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Decolorization of Aqueous Caprolactam Solution by Anion-exchange Resins

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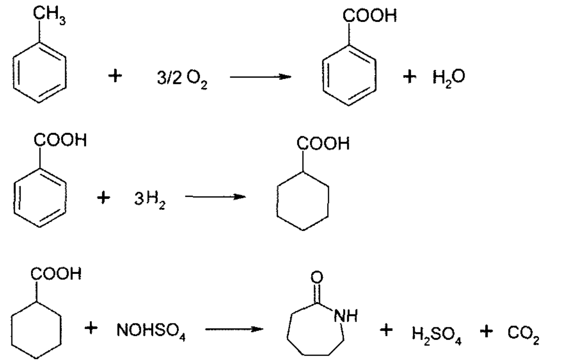
Abstract: Caprolactam is the most important raw material for making Nylon 6 fibers and its quality directly determines the quality of Nylon. So it is necessary to study the techniques and methods to remove the colorful impurities from caprolactam. In this paper, the decolorization of caprolactam aqueous solution by anion exchange resins was studied and the decoloring abilities of five commercial resins were investigated. The regeneration of the resins was also studied, too. This study shows that the resin AMTX202 have excellent decoloring ability in the column experiment and that the decoloring efficiency is correlated with the volume of resins packed and is slightly affected by the flow rate and regenerating times. The fact that the resins can be regenerated and reused without affecting the efficiency of decolorization will decrease the cost of the treatment and operation in the industry. The adsorption of colored compounds with anion exchange resins in the packed columns seems to be technically feasible.

Keywords: Decolorization, Caprolactam, Resin, Ion exchange, Nylon

Introduction

Caprolactam is an important organic chemical material which is mainly used in the manufacture of nylon 6 fibers [1-5]. The two main raw materials in world to produce caprolactam are the benzene introduced by the BASF and DSM companies as well as the toluene developed by the SNIA group [6-9]. Compared with benzene, toluene is less detrimental to environment and human body, so the toluene-based caprolactam was supposed to be more competitive than the benzene-based one. However, the caprolactam made from toluene contains colorful impurities, which seriously affects the qualities of nylon 6 fibers made of it. Therefore, most enterprisers and researchers have rarely paid their attentions to the SNIA process to produce caprolactam and a vast array of factories making toluene-based caprolactam slipped into plights. The factory in Marflidonia went bankrupted in 1989, the one in Circik also was shut down in 1996, and the one in Torviscosa was closed in 1999. The only toluene-based caprolactam producing manufacturer in China built in 1999 encounters the same difficulty now and this paper gives a method to solve this problem.

The SNIA process of producing caprolactam from toluene consists of three main steps. First, the oxidation of toluene to benzoic acid (Reaction 1). Second, the hydrogenation of benzoic acid to hexahydrobenzoic acid (Reaction 2). Third, the nitrosation of hexahydrobenzoic acid to caprolactam (Reaction 3). The first and second steps are mature technologies and most of impurities are generated in the third step. There are two possibilities in the third step reaction: one possibility is that the hexahydrobenzoic reacts with nitrosyl sulfuric acid to produces caprolactam; the other possibility is that hexahydrobenzoic doesn't react with nitrosyl sulfuric acid but reacts with other parts of hexahydrobenzoic to create impurities. No matter what the impurities are, colorful or colorless, the carboxyl group remains. As the aqueous caprolactam solution is alkalescent, the carboxyl acid group is ionized (Reaction 4) and those impurities containing carboxyl acid group can ion-exchange with resins (Reaction 5). In this case, anion exchange resins will work.



(1)

(2)

(3)

$$R{-}COOH + OH^- \longrightarrow R{-}COO^- + H_2O \quad (4)$$

$$R{-}COO^- + Resin{-}OH \longrightarrow Resin{-}OOC{-}R + OH^- \quad (5)$$

Water treatment engineers usually utilize ion-exchange resins to remove the ions in aqueous solutions to purify water [10-13]. The advantage of using resins is that they can be regenerated, thus cut down the cost of operation, and they allow the process in a continuous mode. The resins, which have relatively large surface of ion-exchanging areas, can provide effective adsorptive sites for organic or inorganic ions. The mixed resin bed can even produce the purified water to meet the standards for power plants and electronic industry. This paper has studied the feasibility of several anion exchange resins to remove the colorful impurities from caprolactam aqueous solution.

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Table 1. Characteristic properties of the ion exchange resins investigated

Resin	Matrix	Functional group	Type	Total ion exchange capacity (mmol/g)	Particle size (mm)
IRA900	Polystyrene	$N^+(CH_3)_3$	High porous	4.2	0.3-1.2
201	Acrylic acid	$N^+(CH_3)_3$	Gel	1.5	0.650-0.820
AMTX202	Acrylic acid	$N^+(CH_3)_3$	Gel	6.2	0.315-1.25
D730	Polystyrene	$N^+(R)_3$	Porous	0.8	0.315-1.25
D-2	Polystyrene	$N^+(CH_3)_3$	High porous	3.4	0.45-1.25

Experimental

Materials and Methods

The raw material is the 30 % aqueous caprolactam solution provided by the caprolactam manufacturing factory in Shijiazhuang, Hebei Province, China, without any further treatment. The solution is nigger-brown color, smelly, with the conductivity of 689 μS/cm. And the pH of the solution is 9.23, alkalescent. The resins employed here were IRA900 and 201 offered by Rohm and Hass, Philadelphia, PA, USA. AMTX202, D730, and D-2 in Chinese commercial market were also employed. Their characteristics are given in Table 1.

The color of the vinegar samples was evaluated by modified color intensity (MCI), which is the absorbance at wavelengths of 290 nm (1-cm pass). These measurements were conducted on 752 UV spectrophotometer. In order to normalize the values of decoloring efficiency (DE), it was defined as below:

$$DE = 100\left(\frac{MCI_0 - MCI}{MCI_0}\right)$$

DE: decoloring efficiency
MCI: modified color intensity
MCI_0: the MCI before going into the column

Column Experiment

The Figure 1 shows a schematic diagram of the fixed-bed. The adsorption column was made of glass with an inner diameter of 20 mm and a length of 300 mm. Different resins were packed into the column and sustained by a dank ceramic sheet in the bottom, and the volume of resins used depended on the experiment. The solution was introduced into the column from the top. All the packing procedures were conducted under water to avoid the generation of bubble in the column. After experiment was started, samples were periodically taken at the determined time intervals. Stock solutions were prepared in a glass tank of 5 *l* volume, and all the experiments were carried out at room temperature (25 °C). The flow was delivered by a variable-speed pump, which was operated in the upward mode. Distilled water was supplied into the column at the flow rate of 100 m*l*/min as the aqueous solution for about 10 mins prior to the start of the experiment to fill the bed with water and to prevent sudden disturbance of the experimental system at the beginning of the experiments.

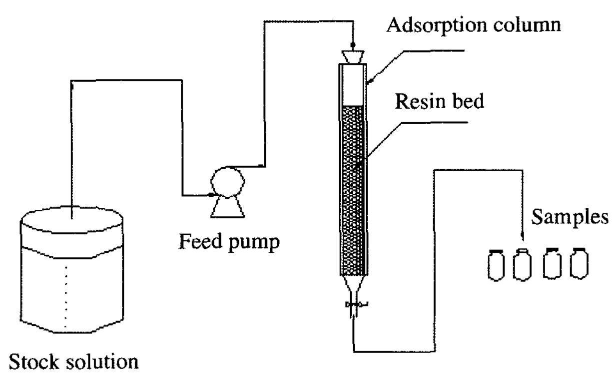

Figure 1. Schematic diagram of fixed bed apparatus.

The resin regeneration was also carried out at room temperature (25 °C). The regenerating eluent was 4 % (w/w) NaOH aqueous solution (recommended by the resin manufacturer). The eluent was pumped into column at a flow rate of 5 m*l*/min for 40 mins. To prevent channeling and to enhance the distribution of the solution through the column, back wash was also introduced. All regenerations were conducted at this condition.

Results and Discussion

The Comparison of Different Resins

Figure 2 illustrates the variation in DE during decolorization in column process with different resin beds versus the eluted volume/bed volume (EV/BV). The EV/BV is defined as the ratio of the volume of the aqueous caprolactam solution treated to the volume of resins packed in the column. The figure shows the decolorization process for caprolactam solution using five different resins, so their performance could be compared. Each experiment was conducted at the flow rate of 100 m*l*/min and with 50 m*l* resins packed All five resins have the ability to eliminate the colorful components and resin AMTX202 seems to be most efficient. The reason could be explained by the fact that the resin AMTX202 has a relative larger ion exchange capacity compared with the other resins (Table 1). For making a fair comparison, all the resins used in the Figure 2 are new.

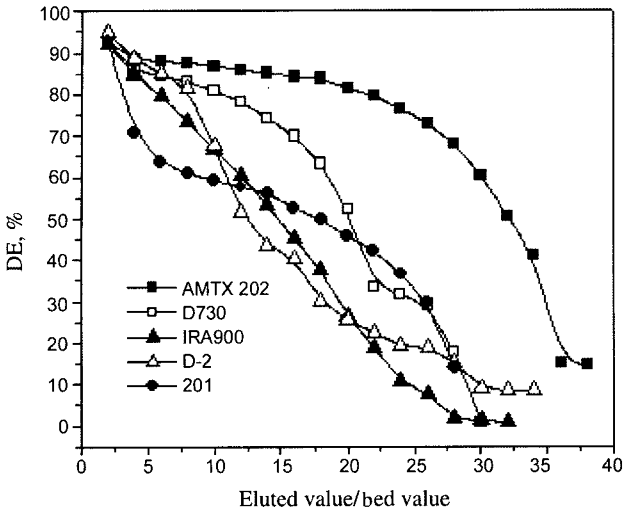

Figure 2. Variation in the DE with different resins in column process.

Figure 3. Top: The 30 % caprolactam aqueous solution before decolorization; Bottom: The 30 % caprolactam aqueous solution after decolorization.

Figure 3 also shows the comparison of decolorization visually. The picture on the top is the aqueous caprolactam solution before decolorization and the bottom picture is the solution after decolorization. All the aqueous caprolactam solutions contained in the bottles are clearly seen to become more transparent and less yellowish after decolorization with the resin AMTX202.

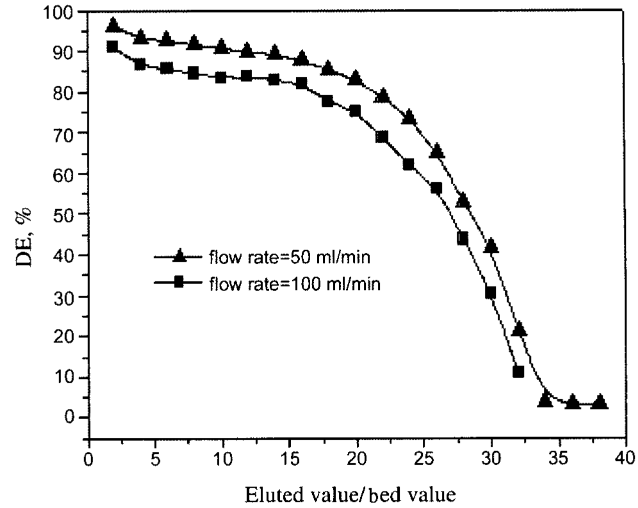

Figure 4. Effect of flow rate on the decoloring efficiency on resin AMTX202.

Effect of Flow Rate

The effect of different flow rates on the DE was also studied. The comparison of the DEs in column process at two different flow rates (ca. 50 m*l*/min and 100 m*l*/min) is profiled in the Figure 4. It can be observed that there is a minor increase in decolorization efficiency with a decrease of the flow rate, but the influence is not significant. For an instance, the DEs at the flow rates at 100 m*l*/min and 50 m*l*/min were 84 % and 87 % (the minimum range of DE which can indeed be used for the production of high quality of nylon 6 fibers is 80 %) at an EV/BV of 16, respectively. These results suggest that the flow rate didn't have conspicuous effect on the decoloring efficiency. To test the running stability of the flow rate, the resins used in the Figure 4 have been regenerated one time.

Effect of Regeneration

Regeneration experiments of the used resins were carried out. Decoloring efficiencies of new and regenerated resins in the flow rate of 100 m*l*/min are presented in Figure 5. To investigate the feasibility of applying resin AMTX202 in industry by making sure that the resin has an enough life-span for industrial service, the regenerating experiments were conducted as a function of the number of regeneration cycles. The decolorization efficiencies of a new resin AMTX202 and regenerated one show somewhat difference, but not dramatically. But the decolorization efficiency profiles of the regenerated resins are practically the same, no matter how many times it is regenerated. The results demonstrate that after the regeneration procedure, resin AMTX202 recovered its decolorization capacity. These results clearly show that the regeneration of resins AMTX202 is feasible in industry,

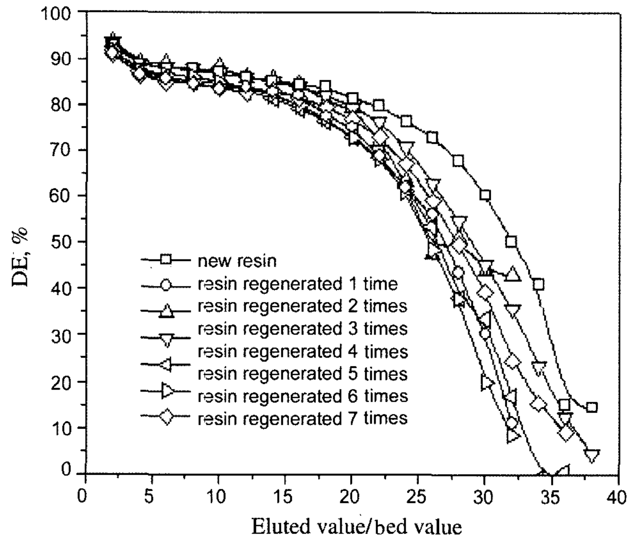

Figure 5. Variation in DE with BV for new and regenerated resin AMTX202.

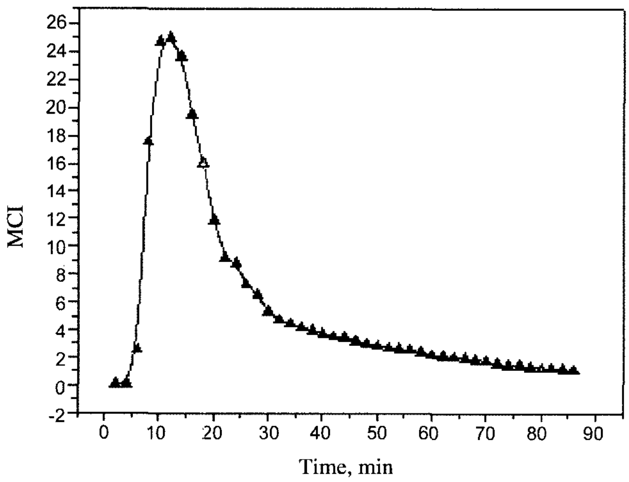

Figure 6. Change of the MCI (modified color intensity) in the exit regenerating solution from AMTX202 resin bed as a function of time with a 5 m*l*/min flow rate of 4 % NaOH solution.

which means that the decolorization in continuous process will be cheaper in the long run.

Regeneration of the AMTX202 resins is needed when the breakthrough point is reached or when the resins are completely saturated. Regeneration of the exhausted resins were conducted by feeding the 4 % (w/w) NaOH solution at a 5 m*l*/min flow rate to the top of the resin column. The MCI (modified color intensity) in the exit of NaOH solution was measured every 2 min. Figure 6 depicts the change of exit MCI as a function of time. Regeneration was essentially completed in about 90 min. The total NaOH solution required for complete regeneration was thus 450 m*l*. In the Figure 6, we can figure out that the MCI was inclining to equilibrium after 40 min, requiring 200 m*l* regenerant approximately. With a 50 m*l* bed volume (BV) of the present resin column, regeneration of the exhausted resins requires approximately 4BV of regenerant for each.

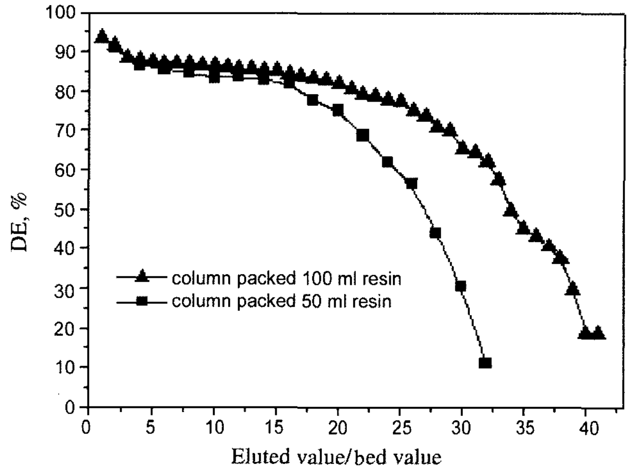

Figure 7. Effect of volume of column on the decoloring efficiency on resin AMTX202.

Effect of Volume of Column

We have shown above that DE is affected by the kind of resin and flow rate at the same regeneration condition has no significant influence on DE in the long run. To assess whether the process can be scaled up, experiments with varying volumes of column were carried out. The volume of resin AMTX202 used was 100 m*l* and 50 m*l*, respectively and the flow rates were kept the same in 100 m*l*/min. The DE obtained using these conditions and the DEs for different volume of column were compared in Figure 7. The results show that the decolorization efficiency profiles of the large column are practically better than that of the small one. Because the aqueous solution of caprolactam has relatively more contact time in the larger column than in the small column, the ion exchange resins in the larger column can fully retain the colorful impurities in solution and consequently increase the decoloring efficiency. In experiment, the DEs for resin volume of 50 m*l* and 100 m*l* were 83 % and 85 % at the EV/BV of 18, and the DEs for resin volume of 50mL and 100 m*l* were 14 % and 62 % at the EV/BV of 36, respectively. These results show that increasing the volume of resins does significantly affect the DE if the flow rate is maintained constant. To test the running stability of the apparatus, the resins used in the Figure 7 have been regenerated one time.

Conclusion

This study shows that the resin AMTX202 have excellent decoloring ability in the column experiment, and the decoloring efficiency was correlated with the volume of resins used and it was slightly affected by the flow rate and regenerating times. The fact that the resins can be regenerated and reused without affecting the efficiency of decolorization will decrease the cost of the treatment in industry. One important advantage of column process is the corresponding decrease in pollution since the sorbent such as activated carbon can be used only once and it generates a considerable amount of solid residue. Ion exchange resins can decrease the amount of solid waste in toluene based caprolatam production.

Acknowledgements

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