Purification of caprolactam by means of an electrodeionization technique

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Abstract

In this study an experimental method for purification of a system containing a 30% caprolactam aqueous solution was attempted at room temperature. The impurities in the system were removed by using the continuous electro-deionization (EDI) device, which is an ion-exchange membrane stack with 40 diluting compartments filled with mixed ion-exchange resin beads. The optimal working parameters for this technology were obtained during a 5-month test. It was shown that the conductivity of the treated caprolactam solution was considerably lower (10 μS/cm) in comparison to the feed caprolactam solution (30 μS/cm). In addition the absorption value had decreased by 20%.

Keywords: Caprolactam; Electrodeionization; Purification

1. Introduction

Caprolactam is an important raw material of both nylon-6 and polyamide fiber. Specifications for this material are extremely stringent, requiring extensive purification. The most common industrial process for the production of caprolactam is the Beckman rearrangement of cyclohexanone oxime, obtained from cyclohexanone.

The 30% caprolactam aqueous solution used in this study comes from extraction with benzene and re-extraction with water after the Beckman re-arrangement. Ion-exchange beds are used in the system to purify caprolactam and remove impurities. In 1 year of operation the cation and anion exchangers were regenerated approximately 60 times in a chemical plant in Yueyang, Hunan, China. The regeneration of ion-exchange resins consumes 450,000 kg HCl (31%) and 486,000 kg NaOH (100%) respectively, and produces 36,000 m³ of wastewater. A continuous electrodeionization (EDI) device can overcome these shortcomings, for it has little wastewater discharge and does not use chemicals.

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In this paper the EDI device was employed to replace the ion-exchange beds. The objective of the study was to determine whether the EDI device enabled impurities (mostly ammonium sulfate) in a caprolactam aqueous solution to be eliminated effectively.

2. Experimental

2.1. Principle of continuous electrodeionization

The principle diagram is shown in Fig. 1. In the diluting compartments ions such as NH_4^+ and SO_4^{2-} in the caprolactam aqueous solution first transfer into the resin beads by diffusion, and then from the resin beads onto the membranes by direct current. Resins are regenerated by means of H^+ and OH^- ions which appear as water-splitting occurs in order to keep the current unchanged when NH_4^+ and SO_4^{2-} in the caprolactam aqueous solution decreased. This takes place in some parts of the diluting compartments. The H^+ and OH^- ions formed are separated before they can recombine into water [1,2].

2.2. Materials

The caprolactam aqueous solution used in this study was obtained from a chemical plant in Yueyang, Hunan, China. It was used directly, i.e., without any additional treatment.

2.3. Apparatus

2.3.1. Description of the tests

The EDI module is comprised of 40 diluting compartments (cell pairs) filled with mixed ion-exchange resins. The voltage applied was 7.5 V per cell pair. The device was installed in a chemical plant. The caprolactam aqueous solution was obtained from a smaller channel which ran from the main process in the chemical plant and was pumped into the EDI; the flow rates of feed remained stable (about 15–20 l/min; the concentrate compartment flow rates ranged between 1 and 3 l/min with little electrolysis water discharge). The current was controlled between 2 A and 3 A.
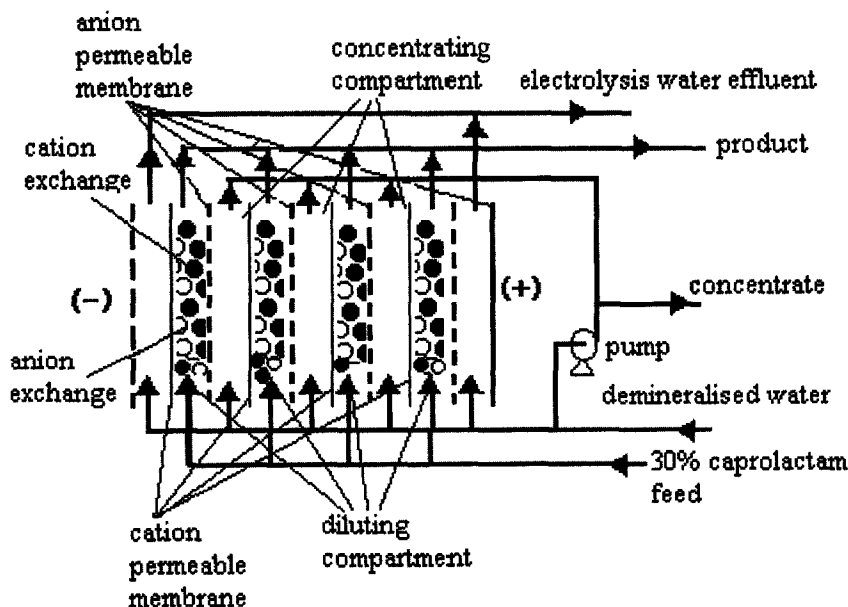

Fig. 1. Diagram illustrating the principle of continuous electrodeionization.

2.3.2. Criterion of production

The pilot plant was designed to achieve the following performances:

- Conductivity:　　　<10 μS/cm
- Absorption value:　<0.8

2.4. Analysis

The conductivity was determined by a 303A conductivity device (China); absorption value was detected using an UV-1601 ultraviolet spectrophotometer (Shimadzu, Japan), with an absorbency wavelength of 290 nm. The impurities in the caprolactam were checked by an Agilent 6890-5973 (USA) gas chromatography–mass spectrometer.

3. Results and discussion

3.1. Pilot plant experiments

During the tests, conductivity and absorption values were monitored once a day in both the feed and the treated solutions. Fig. 2 shows that the conductivity of the feed solution was consistently reduced in comparison to the treated solution during the 138-day test period. The conductivity of the product solution remains reliably low even during periods when the feed solution has relatively high conductivity.

Fig. 3 shows that the UV absorption value decreased during the same test period, and the value at the intake compared to the EDI device effluent was reduced. The UV absorbance of the
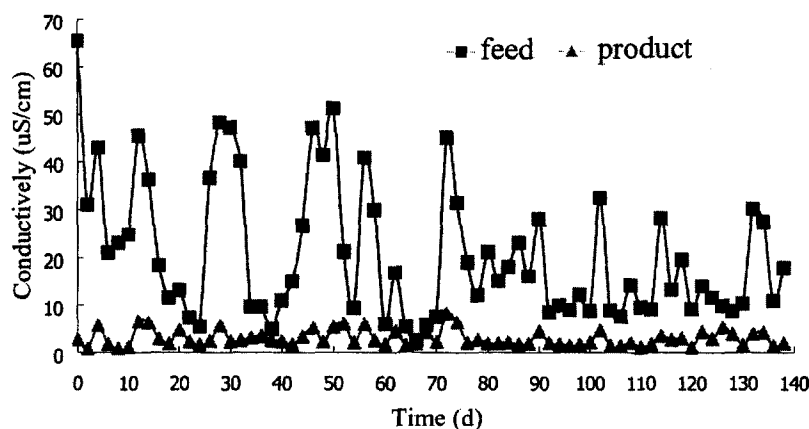

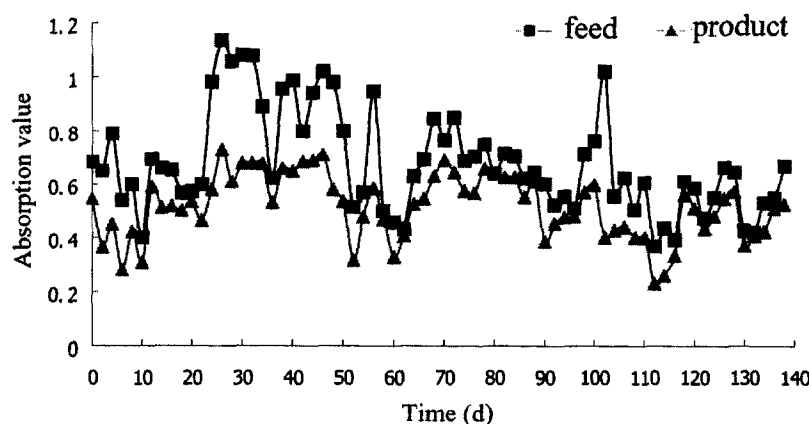Fig. 2. Measurement of conductivity in a 30% caprolactam aqueous solution.

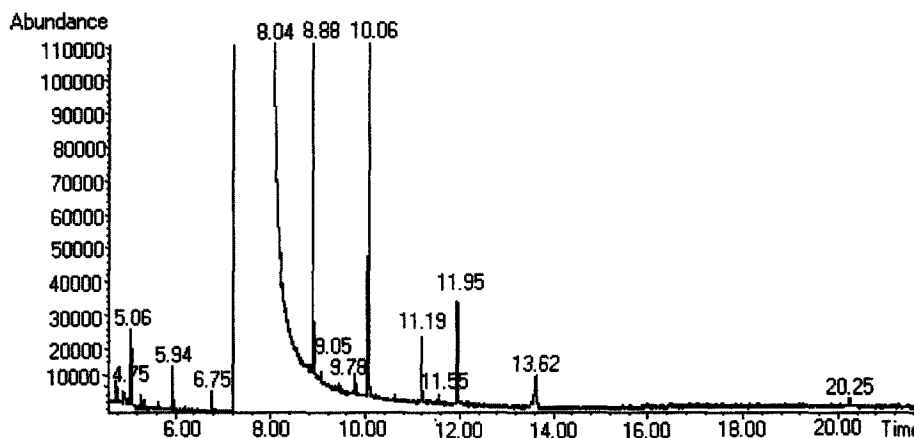Fig. 3. Measurement of absorption value in a 30%caprolactam aqueous solution.

Fig. 4. Total ion current chromatography of impurities in a 30%caprolactam aqueous solution without treatment.

EDI device effluent was consistently lower than 0.8, and the reduction in absorption was always in excess of 20%.

It is evident that the EDI device efficiently removes the impurities from a 30% caprolactam aqueous solution, and the product quality complies with the criteria.

3.2. Determination of impurities in the system

Impurities in caprolactam are usually determined by chromatographic techniques. The main problem faced in the determination of impurities comes from low concentrations and great variety. The common methods of caprolactam purity control in industry are non-specific, e.g., permanganate extinction number, volatile bases and so on [3]. The samples can be analyzed directly by capillary gas chromatography–mass spectrometry (GC–MS). For most of compounds, the retention time and identification can be obtained by GC–MS, which can be used to monitor the change of these impurities by GC with a flame-ionization detector. The resolution capacity of a capillary column is higher than a packed column, and therefore, a capillary column is used to separate the impurities in the system [3].

Figs. 4 and 5 show the results of total ion current chromatography of the samples before and after the EDI treatment. Fourteen compounds were well separated in Fig. 4, and can be seen in lower concentrations in Fig. 5.

For the peak identification, the mass spectra obtained were compared with the mass spectra published in the data tables [4]. Not all of the chromatography peaks gave mass spectra suitable for interpretation. As shown in Fig. 4, peaks 5.10, 5.96, 6.75, 8.88, 10.06, 11.19, 11.95, 13.63 and 20.25 were 5-ethhyldihydro-2 (^{3}H)-furanone, aniline, 4, 5, 6, 7-Tetrahydro benzofurazan, N- (N – acetyl – L-ananyl)-glycine butyl ester, 14 hexanoic acid, N – ethyl – N - (1-methylethyl) – 2-propanamine, methyl butanedioic acid, 8-methyl-2,4(^{1}H,^{3}H)-pterdinedinedione, 7-methyl caprolactam, 1,2-benzenedicarboxylic acids diethyl ester, respectively. Peaks 4.75, 8.04, 9.05, 9.78 and 11.55 cannot be identified by a comparison of the mass spectra published [4]. In Fig. 5, peaks 5.10, 5.96, 11.95 were 5-ethhyldihydro-2 (^{3}H)-furanone, aniline and 8-methyl-2,4 (^{1}H,^{3}H)-pterdinedinedione, respectively.

The impurities may originate from raw material and a side reaction. The impurities in the 30% caprolactam aqueous solution after EDI
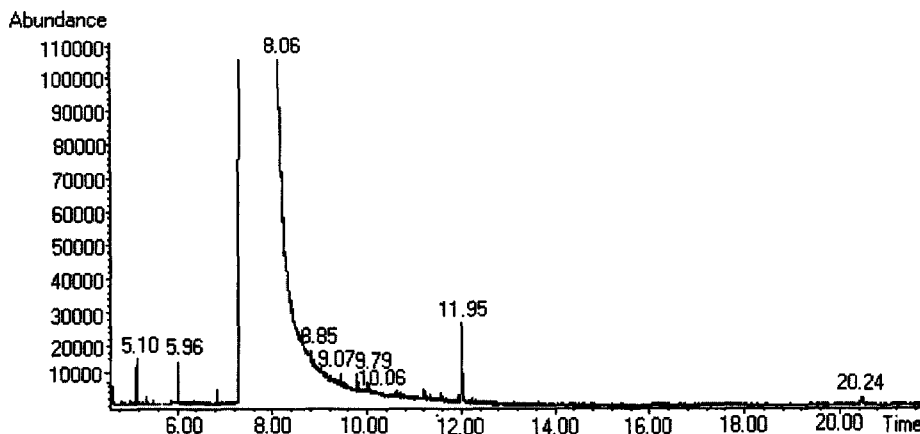
Fig. 5. Total ion current chromatography of impurities in a 30% caprolactam aqueous solution after treatment.

treatment were reduced in comparison with others. Peaks 5.10, 5.96, and 11.95 decreased little. Their existence may be undesirable.

4. Evaluation of the treatment cost

The investment required for the installation of a continuous EDI device that can effectively treat a flow rate of 62 m^3/h is estimated at around $350,000. The only operational cost is electricity, the consumption of which is estimated to be 10 KW/h ($34,000/y). No chemicals are consumed, and very little maintenance is required.

This can be compared to the Yueyang chemical plant in Hunan, which treats the same flow but uses simple ion exchange. Its costs are currently in the region of $182,000/y, consisting of chemicals, demineralised water, and waste water treatment ($165,500, $10,500, and $6,000, respectively).

5. Conclusions

The results of the tests demonstrate that continuous EDI is a plausible replacement for ion exchange in purification of a 30% caprolactam aqueous solution. From this study it was possible to determine that conductivity of the treated solution remained stable and lower than 10 μS/cm. The reduction of the absorption value was always in excess of 20%, and impurities were lower after EDI treatment.

References

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