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Pilot-scale integrated membrane system for the treatment of acrylonitrile wastewater

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HIGHLIGHTS

- Acrylonitrile wastewater with high concentration was treated by a novel integrated membrane system (IMS).
- UF, NF and RO were included in IMS; pilot-scale plants of IMS were built and tested for 1600 h.
- Technical and economic analyses of pilot scale-plants were studied and compared with present four-effect evaporation system.
- IMS has a good application in acrylonitrile wastewater treatment instead of four-effect evaporation.

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ABSTRACT

The production of acrylonitrile exceeds 5 million tons every year throughout the world, which leads to the huge emission of acrylonitrile wastewater. Hence, treating the acrylonitrile wastewater remains challenging. In this study, a pilot scale integrated membrane system (IMS) consisting of ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) was proposed to treat the highly concentrated acrylonitrile wastewater from petrochemical plants. A preliminary techno-economic study for a 24 m^3/day wastewater treatment pilot plant was conducted. The system runs smoothly in 1600 h operation. In treating acrylonitrile wastewater with COD 22,000–30,000 mg/L, NH_3-N 14–40 mg/L, CN^- 20–55 mg/L, the effluent water quality of IMS was COD < 3000 mg/L, NH_3-N < 10 mg/L, CN^- < 5 mg/L. The results show that the developed IMS is effective for the treatment of acrylonitrile wastewater and industrialization of IMS is prospective.

1. Introduction

Acrylonitrile is an important material applied in the synthesis of plastics, acrylic fibers, and synthetic rubber. Statistics data from 2005 to 2012 show that production capacities of acrylonitrile have exceeded 5 million tons per year throughout the world. Asia is the main production region which contributes 49.9% of the capacity. To date, acrylonitrile production capacity in China is approximately 1.4 million tons per year [1,2]. Generally, equivalent amount of wastewater containing hazardous materials is generated in producing every ton of acrylonitrile. Considering the stringent regulations on wastewater emission and the crisis in water safety, it is urgent for acrylonitrile enterprises to explore safe and low-cost treatment technology.

There are various types of pollutants in acrylonitrile wastewater such as alkenes, aldehydes, ketones, aromatic compounds, oligomer and cyanogen, which are very stable in environmental degradation. Besides, the great quantity, the complex and variable water quality make the degradation of acrylonitrile wastewater very difficult. Many treatment methods of acrylonitrile wastewater were investigated, such as supercritical water oxidation [3,4], wet air oxidation [5,6], ozonation [7], radiation [8], biodegradation [9,10], adsorption [11] and combination technology of the above [12–15]. However, most of these methods reported are limited to laboratory research due to their disadvantages, such as expensive investment of instruments, intensive energy consumption or high cost of operation. Furthermore, they are difficult to be industrialized. At present, the mainly used acrylonitrile wastewater treatment method in China is four-effect evaporation and incineration technology [4,8]. Nevertheless, this method is energy-intensive and operation-complicated.

Membrane technology is effective in separating, purifying and refining various species from complex mixtures. Membrane separation process is efficient, energy saving and easily operated. Specifically, nanofiltration (NF) and reverse osmosis (RO) have been widely used in the treatment of various wastewater, such as papermaking wastewater [16,17], dyeing wastewater [18], food-processing wastewater [19], nuclear wastewater [20], and petrochemical wastewater [21]. However,

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Table 1
Characteristics of acrylonitrile wastewater and treatment target.

Parameters	Value	Target
pH	5.4–5.8	6–8
T (°C)	110–120	<40
COD (mg/L)	22,000–30,000	<3000
NH_3-N (mg/L)	14–40	<40
CN^- (mg/L)	20–55	<5

Table 2
Characteristics of the NF and RO membranes.

Items	NF	RO
Manufacturer	Dow	CSM
Material	PA composite	PA composite
Effective area (m^2)	7.6	7.9
Inflow. max (m^3/h)	3.6	3.6
Operation pressure. max (MPa)	4.1	4.1

severe membrane fouling was observed if NF or RO was separately used. In the meantime, the conglutination of oligomers on membrane surface can accelerate concentration polarization during membrane process, resulting in flux decline and serious membrane fouling. To minimize fouling of NF and RO membranes, pretreatment with filters to remove coarse particles and colloids is needed. Both granular media (e.g., anthracite coal, sand filtration) and membrane filtration pretreatment technologies may offer advantages or face challenges depending on the source water quality and origin. Therefore, selecting the most suitable pretreatment technology for a given project should be based on side-by-side pilot testing. In addition to pretreatment, adjustment of the NF/RO filtration conditions (e.g., operation pressure, internal reflux, membrane cleaning) also results in fouling control. There is limited information in literature using only membranes to treat acrylonitrile wastewater. Besides, NF in combination with RO appears a highly promising technology that of course requires further development and commercialization.

The objectives of this paper are: 1) promoting a novel acrylonitrile treatment technology with an integrated membrane system; 2) elaborating a practical implementation of integrated membrane through a pilot scale plant during 1600 h run; and 3) optimizing the operation conditions of integrated membrane from the process intensification view. An integrated membrane system (IMS) for the treatment of acrylonitrile wastewater is proposed. Highly efficient sand filtration, ultrafiltration (UF), NF and RO are integrated in the system. A pilot plant with 1 m^3/h treatment capacity was designed. The effect of inhibitor on permeate flux was studied. Internal refluxes of NF/RO, operation pressure of RO, NF/RO membrane element were optimized. The techno-economic evaluation was investigated and compared with four-effect evaporation.

2. Experimental

2.1. Acrylonitrile wastewater

Acrylonitrile wastewater was obtained from a petrochemical factory located in Anqing, Anhui Province, China. The characteristics of the acrylonitrile wastewater are listed in Table 1.

Acrylonitrile wastewater is toxic and non-biodegradable because acetonitrile, acrylonitrile, cyanide (HCN) and cyano-oligomer are contained. At present, acrylonitrile wastewater is treated by four-effect evaporation [22] and incineration. The schematic and water balance in four-effect evaporation are presented in Fig. 1. 20 m^3/h of acrylonitrile wastewater is evaporated in four huge evaporators (namely E-510, E-511, E-512, E-513) using steam. The dilute, 11 m^3/h is discharged to wastewater treatment plant (WWTP). The concentrate, 9 m^3/h is sent to incinerators for incineration along with air and fuel oil.

2.2. Integrated membrane system (IMS)

The IMS consists of highly efficient sand filter, UF, NF, and RO. UF membrane is polyether sulfone hollow fiber with MWCO 20,000. NF and RO membranes in this study are commercially available as listed in Table 2. A schematic diagram of this system is shown in Fig. 2. The pilot plant as shown in Fig. 3 was installed in-site.

When the system is online, 1 m^3/h of acrylonitrile wastewater is pumped into the IMS. As the original acrylonitrile wastewater is 120 °C, wastewater was cooled under 40 °C by a heat exchanger and then pumped through sand filter. Sand filter was used to remove mechanical impurities and large solid particles. Backwash of sand filter was usually once every 24 to 48 h and spent (waste) backwash volume is 2% to 5% of the intake wastewater. The use of NF retentate instead of cooling water as backwash allowed reducing operation cost. UF was utilized to remove small particles and colloids. Similarly, the backwash of UF (50–100 L/h) was from NF retentate. UF permeate was fed into NF to remove oligomers and multivalent salts. The resulted permeate from NF unit was then treated by RO membranes. The removal of low molecular weight compounds and CN^- was achieved by RO. Permeate of RO, 0.7–0.72 m^3/h was discharged to WWTP, indicating that 70–72% of the wastewater was recovered by IMS. Retentate of RO, 0.3 m^3/h was recirculated as the inflow of NF. Hence the inflow of NF was 1.3 m^3/h. Concentrate of NF unit, UF retentate and backwash liquid of pretreatment (0.3 m^3/h in total) were fed into an incinerator. Incineration was taken

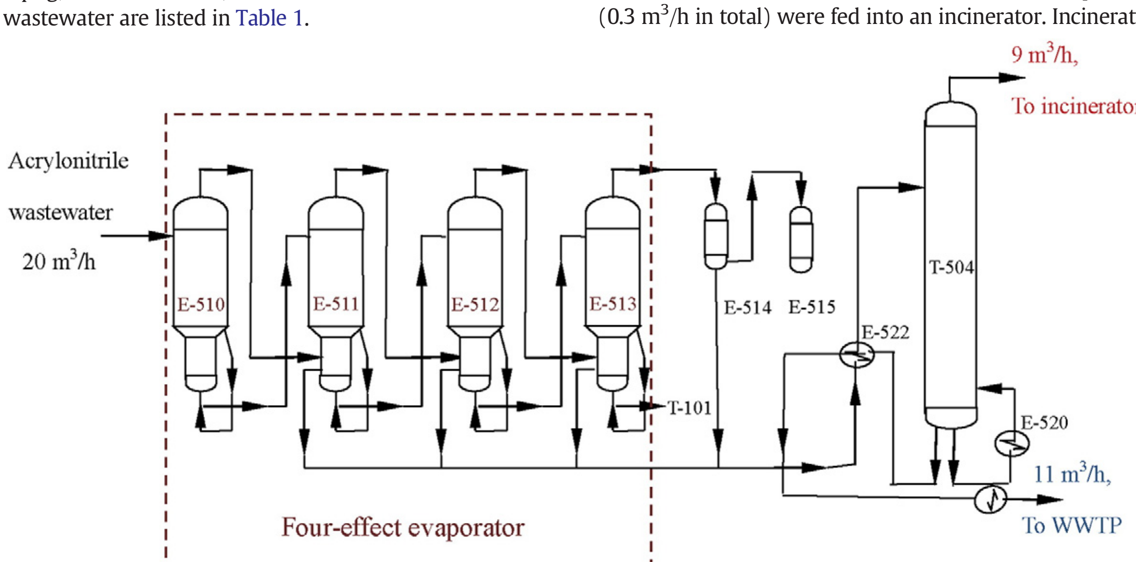

Fig. 1. Schematic of four-effect evaporation and water balance in the system.