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Removal of Alkaline Catalysts from Polyols by Ion Exchange: Regeneration Process Optimization

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ABSTRACT

Resin regeneration is crucial in the feasibility of polyol purification by ion exchange. In order to get an economically viable commercial process, a new regeneration process, including initial and final methanol flushing steps and treating with a 4.5 M aqueous mineral acid solution, has been investigated. An important reduction in regeneration costs was reached by minimizing the amount of acid used and recycling one part of the regenerant solution to the process. The composition of regeneration effluents has been studied in order to recover their valuable components. This simple resin regeneration technique lends itself to a technically and economically viable commercial process for the treatment of polyol products.

Key Words. Ion exchange; Polyols; Regeneration; Organic media

INTRODUCTION

Ion exchange seems to be a promising operation for purifying polyols. Numerous patents describe the use of ion-exchange resins for alkaline catalysts removal (1–3). Most of these applications, however, have not progressed beyond laboratory use. One of the problems in commercializing such a process is the difficulty involved in regeneration of loaded resin (4).

In a previous work (5), Amberlite 252, a macroporous strong cation-exchanger, was selected for polyol purification. This resin showed good chemical and physical strengths, high capacity, and a high rate of exchange. Furthermore, it was demonstrated the loaded resin could be regenerated using 4.5 M hydrochloric acid solution.

Current techniques for resin regeneration utilize aqueous and water-soluble solutions. Upon exhaustion of the cation-exchange loading capacity, the column is flushed with a solvent miscible with both water and organic media. An aqueous solution, such as HCl, is passed over the ion-exchange column to dilute the adsorbed ions and then flushed with a solvent miscible in both water and organic media before reuse (6). The different solvents used in the flushing steps have to be treated and recycled to the process, leading to an expensive operation. The amount of solvent employed has to be minimized in order to reduce the costs required for its recovery (7).

The goal of this investigation was to optimize the different regeneration steps in order to get an economically feasible process. In this paper we present experimental data showing the influence of concentration, acid type, and total amount of acid used in the regeneration process. Finally, we investigated the reutilization of concentrated acid in consecutive cycles of regeneration and the evolution of effluent concentration.

EXPERIMENTAL SECTION

Polyol

Experiments were limited to the use of F-148 grade polyol, made by Repsol Quimica S.A. The alkaline metal content is about 2200 ppm (Na + K), and the average molecular weight is 3500.

Ion-Exchange Resin

Amberlite 252 (Rohm and Haas Co.), a macroreticular sulfonated polystyrene–divinylbenzene resin, was selected in a previous paper (5) for polyol purification. The physical properties and the treatment of the resin are reported in Ref. 5.

Breakthrough Experiments

Breakthrough and regeneration experiments were carried out with the apparatus shown schematically in Fig. 1. In breakthrough experiments, about 60 g of fresh resin beads, with an average diameter of 0.55 mm, were charged to a 22 mm i.d., 600 mm length stainless steel column. The polyol was then pumped through the resin bed at a fixed superficial veloc-

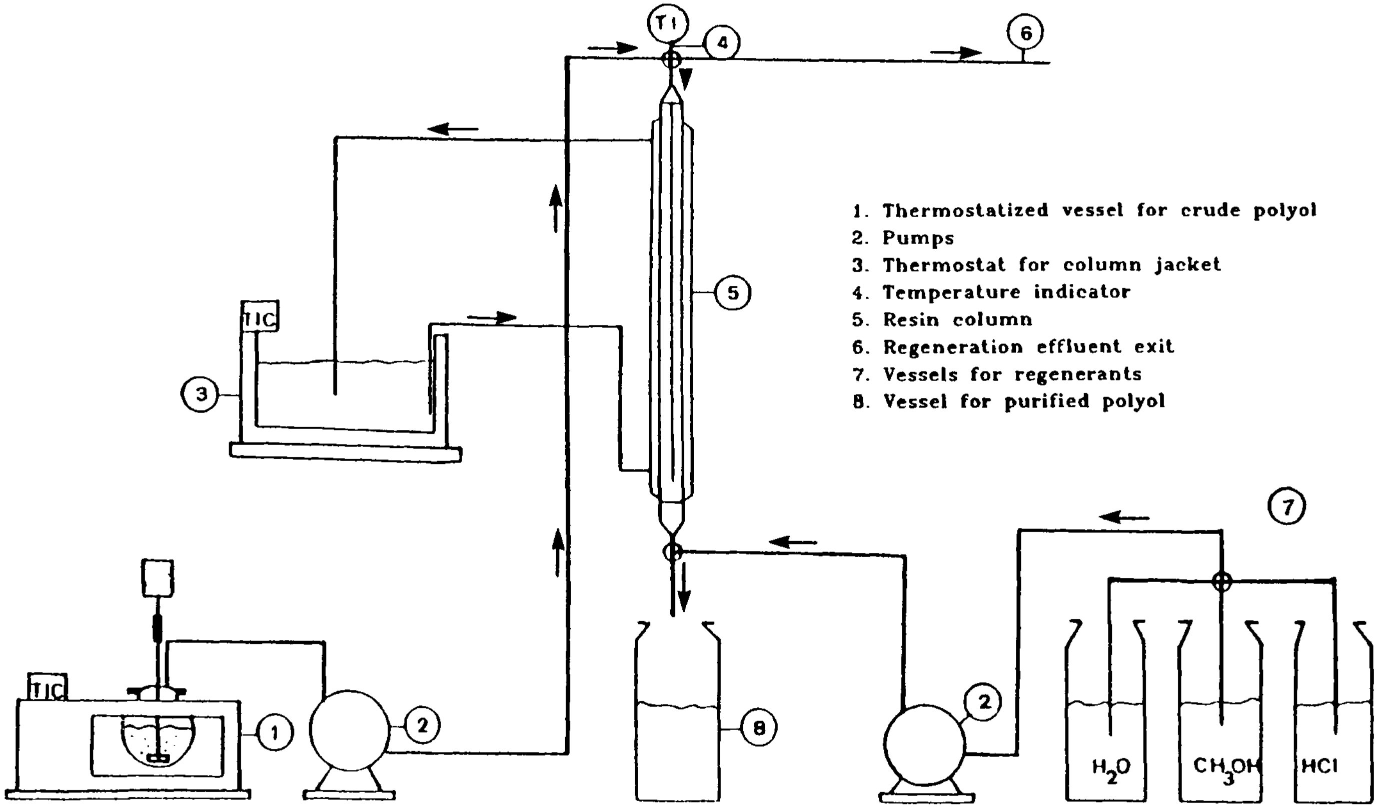

FIG. 1 Experimental setup for breakthrough curves.

ity of 2.5 cm/min (4 bed volumes/h) at 100°C. Samples of the effluent polyol were taken and analyzed for potassium content by atomic emission spectrometry.

Regeneration Procedures and Effluent Compositions

After completion of a breakthrough curve, the spent resin bed was regenerated by consecutive flushing with solvents (methanol and water), contacting with an aqueous acid solution and rinsing with water and methanol. The flow rate of the regenerant solutions was about 0.4 bed volumes/min. Polyol concentration in methanol effluent was determined by weighing the amount of residual polyol after methanol elimination. Water concentration in water–methanol mixtures was determined by automatic amperometric titration using Karl-Fisher reagent.

RESULTS AND DISCUSSION

In a previous paper (5) it was concluded that 4.5 M hydrochloric acid solution is necessary to complete resin regeneration. However, the amount of solvent used and the period of time of each step were not specified.

Taking into account the results obtained in a previous screening (8), the following regeneration procedure is initially proposed. The loaded column is successively flushed with 4 bed volumes of CH_3OH and 4 bed volumes of deionized water. The flushed column is regenerated with 8 bed volumes of 4.5 M aqueous hydrochloric acid solution, and finally the regenerated column is made ready for the next cycle by flushing successively with 4 bed volumes of H_2O and CH_3OH. The total period of time for the regeneration cycle, approximately 1 hour, was acceptable from the viewpoint of its industrial application.

Regeneration cycles were carried out using the above described method. Breakthrough curves obtained in successive operation–regeneration cycles are identical, as is shown in Fig. 2, confirming the adequate regeneration of resin bed.

However, polyol shows premature breakthrough at the leading edge of the breakthrough curve. Only 10% of the potential resin capacity is utilized at the breakthrough point (C_K = 5 ppm). These data indicate that Amberlite 252 is not able to exchange its full potential capacity in pure polyol media. Other investigators have also observed this lack of efficiency when investigating the adsorption of large molecules by ion-exchange resins in

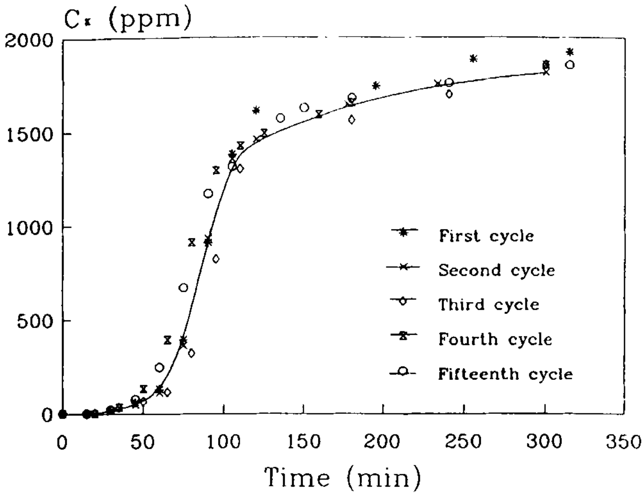

FIG. 2 Comparative breakthrough curves for a series of recycle runs: $v = 2.5$ cm/min; $T = 100°C$; $W_r = 60$ g; $d_p = 0.55$ mm.

organics or aqueous media (9–11). This apparent low ion-exchange capacity could be due to the slow ion-exchange rate resulting from a low degree of dissociation and the large size of the molecule. Steric blocking of adjacent sites by adsorbed molecules, the high flow rate used for the breakthrough curve, and the exclusion of the larger polyol molecules from the smaller pores have been pointed out as other possible causes of this loss of efficiency.

Influence of Acid Concentration

A brief, economical analysis of this regeneration method shows that the high concentration of hydrochloric acid required is problematic for the economical feasibility of this process.

In order to reduce acid consumption, we investigated the regeneration of the spent resin column with an acid concentration lower than 4.5 M. As shown in Fig. 3(a), a reduction of the acid concentration of the regeneration solutions produces a certain decrease in the exchange capacity, corroborating the results presented in a previous paper. Only by using an acid concentration greater than or equal to 4.5 M can satisfactory resin regeneration be reached due to *O*-protonation at the polyol chain in a very strong aqueous acid media (5).

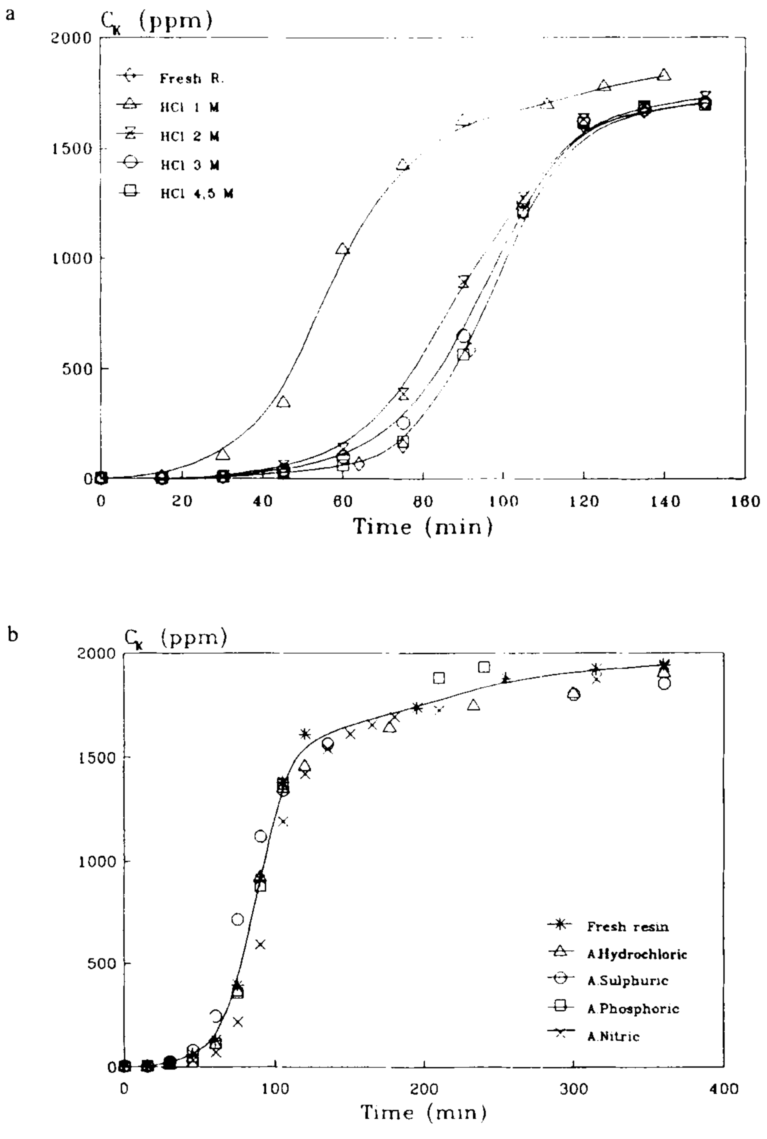

FIG. 3 Comparative breakthrough experiments. a) Influence of acid concentration. b) Influence of acid type. v = 2.5 cm/min; T = 100°C; W_r = 60 g; d_p = 0.55 mm.

Influence of Total Amount of Acid Employed in Regeneration Step

The aim of this study was to reach a significant reduction of regeneration costs. With this in mind, the possibility of reducing the total amount of acid used in the regeneration step was investigated. In this regard, the importance of optimizating the regeneration process was recently pointed out by other investigators (12, 16).

A series of comparative experiments were carried out regenerating spent resin with 4, 6, and 8 bed volumes of 4.5 M hydrochloric acid solution (below 4 volumes, operational problems arise). The breakthrough curves obtained in each case were identical, showing that the column could be adequately regenerated using only 4 bed volumes of acid solution, a reduction of 50% in acid consumption.

Influence of Acid Type

In order to test the possibility of resin regeneration using different mineral acids (13), a series of comparative experiments were carried out employing 4.5 M aqueous solutions of different acids, hydrochloric, sulfuric, phosphoric, and nitric, in the regeneration step.

As shown in Fig. 3(b), the breakthrough curves obtained using regenerated resin with different acids are identical. These results indicate that regeneration with strong acids is technically feasible and offers new alternatives for the regeneration process.

Reuse of Hydrochloric Acid Solutions

Since a reduction of acid concentration was not possible, the total or partial reutilization of the acid solutions in successive regeneration cycles was investigated in order to reduce the regeneration costs.

A more detailed economic analysis showed that 2 bed volumes was the maximum amount of 4.5 M acid solution which could be used in regeneration to make this process economically feasible. Economic analysis of the process and operating conditions details are not presented here because they are proprietary information.

The acid regeneration step was subdivided into two parts: during the first, two reused acid volumes coming from the previous regeneration cycle were used; in the second, 2 volumes of 4.5 M acid solution were passed through the resin bed and later reused during the following regeneration cycle.

Figure 4 shows the breakthrough curves obtained under identical conditions using resin regenerated by the above-described method. The loading

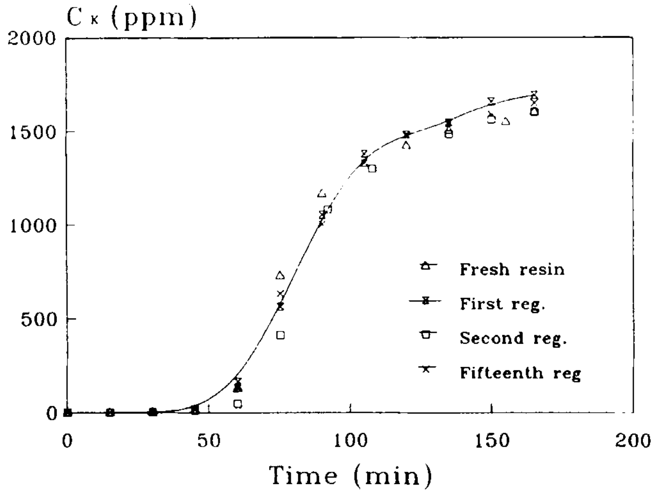

FIG. 4 Reuse of hydrochloric acid solutions: v = 2.5 cm/min; T = 100°C; W_r = 60 g; d_p = 0.55 mm.

curves obtained are identical even after 15 regeneration cycles, demonstrating efficient resin regeneration. This reduction of acid consumption results in an important improvement in the economic feasibility of the process.

Evolution of Effluent Composition

The economic feasibility of this regeneration process depends not only on acid costs but on a complete recovery of methanol solvent and polyol displaced in the resin bed. Therefore, it was very important to know the composition of the different regeneration effluents in order to design and set the dimensions of the industrial equipment needed to recover these effluents (14, 15).

The evolution of polyol concentration in methanol effluent corresponding to the first regeneration step and the total amount of polyol removed by each methanol volume expressed as gram of polyol per gram of resin bed is shown in Fig. 5(a). The highest total amount of polyol eliminated and later recovered in this regeneration step can reach 1.29 g/g when using at least 8 bed volume of methanol. As shown in Fig. 5(a), by using only 4 volumes of methanol (as in the above-described method), the polyol eliminated is 1.23 g/g, the remaining 0.06 g/g polyol retained in the column cannot be recovered under these conditions. Based on actual polyol prices, the polyol losses are acceptable from an economic viewpoint.

Figure 5(b) shows the evolution of methanol concentration in the water effluent during the second regeneration step and the amount of methanol displaced from the resin column by each water volume. It can also be observed that there is complete methanol exhaustion of the column when using 4 water volumes. The methanol present in the rinsed water solution (approximately 5% by weight) must be recovered in order to optimize the process.

Figure 5(c) shows the concentration history of potassium in the effluent solution during the treatment step with acid. Potassium is completely removed from the resin after the fourth HCl bed volume, confirming the suitability of the proposed regeneration method. The concentration curve shows a sharp peak characteristic of ion-exchange regeneration curves. This peak did not appear in the preceding elution curves since the solvents were not chemically adsorbed in the resin and only existed in the void volume of the bed before elution (16).

In the fourth regeneration step, the use of 4 volumes of deionizated water decreases the conductivity of the effluent solution to under 200 μS, which is an acceptable value at the end of the regeneration step.

The regenerated column was made ready for the next cycle by flushing it with 4 bed volumes of methanol. As shown in Fig. 5(d), water is completely eluted from the column. The average water concentration in the methanol solution is 13% by weight. This water content must be eliminated by distillation in order to recycle methanol to the process.

Our study of effluent compositions has shown that the proposed regeneration method allows the total elimination of undesirable compounds retained in the column and minimizes the total amount of different regenerants and the time period needed for the regeneration process. An industrial process for polyol purification and effluent recovery is shown schematically in Fig. 6.

The industrial equipment consists of two resin columns; while one unit is operating in polyol purification, the other one is operating in the regeneration cycle. The methanol–polyol solution obtained in the first regeneration step is treated by flash vaporization to recover commercial polyol and methanol which is recycled to the methanol vessel. Methanol–water solutions obtained in the second and the fifth regeneration steps are recovered in the distillation column. The first two volumes of recycled acid solution are sent to wastewater treatment and the other two volumes of virgin hydrochloric acid solution are stored in a intermediate vessel awaiting reuse.

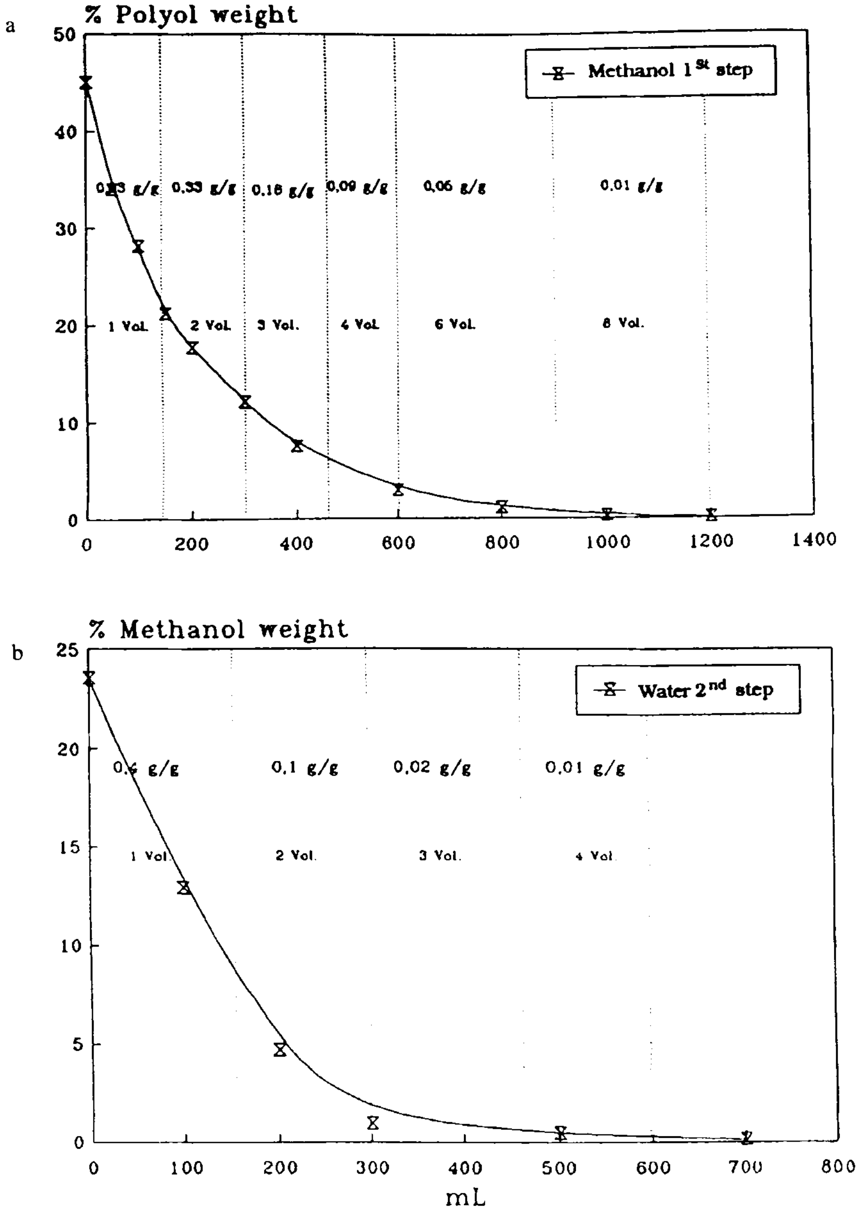

FIG. 5 Concentration histories of regeneration effluents. a) Elution curve of polyol (1st regeneration step). b) Elution curve of methanol (2nd regeneration step). c) Elution curve of potassium (3rd regeneration step). d) Elution curve of water (5th regeneration step). v = 15 cm/min; T = 25°C; W_r = 60 g; d_p = 0.55 mm.

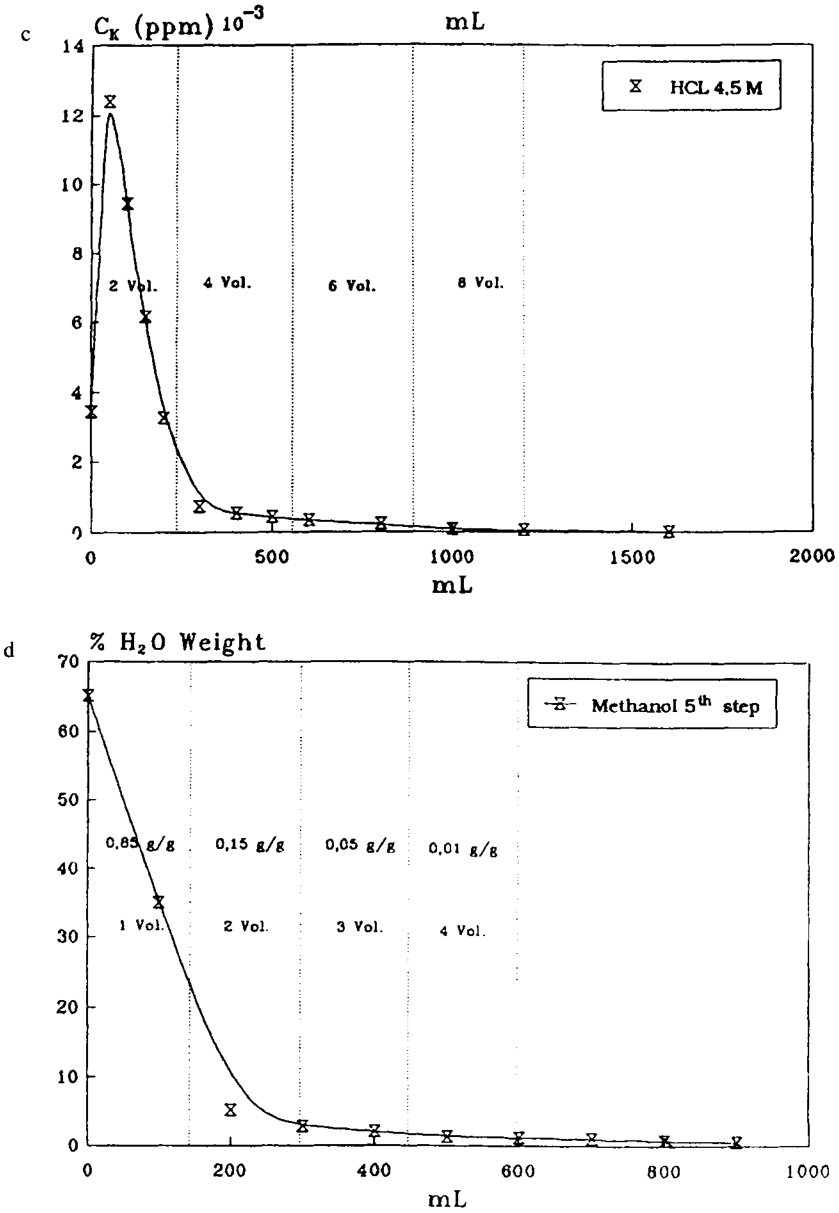

FIG. 5 Continued.

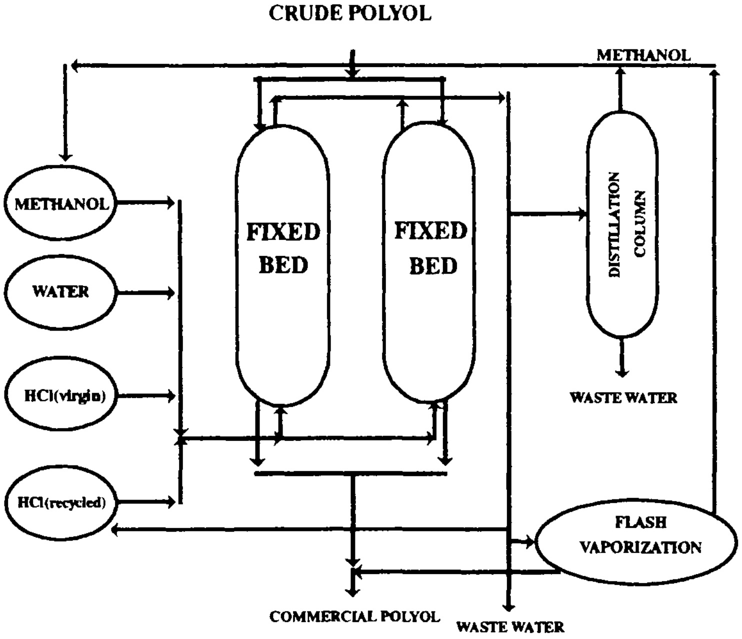

FIG. 6 Scheme of industrial process for polyol purification.

From the operation conditions for polyol purification (5) and resin regeneration established above, the Spanish Petrochemical Company (Repsol Química S.A.) confirmed the economic feasibility of this ion-exchange method for polyol purification.

CONCLUSIONS

In this work a new regeneration process, including initial and final methanol flushing steps and treatment with a 4.5 M aqueous mineral acid solution, has been developed.

Regeneration with different strong mineral acids is technically feasible and offers new alternatives for the regeneration process. By minimizing the acid consumption in each cycle and recycling the acid solution, the proposed method became economically feasible. A study of regeneration effluents has pointed out the minimum amounts of each regenerant required for an adequate regeneration of the resin and the compositions of the resulting effluents.

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