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Removal of VOCs from aqueous solutions using pervaporation process

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Abstract

The contamination of groundwater and surface water by Volatile organic compounds (VOCs) is a problem at many industrial sites. VOCs are present in effluents from industries such as petroleum refineries and chemical plants. Acrylonitrile, which is toxic to humans, is one of the VOCs used in large quantities as an important industrial material for production of synthetic polymers; consequently, it is present in many industrial effluents. More stringent requirements for the removal of VOCs from wastewater in recent years have increased the need to develop new technologies for removal of VOCs from dilute streams. Membrane pervaporation is an attractive and potentially cost-competitive alternative to traditional methods for removing low concentration of VOCs from wastewater. In this study, the batch removal of acrylonitrile, as a VOC, from aqueous solutions using pervavoration process under different experimental conditions was investigated. The influences of temperature, initial concentration, permeate pressure, feed flow rate and membrane thickness on the acrylonitrile removal efficiency was investigated. The results of experiments confirmed that pervaporation applied to the separation of organic compound from water and wastewater is very promising method. PDMS membrane showed very good properties in the separation of acrylonitrile, reaching 99.6% removal of that compound.

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Introduction

The contamination of groundwater and surface water by VOCs has become a worldwide environment problem because of the many adverse effects of these pollutants. The level of VOCs allowed in discharged wastewater or drinking water is lowered every few years (Hilmioglu et al., 2010). Acrylonitrile, which is toxic to humans, is one of the VOCs used in large quantities as an important industrial material for production of acrylic fibers, plastics, synthetic rubbers and acrylamide; consequently, it is present in many industrial effluents. Acrylonitrile enters the environment during the manufacture, use, and disposal of acrylonitrile-based products. Adverse effects of acrylonitrile on human health and the environment are well documented (Collins et al., 1989; Xu et al., 2003). The most important physical/chemical properties of acrylonitrile are summarized in Table 1.

Traditional VOC control technologies such as adsorption (Kumar et al., 2008) and biological treatment (Shakerkhatibi et al., 2010) have been studied for the removal of acrylonitrile from aqueous streams. However, these technologies do not always provide a complete and economic solution for some of these wastewater applications.

An alternative technology for the removal of acrylonitrile from aqueous streams is pervaporation process. Pervaporation is a membrane separation process in which a liquid stream containing two or more components is placed in contact with one side of a non-porous polymeric membrane while a vacuum or gas purge is applied to the other side. The components in the liquid stream sorb into the membrane, permeate through the membrane, and evaporate into the vapor phase. The condensed permeate liquid often separate into two phases due to limited solubility of VOCs in water. The organic phase can be treated for reuse, and aqueous phase saturated with VOCs can be recycled to the feed stream for reprocessing.

Pervaporation appears as an energy-sparing process because only part of the mixture is vaporized, which corresponds to the pervaporate fraction. As no solvent is used, pervaporation is seen as a clean process. Compared to conventional VOC control technologies such as air stripping, adsorption and biological treatment, pervaporation offers advantages such as high selectivity, compact and modular design and easy integration with existing processes to form hybrid process.

Materials and methods

Materials

PDMS/PVDF/PP composite membrane with functional layer of polydimethylsiloxane (18 μm thickness) used in the experiments was kindly supplied by GKSS Forschungszentrum (Geesthacht, Germany). Membrane was cut into 15×20 cm pieces and hold in a flat frame membrane module. Acrylonitrile (99.9%) was purchased from Merck Co. Ltd. (Darmstadt, Germany) and deionized laboratory water was used for making aqueous mixtures.

Pervaporation experiments

A schematic diagram of the test unit is shown in Fig.1. The system was operated in batch mode with continuous recirculation of the aqueous phase to the feed tank. A flat frame membrane module with effective area of 138cm^2 was used in cross-flow mode. A peristaltic pump was used to recirculate the feed from the feed tank (2 lit) through the membrane. The temperature of feed stream was controlled by a PID controller. During the experiments the membrane downstream pressure was controlled by a needle valve and a vacuum pump (Busch Inc., Switzerland). A pressure meter calibrated by a vacuum gauge was used to measure the downstream pressure. The condenser system consisted of two traps refrigerated by liquid nitrogen that can be used alternately, allowing the permeate stream to be sampled continuously without interrupting operation of the unit. The feed flowrate was measured by a rotameter. The possibility of recirculating the saturated aqueous condensate to the feed tank was not applied in this work.

Sampling

Sampling of feed and retentate was done carefully to avoid any loss. Samples were collected in a small 10 ml glass vial and capped immediately with a teflon-lined cap to avoid acrylonitrile loss.

The vacuum trap containing the permeate was weighed (after warming to room temperature) to obtain the mass of the permeate, which was typically less than 6 g. The permeate was then dissolved in deionized water in order to fall within the calibration range of the HPLC.

Analytical facilities

Aqueous acrylonitrile concentration was measured by HPLC (Adept, Cecil Instruments, UK) equipped with a reverse-phase C18 Hichrom column (5μm, 4.6×150mm). The mobile phase was 75% acetonitrile and 25% deionized and filtered water. Acrylonitrile concentration was determined using an injection volume of 20 μl at 195 nm wavelength (UV detector) and a mobile phase flow rate of 1 ml/min. For every sample analyzed, two injections were made; the average was taken as the actual response.

In the present study, the effect of feed flow rate (3, 5 and 7 l/min), initial feed concentration (20, 50 and 150 ppm), feed temperature (30, 45 and 60°C), permeate-side pressure (1, 10, 20 and 30 mmHg) and membrane thickness (1, 18μm) on the removal efficiency of acrylonitrile was investigated. The experiments were carried out for 8 h. All experimental conditions were repeated three times and the average values are reported.

Removal efficiency of acrylonitrile was calculated using the following equation:

$$\%\boldsymbol{Removal} = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 is the initial concentration of acrylonitrile, and C_t is the concentration of acrylonitrile at time t.

Results and discussion

Effect of duration time

Effect of duration time on the removal efficiency was investigated in various acrylonitrile feed concentration. As shown in Fig. 2, after 8 h of treatment, the acrylonitrile concentration in the retentate reached 42, 10 and 2.3 ppm for initial concentration of 150, 50 and 20 ppm, respectively. As expected, the removal efficiency of acrylonitrile increased with time. At the beginning, the acrylonitrile flux decreases sharply, because the acrylonitrile concentration in feed is high. As time goes on, the acrylonitrile concentration decreases more slowly. This is because the acrylonitrile concentration in feed decreases, and also the mass transfer resistance in the boundary layer increases.

Table 1. Physical and chemical properties of acrylonitrile (MacKay *et al.*, 2006)

Properties	**Value**
Molecular weight	53.063
Boiling point	77.30 °C
Density at 20 °C	0.8060 g/cm^3
Solubility in Water at 20 °C	73.5 g/lit
Vapor pressure at 20 °C	11694 Pa
Henry's law constant at 25 °C	11.4 atm-m^3/mol

Effect of feed flow rate

The effect of feed flowrate was investigated using the following flows: 3, 5, and 7 l/min. Fig. 3 shows the evolution with time of the concentration of acrylonitrile in the feed tank as a function of flowrate of the aqueous phase, It can be seen that the higher the flowrate the faster the acrylonitrile removal. This fact demonstrate that the mass transfer resistance of the liquid boundary layer has a strong influence on the transport rate of acrylonitrile and minimization of polarization layer reduces liquid film resistance and significantly increases removal efficiency. Similar results have been reported by other authors (Yahaya, 2008) in the separation of aqueous binary mixtures containing volatile organic compounds.

Additionally, It was found that water flux is independent of feed flowrate and the selectivity of the separation process increases with increasing Reynolds number, due to the increase in the flux of acrylonitrile.

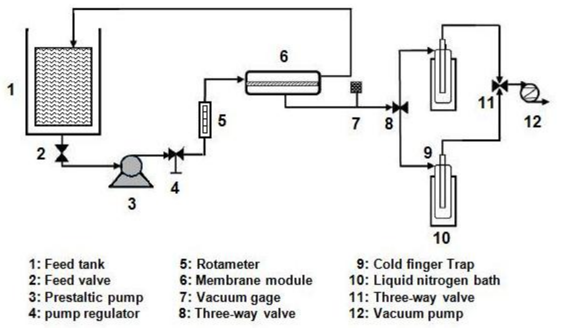

Fig. 1. Schematic diagram of the pervaporation system used in this study.

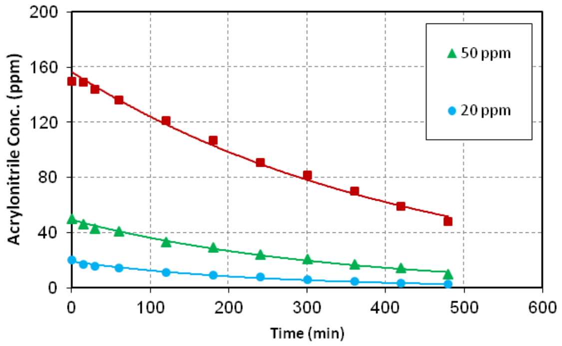

Fig. 2. The effect of duration time on the pervaporation process.

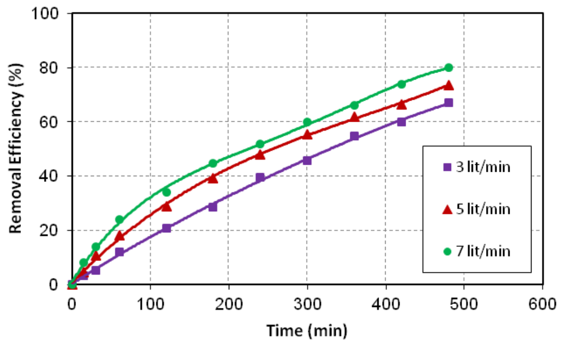

Fig. 3. The effect of feed flowrate on the removal efficiency.

Effect of permeate-side pressure

In this work, the influence of the permeate pressure on the removal efficiency of acrylonitrile in pervaporation system was experimentally analyzed. Fig. 4 depicts the influence of permeate-side pressure on the removal efficiency. The data were obtained from the pervaporation experiment which was carried out at 30°C, feed flowrate of 7 l/min, acrylonitrile feed concentration of 50 ppm and at permeate pressure in the range of 1-30 mmHg.

As shown in Fig. 4, permeate-side pressure is a key factor in permeation rate in the pervaporation process. With an increase in downstream pressure the flux of permeating component normally decreases due to the reduction of effective driving force across the membrane and approaches to zero at component saturation pressure. However, an increase in permeation rate by employing a high vacuum in downstream side is accomplished in expense of high operation cost. Therefore, a general tendency exists in industry, for employment of a moderate vacuum (Ghoreyshi et al., 2008).

As can be seen from Fig. 4, acrylonitrile removal efficiency decreased significantly (from 80% to 39%) with increasing permeate-side pressure from 1 to 30 mmHg.

Effect of feed temperature

The studies of the influence of the operating temperature were performed to see how varying the temperature affects acrylonitrile removal efficiency. The experiments operated at feed flowrate of 7 l/min and permeate pressure of 1 mmHg, acrylonitrile feed concentration of 50 ppm and various temperature ranging from 30 to 60°C.

The influence of temperature on the removal efficiency is shown in Fig. 5. Results showed that acrylonitrile removal efficiency improved significantly (from 80% to 99.6%) with increasing process temperatures from 30 to 60°C. The explanation is that, temperature is a key factor in pervaporation process and affects all of the constituent steps of solute transport as well as the driving force for mass transfer.

Effect of membrane thickness

The experimental data for membrane thickness influence on the removal efficiency is shown in Fig. 6. The experiments were operated at feed flowrate of 7 l/min and permeate pressure of 1mmHg, feed concentration of 50 ppm and at 30°C.

As shown in Fig. 6, acrylonitrile removal efficiency was impacted significantly by changing membrane thickness. Decreasing membrane thickness from 18 to 1 µm, resulted in increasing removal efficiency from 80 to 99.1%.

This is due to the fact that at higher membrane thickness the feed components diffuse through a longer tortuous path to reach the downstream side and thus the resistance towards diffusion increases.

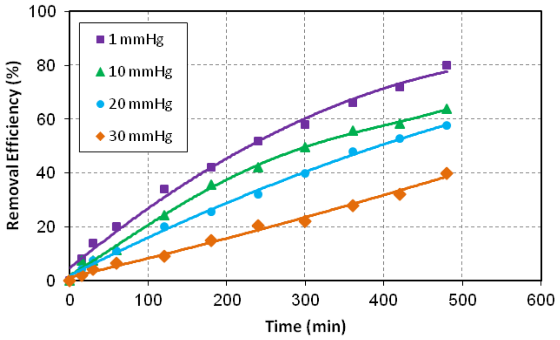

Fig.4. The effect of permeate-side pressure on the removal efficiency.

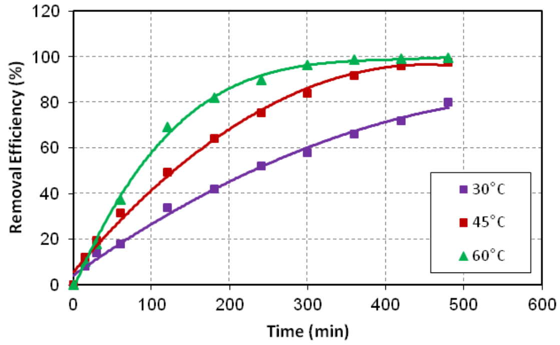

Fig. 5. The effect of feed temperature on the removal efficiency.

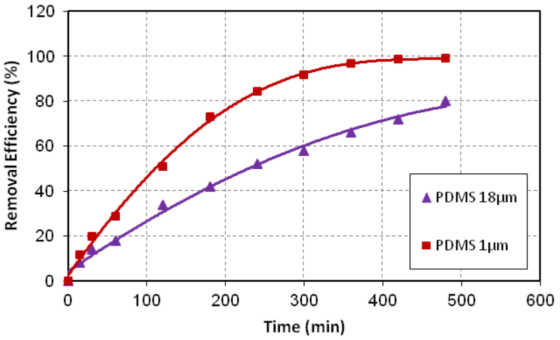

Fig. 6. The effect of membrane thickness on the removal efficiency.

Conclusions

Experimental study was conducted on the pervaporation process for separation of acrylonitrile from aqueous solutions. PDMS membrane showed very good properties in the separation of acrylonitrile, reaching more that 99.6% removal of that compound. Acrylonitrile removal efficiency improved significantly with increasing process temperatures from 30 to 60°C. Moreover, acrylonitrile removal efficiency decreased from 80% to 39% with increasing permeate-side pressure from 1 to 30 mmHg. Results also showed that, the higher the flowrate, the higher removal of acrylonitrile. These results are in agreement with the fact that minimization of polarization layer reduces liquid film resistance and significantly increases removal efficiency. Additionally, acrylonitrile removal efficiency was impacted significantly by changing membrane thickness. Finally, it can be concluded that pervaporation with PDMS membrane offers an interesting prospect for its application to the treatment of wastewater streams containing VOCs such as acrylonitrile.

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