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Concentration and treatment of ceric ammonium nitrate wastewater by integrated electrodialysis-vacuum membrane distillation process

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HIGHLIGHTS

- A designed ED/VMD system was used to treat acid cerium wastewater.
- NO_3^- and Ce^{4+} were separated efficiently by ED system.
- More than 99.9% of Ce^{4+} was blocked and concentrated by PVDF VMD system.
- Vapor condensation inside the pores was the main reason caused membrane fouling.

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ABSTRACT

Ceric ammonium nitrate manufacture generated a large number of acidic wastewater, which contained a certain amount of ceric. To treatment this wastewater and recovery the ceric resource and waste acid, an electrodialysis-vacuum membrane distillation (ED-VMD) hybrid system was introduced. To establish a stable and efficient system, a series of membrane materials, performance parameters and solution properties were investigated. It was found that NO_3^- could be separated from Ce^{4+} and recovered efficiently in ED system. pH value of Cerium wastewater decreased in the ED process which ensured a stable and reliable operation of the following concentration technology. The high resistance of Ce^{4+} and high NO_3^- recovery efficiency in ED anode compartment supplied an opportunity for industry waste acid recycling as well. The VMD process provided more than 99.9% rejection of Ce^{4+} and concentrated it maximally. Furthermore, membrane cleaning procedures were discussed in order to keep the high efficiency of VMD system. The results implied that vapor condensation inside the pores was the main reason caused membrane fouling and flux decreasing. And the drying procedure was the most efficient cleaning method. This work provided a potential treatment process for rare earth metals wastewater treatment, which decreased the wastewater discharge and recycled the resource in some field.

1. Introduction

Global demand for rare earth metals (REMs) is increasing dramatically in recent years and prices of REMs are increasing accordingly. Cerium, as the most plentiful element in the family of REMs or lanthanide elements find several applications in areas such as chemical engineering, luminescence, agriculture, catalysis, nuclear energy, metallurgy microelectronics [1]. Ceric ammonium nitrate is one of the most widely used cerium products, which was considered as catalyst, oxidant and initiator of polymerization reactions [2,3]. While during the production of ceric ammonium nitrate, a large amount of nitrate acid was consumed and waste acid was generated simultaneously. Although acid recycle technology was generalized, the discharge of waste acid with cerium was inevitable. As a valuable and toxic metal, recycling and reusing cerium seem to be an imperative work. Thus, the separated collection and treatment of ceric wastewater has attracted more attention. Although a concentration and reclamation method for ceric wastewater is necessary, little work has been reported. The concentration process should have the properties of high stability, high efficiency, low energy consumption and easy operation [4].

Membrane technology is an emerging technology that presents a superiority for concentration. Membrane Distillation (MD) process consists in a thermal process in which only vapor molecules pass through a porous hydrophobic membrane. The driving force of the process is the vapor pressure difference through the membrane, which causes the evaporable components penetrate, and nonvolatile

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components retain. MD process emerges a number of advantages that makes it competitive in more applications, such as low operating temperature and hydraulic pressure, low sensitivity to salt concentration, a small footprint, a near 99.9% rejection of non-volatile solutes [5], independent performance of high osmotic pressure or concentration polarization [6,7], and potentially low maintenance requirement [8]. Furthermore, as a thermal driving process, 90% of the total energy consumption of the MD system utilized for heating the feed solution [9]. As a result, using free heating resource such as waste heat, solar or geothermal energy can reduce the total energy consumption remarkably [10,11]. Four major MD patterns have been well developed, the direct contact MD (DCMD), the vacuum MD (VMD), the air gap MD (AGMD) and the sweeping gas MD (SGMD). Although most of the studies focused on DCMD system due to the simplicity of configuration design and the possibility of internal heat recovery, the VMD process with higher permeate flux and less conductive heat loss was more attractive in desalination and some coupled processes [12–14]. VMD process has been successfully used for radioactive wastewater separation [15], urine treatment [16], brine water treatment [17], in which nearly 99% rejection of pollutants was achieved. Although some advantages of MD process were impressive, wetting phenomenon was a non-negligible problem of hydrophobic membrane materials. It has been evidenced that liquid intrusion was a factor in causing membrane wetting [18]. In the case of treatment of titanium white sulfuric acid by MD technique, the $FeSO_4$ and cubic NaCl crystallization caused membrane wetting was observed [18]. A positive correlation between wetting and crystallization has been reported by many researches as well [19,20]. Considering the precipitation of ceric ammonium nitrate in concentrated nitrate acid, and the damage of concentrated acid on membrane materials, a former acid separation technic was suggested to introduce to avoid membrane wetting caused by salt crystallization.

Electrodialysis (ED) technology is an important technique for separation or recovery of the pure compound form different contaminated wastewater. It has been widely used for separation of acid and metal elements [21]. In ED process, an alternate installation of the anion exchange membranes (AEMs) and cation exchange membranes (CEMs) allows the relevant ions able to cross the CEM and to be stopped by the AEM and vice versa. Thus, ED technology was employed in the reclamation of the acid-containing aqueous solution for the water purification and acid concentration [22]. Particularly, the improvements in membrane materials, such as the proton selective AEM and the monovalent selective CEM, promoted the application prospect of ED for the reclamation of waste acid. Monovalent selective AEM was used to separate chloride and nitrate ions from paper, pulp industry wastewater and drinking water [23]. Selvaraj et al. have given a view to separate sodium formate form industry wastewater by using mono selective electrodialysis [24]. ED process was also applied to recovery free acid from stainless steel pickling baths successfully [25]. Chekioua et al. [26] used ED system to remove the iron ions from sulfuric acid pickling bath. The iron ions can be effectively separated and the purification rate achieved to 70.17% maximally.

The current work aims to treat the acidic rare earth element wastewater, recycling Ce^{4+}, HNO_3 and water. In this novel hybrid membrane system employing ED technology for acid separation and recovery, while the VMD process for cerium concentration and water purification. The investigation was performed, to begin with by analyzing the cerium separation rate from nitrate acid in ED process. Considering the formation of anionic complex of cerium in the system, two monovalent selectivity AEMs were chosen to compare with one traditional AEM for nitrate separation. The nitrate recovery rate, cerium retention rate and water flux were examined in ED and VMD processes. Finally, the implications and feasibility of the proposed separation and concentration system were evaluated and discussed. In the ED system, high Ce^{4+} separation efficiency resulted the reuse of HNO_3 in the production process. In the VMD system, Ce^{4+} can be concentrated furthest to avail recycling, and the tremendous rejection of Ce^{4+} promoted the reuse of permeate in interior industry as cooling water.

2. Materials and methods

2.1. Reagents and materials

All chemicals used were analytical grade and without further purification. Ceric ammonium nitrate (99%) and HNO_3 (65–68%) were purchased from Aladdin reagents company (Shanghai, China). All the solutions were made up by ultrapure water (18.2 MΩ·cm).

Three types of AEMs were chosen for ED process, those were CJMA-3 AEM from University of Science and Technology of China (a commercial normal anion exchange membrane), ASV monovalent AEM from ASAHI GLASS CO., Ltd., Japan (commercial), and QPPO monovalent AEM from Zhejiang University of Technology, China (newly developed). Two PVDF hollow fiber membrane modules were produced by Dehong CO., Ltd., China (a commercial membrane module, named DH membrane, pore size of 0.2 μm, pore porosity of 85% and contact angle of 95.8°) and Tianjin University of Technology (newly developed, named TJ membrane, pore size of 0.16 μm, pore porosity of 85% and contact angle of 97.6°) for VMD process respectively. The characteristics of AEMs and VMD membrane modules were shown in Table 1.

2.2. Experiment apparatus

A laboratory scale ED-VMD system was developed to treatment ceric ammonium nitrate wastewater (Fig. 1). The system comprised an ED separation system and VMD concentration system. The ED unit was constructed by 2-cm-thick acrylic resin. The effective volume for each reaction cell was 32 cm^3 (4 cm × 4 cm × 2 cm). The cathode and anode compartments were separated by an AEM. Titanium ruthenium plating iridium electrodes with the effective surface area covered 16 cm^2 (4 cm × 4 cm) were used as the cathode and anode. A variable current supply (0–30 V) was used to generate a constant direct current. Electrodes, pumps and power supply were purchased from China.

The experiments were carried out on synthetic water, which only contained ceric ammonium nitrate and nitrate acid. The feed solution was 300 mL contained 0.2 $mmol{\cdot}L^{-1}$ Ce^{4+} and HNO_3, and was pumped to cathode compartment. A 300 mL portion of 0.01 $mmol{\cdot}L^{-1}$ HNO_3 was used as electrode solution, and was pumped to anode compartment. The flow rate for different cells was the same. The applied current densities were 125 and 62.5 $mA{\cdot}cm^{-2}$ (0.2 A and 0.1 A respectively) and were kept constant during the entire experiment.

The cross-flow hollow fiber VMD experiments were carried out. During the operation, the feed solution was heated firstly and bumped

Table 1
(a) 2 Main characteristics of AEMs used in the experiments. (b) Main characteristics of VMD membranes used in the experiments.

(a)

Membrane type	Thickness (μm)	Ion exchange capacity ($mmol{\cdot}g^{-1}$)	Area resistance ($\Omega\,cm^2$)	pH
ASV	120	–	3.7	0–10
QPPO [53]	–	1.26	4.63	–
CJMA-3	130	0.9	2	0–12

(b)

Membrane type	Material	Membrane number	Module length/cm	Inner diameter/mm	Wall thickness/mm
TJ membrane	PVDF	50	23	0.8	0.15
DH membrane	PVDF	50	11	0.7	0.15