therefore, all measurements of urotropine in wastewater in the next steps were done in this pH.

Fig. 4 shows the residual urotropine concentration in the effluent wastewater vs. various flow rates. According to these results, the flow rate of 12.5 mL/min for 100 mL dry C100H and 150 mL dry Amberlite IR120 resins was suitable for passing the wastewater. Then, the wastewater was passed through the resin in this rate and definite volumes, and urotropine concentration and pH were determined in the effluent wastewater. The results for C100H resin are shown in Fig. 5. The results show that the sudden increase in pH accompanied with the increase in urotropine concentration, which meant that resin was exhausted. According to these results and the data achieved from other measurements, it may be concluded that pH increase is the reason that indicates the resin is saturated. The COD of effluent wastewater was also measured at this point.

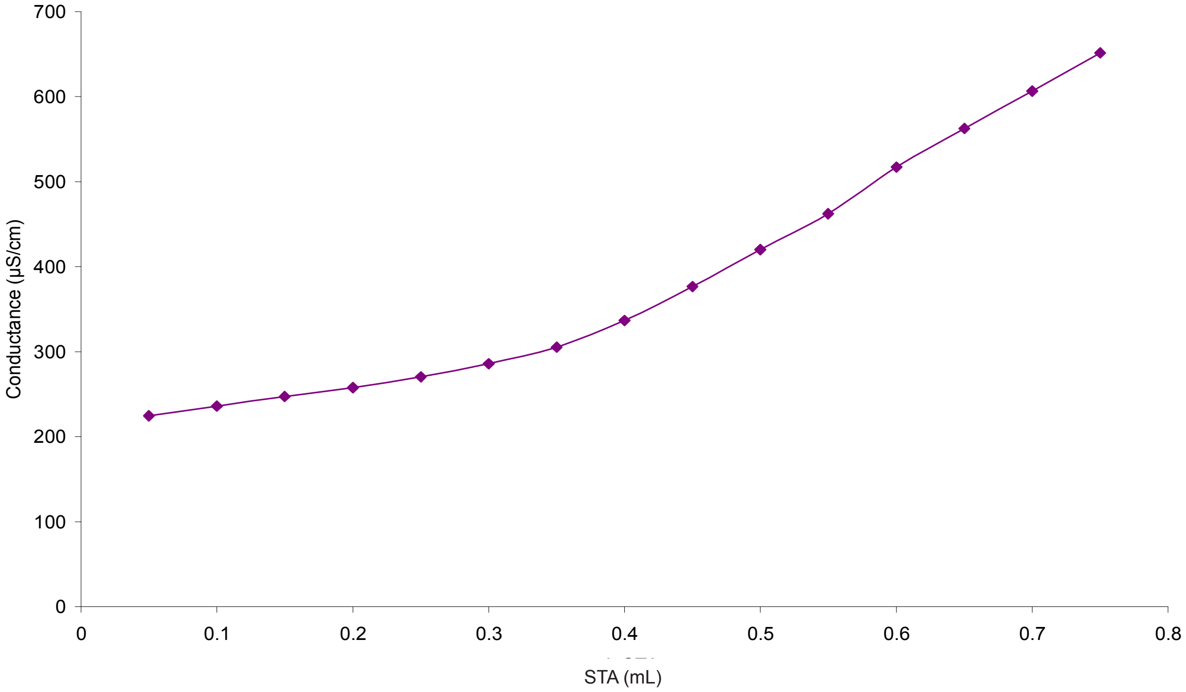

Fig. 2: Conductometric curve obtained for 10 mg of urotropine in the presence of 200 mg/L ammonia; pH= 6.02; 0.05 M silicotungstic acid (STA) as titrant

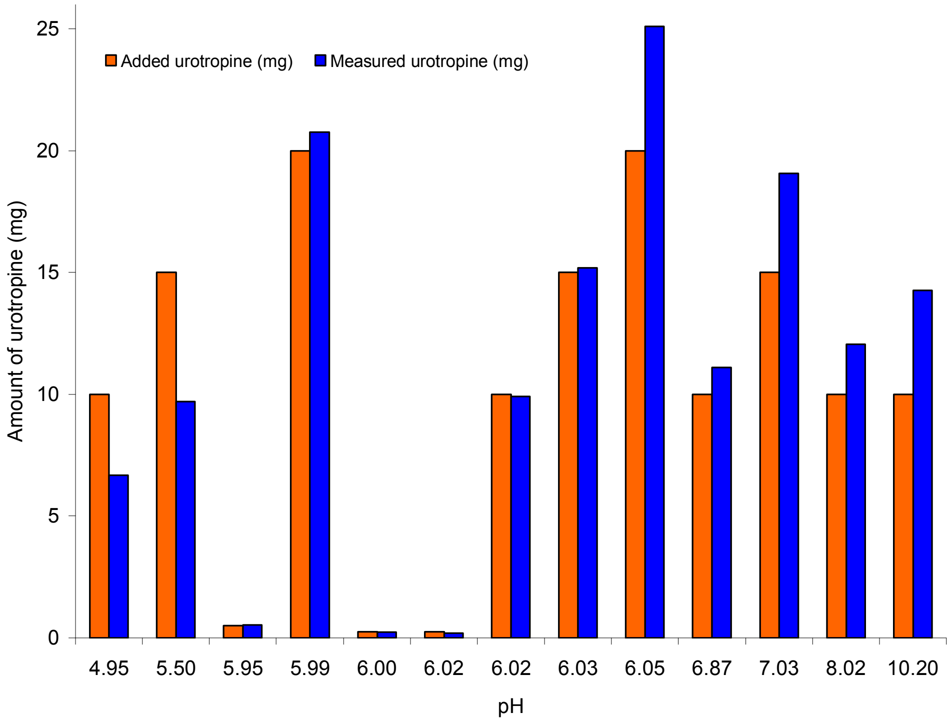

Fig. 3: The optimum pH for determination of urotropine in the presence of ammonia (200 mg/L) by STA as titrant (0.05 M for urotropine content of ≥ 10 mg, 0.0025 M or 0.0015 M for urotropine content of ≤ 0.5 mg)

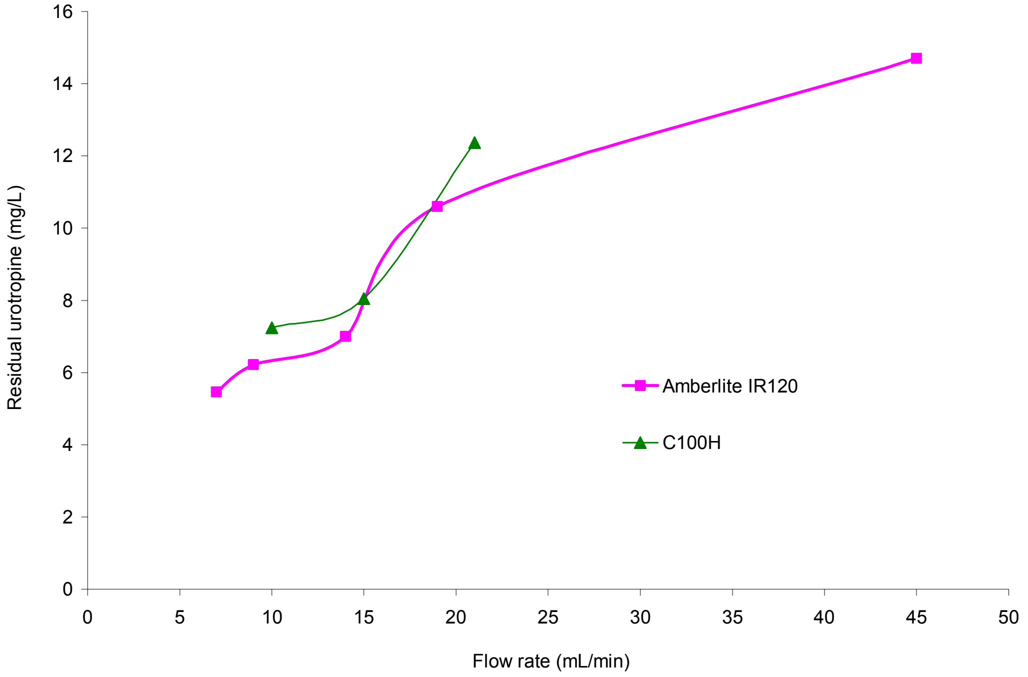

Fig. 4: Residual urotropine (mg/L) in the effluent wastewater vs. flow rate for 100 mL dry C100H and 150 mL dry Amberlite IR120 resins. The initial urotropine concentration in wastewater was 2000 mg/L

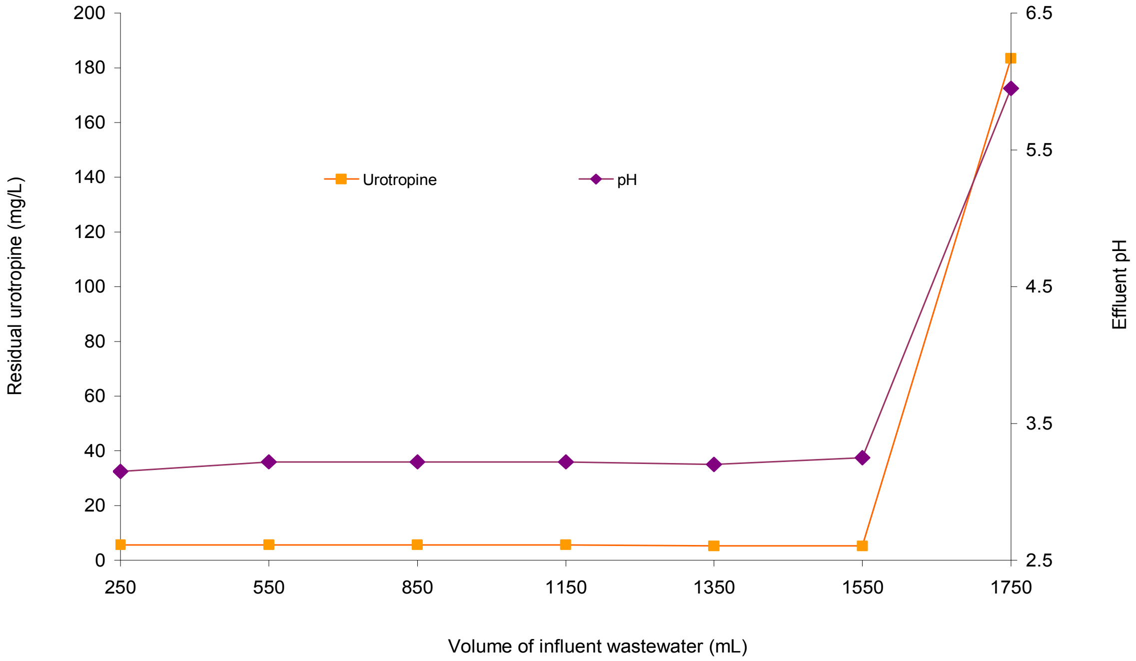

Fig. 5: The dependence of residual urotropine (mg/L) and effluent pH to the wastewater volume passed through 100 mL dry C100H resin. The initial urotropine concentration in wastewater was 2000 mg/L and initial pH was 8.8

The measured COD was much higher than 100 mg/L as the standard COD. So it was obvious that the resin has been exhausted. The results of regeneration of resins are shown in Fig. 6.

The plot of effluent pH against the ratio of volume of influent wastewater to volume of the resin is shown in Fig. 7. The analysis of the waste water before and after treatment by C100H resin in pilot scale is shown in Table 1.

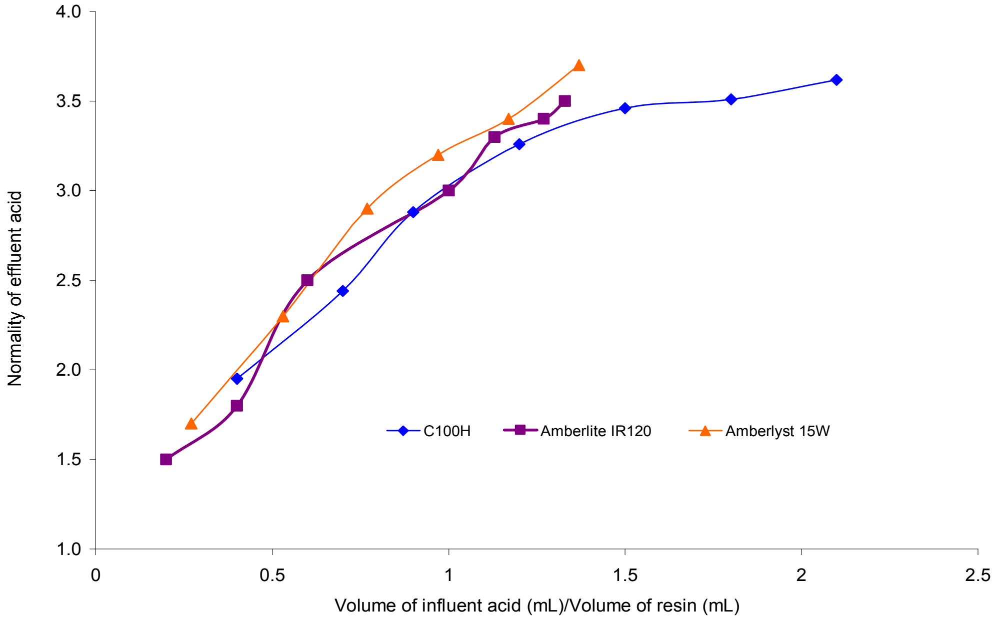

Fig. 6: The normality of effluent acid vs. the ratio of volume of influent acid (10% sulfuric acid) to volume of resin: C100H (100 mL), Amberlite IR120 (150 mL) and Amberlyst 15W (150 mL). The initial normality of acid passed through resins was 3.6

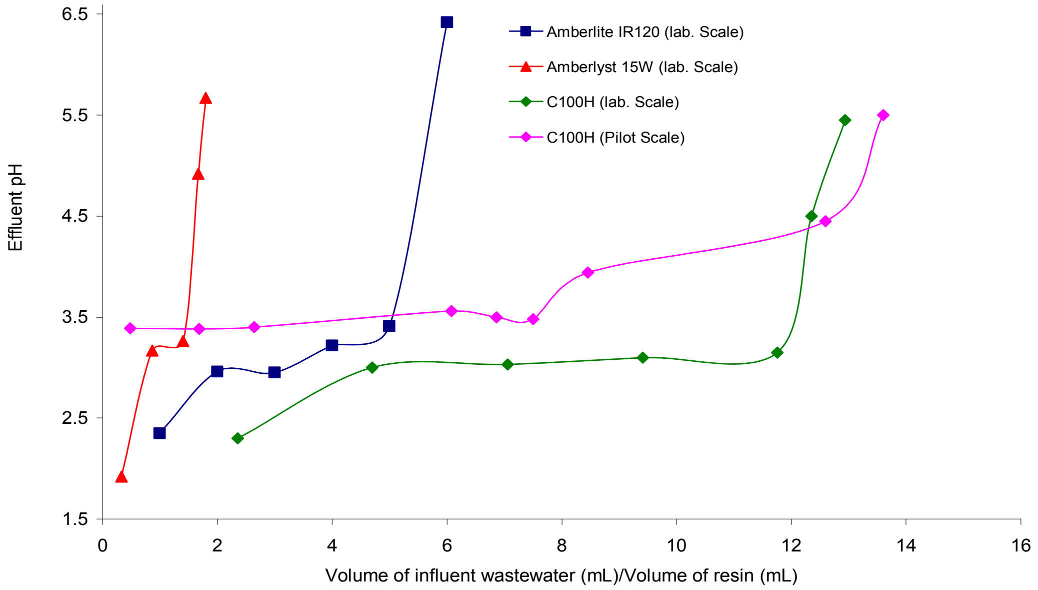

Fig. 7: Effluent pH vs. the ratio of influent wastewater volume to resin volume: C100H (100 mL), Amberlite IR120 (100 mL) and Amberlyst 15W (150 mL). The initial urotropine concentration in wastewater passed through resins was 2000 mg/L and initial pH was 8.8.

Table 1: Analysis of the wastewater used in pilot experiment before and after passing through C-100H resin

Wastewater constituents	Before	After
Urotropine	2800 mg/L	< 10 mg/L
Ammonia	% 0.007	0
Formaldehyde	1000 mg/L	1000 mg/L

DISCUSSION

Determination of urotropine in wastewater in the presence of formaldehyde and ammonia is difficult because most of the methods are indirect determinations based on the determination of the amount of formaldehyde released after hydrolysis of urotropine in acidic condition (Madsen *et al.*, 1996). Therefore, in order to determine the amount of formaldehyde formed from the hydrolysis of urotropine, the amount of formaldehyde originally present must be determined prior to hydrolysis and then subtracted from the amount of formaldehyde formed after hydrolysis.

As described before, coductometric titration with STA solution was used for determination of urotropine in wastewater. In water, methanol and ethanol urotropine forms an insoluble and stable compound with STA in which the stoichiometric ratio of this acid to urotropine is 1 to 4 (Nikolic *et al.*, 1983). Therefore, before the end point of titration relatively small changes in conductivity of the solution are observed; but after the end point of titration, the changes in conductivity are more pronounced due to the presence of hydrogen ions from the excess acid (Fig. 2).

The advantage of this method is that determination of urotropine in wastewater in the presence of formaldehyde is possible without any interference from formaldehyde because STA does not react with formaldehyde, but the presence of ammonia in the wastewater interferes with the determination of urotropine that can be removed by optimizing the pH conditions. Therefore, pH was optimized using standard solutions containing different amounts of urotropine and ammonia. As shown in Fig. 3, decreasing of the pH could bring the measured urotropine closer to the added amounts. It is obvious that in solution with pH=6, the weak base urotropine (pK_a=5.05) acts as nonionic species that react with STA but ammonia (pK_a=9.3) acts as NH_4^+ cation and does not react with STA and therefore does not interfere in the determination of urotropine (Strom and Jun, 1986).

The strongly acidic cation exchange resins in hydrogen form comprise a copolymer of styrene and divinylbenzene and have sulfonate groups as ionizable functions and therefore, can absorb the cations and separate them from other species. Since urotropine in water (pK_a=5.05) acts as a cation, a sufficient cation exchange resin can absorb it from wastewater.

In the present work, the suitable conditions for treatment of urotropine wastewater by the C100H (Purolite), Amberlite IR120 and Amberlyst 15W cation exchange resins were studied. The method comprises passing the wastewater through the strongly acidic cation exchange resins to absorb the cations present in the wastewater. The regenerating of the resins was performed in order to remove the absorbed cations. Fig. 6 indicates that these resins have the same capacity because they need to the same volume of acid for regeneration.

Fig. 7 indicates that these resins can remove urotropine from the wastewater but in the same volume of studied resins, C100H has a higher capability in removing of urotropine in comparison with tow other resins.

The comparison of results for pilot and lab scale indicates that the volume of the wastewater exhausting 5000 mL of the resin in pilot scale is consistent with the volume in laboratory scale. The capability of C100H was 2 and 7 times greater than Amberlite IR120 and Amberlyst 15W, respectively. The breakthrough point for C100H, Amberlite IR120 and Amberlyst 15W was 23520, 10000 and 2800 mg urotropine/Lresin, respectively. Therefore, the efficiency of the three resins is as following:

C100H > Amberlite IR120 >> Amberlyst 15W

C100H resin can act as sufficient cation exchanger for removing of urotropine in wastewater containing the high concentrations of it (Table 1). Although the resin volume was not so much close to the industrial scale, but it could indicate the resin capabilities in trend of increasing the wastewater volume and its flow rate. The other components of urotropine plant wastewater can be removed by current methods and then it may be reused in production process.

The comparison of results with other methods indicates that this method reduces urotropine concentration more effectively. The Fenton method removes urotropine slightly, but electro-Fenton method reduces it to approximately 66 mg/L (0.47 mM) in wastewater containing approximately 2500 mg/L (18.1 mM) urotropine (Chou *et al.*, 1999). The reverse osmosis method by cellulose acetate membrane reduces urotropine concentration to 0.2% in wastewater containing 1% urotropine (Bangxiao and Zhijun, 1986).

Based on these results, it will be possible for urotropine producers to calculate their required amounts of resin and acid for urotropine wastewater treatment in regard to the wastewater flow rate and concentration of urotropine in the wastewater.

ACKNOWLEDGEMENTS

The authors express their appreciation to Sina Chemical Industries Company for supporting this study.

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