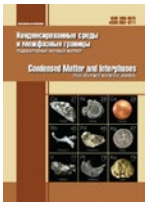

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Low-reagent selective extraction of ammonia nitrogen from wastewater: optimization of the current mode of bipolar electrodialysis coupled with a liquid-liquid membrane contactor

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Abstract

Objectives: Liquid-liquid membrane contactors (LLMC) with gas-permeable membranes are promising systems for the single-stage selective removal of ammonia nitrogen from multicomponent wastewater. A drawback of these systems is the need to dose concentrated solutions of acid and alkali to maintain the desired pH in the LLMC streams. The use of bipolar electrodialysis (BMED) reduces the amount of reagents. The aim of this article is to demonstrate the feasibility of effectively using bipolar electrodialysis in a combined LLMC + BMED process at current densities significantly lower than those currently used.

Experimental: The studies were conducted using a dual-loop laboratory LLMC containing hydrophobic hollow fiber gas permeable membranes made of polysulfone and a laboratory BMED with a two-compartment unit cell consisting of alternating Ralex CMH PES cation-exchange membranes and TWEDBp-1 or Neosepta Bp-1 bipolar membranes. The simulated wastewater with pH of 9.3±0.1 contained NH_4^+, K^+, Cl^-, OH^- ions, and NH_3 molecules. The stripping solution with pH of 3.0±0.1 contained HCl.

Conclusions: It is shown that the use of TWEDBp-1 or Neosepta Bp-1 bipolar membranes for reagent-free generation of H^+ and OH^- ions eliminates the need for alkali dosing in the LLMC feed solution. This result is achieved at an optimal current density of 2 mA cm^{-2}. Under the experimental conditions, this current density is 1.5 times (TWEDBp-1) and 2.0 times (Neosepta Bp-1) higher than the critical current density, which corresponds to the onset of intense H^+ and OH^- ion generation by the studied bipolar membranes.

Keywords: Ammonia nitrogen, Wastewater, Liquid-liquid membrane contactor, Electrodialysis, Bipolar membrane

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Краткие сообщения

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Научная специальность ВАК – 1.4.6. Электрохимия; 1.4.4. – Физическая химия

Малореагентное селективное извлечение аммиачного азота из сточных вод: оптимизация токового режима биполярного электродиализа, сопряженного с жидкостно-жидкостным мембранным контактором

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Аннотация

Цель статьи: Жидкостно-жидкостные мембранные контакторы (ЖЖМК) с газопроницаемыми мембранами являются перспективными системами для одностадийного селективного извлечения аммиачного азота из многокомпонентных сточных вод. Недостаток этих систем состоит в дозировании концентрированных растворов кислоты и щелочи для поддержания заданных значений pH в контурах ЖЖМК. Снизить применение реагентов можно, комбинируя ЖЖМК с биполярным электродиализом (БМЭД). Цель статьи – продемонстрировать возможность эффективного применения биполярного электродиализа в комбинированном ЖЖМК + БМЭД процессе при плотностях тока значительно меньше тех, которые используются в настоящее время.

Экспериментальная часть: Исследования выполнены с использованием двухконтурного лабораторного ЖЖМК, который содержал гидрофобные половолоконные газоразделительные мембраны из полисульфона, и лабораторного БМЭД с двухкамерной элементарной ячейкой, состоящей из чередующихся катионообменных мембран Ralex CMH PES и биполярных мембран TWEDBp-1 или Neosepta Bp-1. Имитат сточной воды содержал ионы NH_4^+, K^+, Cl^-, OH^- и молекулы NH_3 и имел pH 9.3±0.1. Принимающий раствор содержал HCl и имел pH 3.0±0.1.

Выводы: Показано, что применение биполярных мембран TWEDBp-1 или Neosepta Bp-1 для безреагентной генерации ионов H^+, OH^- позволяет обойтись без дозирования щелочи в питающий раствор ЖЖМК. Этот результат достигается при оптимальной плотности тока в 2 мА $см^{-2}$. В условиях проведения экспериментов она в 1.5 раза (TWEDBp-1) и 2.0 раза (Neosepta Bp-1) превышает критическую плотность тока, которая соответствует началу интенсивной генерации ионов H^+, OH^- исследованными биполярными мембранами.

Ключевые слова: аммиачный азот, сточные воды, жидкостно-жидкостный мембранный контактор, электродиализ, биполярная мембрана

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1. Introduction

Ammonia nitrogen is found in municipal wastewater, livestock effluents, and nitrogen fertilizer production. Entering the hydrosphere, it causes the eutrophication of water bodies, leading to ecosystem degradation [1]. In recent years, there has been a clear trend not only to neutralize ammonia nitrogen in wastewater but also to extract it as pure salts using liquid-liquid membrane contactors (LLMCs) [2, 3]. Typically, LLMCs contain a bundle of hydrophobic, gas-permeable hollow fiber membranes (HFMs) [4]. An ammonium-containing feed solution with a pH>8 flows over their shell surface. A stripping acid solution with a pH ⩽ 3 is pumped through the lumen of the HFMs [5]. In an alkaline feed solution, some of the NH_4^+ cations are converted to NH_3, which is transferred through the HFMs

to the stripping solution. There, it reacts with a proton and again becomes an NH_4^+ cation. The dense skin layer on the shell surface of the HFM is impermeable to hydrated ions, ensuring the production of pure ammonium salt in the stripping solution [5]. Dosing concentrated acid and alkali allows maintaining specified pH values in the stripping and feed solutions, respectively [6]. Alkali dosing can be eliminated by compensating for the consumed hydroxyl ions in the feed solution with OH^- ions generated by a bipolar membrane [7] (Fig. 1). For these purposes, electrodialyzers with a two-compartment unit cell formed by alternating cation-exchange and bipolar membranes (BMED) are most often used [7]. However, the current densities applied to generate H^+ and OH^- ions exceed 10 mA cm^{-2} [7], resulting in high energy consumption, calling into question the environmental and economic feasibility of the low-reagent process (LLMC + BMED) compared to the reagent one (LLMC).

The aim of this study is to demonstrate the feasibility of effectively using bipolar electrodialysis in a combined LLMC + BMED process at current densities significantly lower than those currently used.

2. Materials and methods

The laboratory-scale LLMC contained a bundle of polysulfone HFMs produced by Nova Service Company LLC, Krasnodar, Russia. The total shell surface area of the HFMs was 168±1 cm^2. The average linear flow velocities of the feed and stripping solutions were 0.4 and 1.3 cm s^{-1}, respectively. Before the process, the feed solution with a volume of 250±1 cm^3, simulating the wastewater composition, contained 410±1 mM NH_4Cl and KOH in an amount required to achieve pH 9.3±0.1; the stripping solution with a volume of 100±1 cm^3 contained 10 mM HCl and had a pH of 3.0±0.1. In the case of the reagent process, a KOH solution with a concentration of 1000±1 mM was continuously dosed into the feed solution. In the case of a low-reagent process, the feed solution after the LLMC was pumped (0.4 cm s^{-1}) through the alkaline chamber of the BMED (1) and again fed into the LLMC (Fig. 1). A 410±1 mM KCl solution was circulated through the acid chamber of the BMED (2). The 40±1 mM acid solution was added to the stripping solution of the LLMC identically in both processes. Each experiment lasted 5 hours. A detailed description of the experimental setup and the data processing methodology are given in [8].

The current-voltage curves of the bipolar membranes were obtained under conditions identical to those specified in the combined LLMC + BMED process.

The current-voltage curves were recorded in the potentiodynamic mode at a linear current-density sweep rate of $2.5 \cdot 10^{-3}$ mA cm^{-2} s^{-1} using a Keithley 2400 SourceMeter (Keithley Instruments, USA). The concentration of ammonium ions in the feed and stripping solutions was determined spectrophotometrically using Nessler's reagent with a UV-1800 spectrophotometer (ECOVIEW, Russia); pH was monitored using an Expert-001

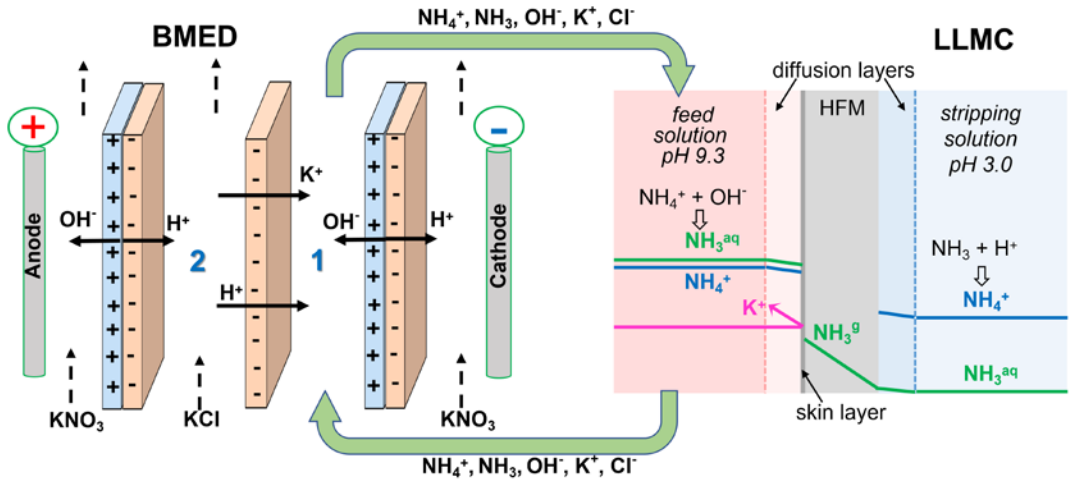

Fig. 1. Schematic diagram of the coupled membrane unit. Explanations are in the text

pH meter (Russia) equipped with a combined glass electrode.

The laboratory electrodialyzer BMED contained a Ralex CMH PES cation-exchange membrane (MEGA, Czech Republic) and Neosepta Bp-1 (Astom, Japan) or TWEDBp-1 (Shandong Tianwei Membrane Technology Co., Ltd., China) bipolar membranes. The membrane polarized area was 4.0±0.1 cm^2, and the intermembrane distance was 0.66±0.01 cm. All experiments were performed at least three times.

3. Results and discussion

Fig. 2 shows the current-voltage curves of the bipolar membranes and the amount of ammonia nitrogen ($n^{NH_4^+)}$) extracted from the feed solution and accumulated in the stripping solution vs the current density (i) in the BMED. Neosepta Bp-1 and TWEDBp-1 membranes are characterized by close values of critical current densities, i_{cr} (1.0 and 1.3 mA·cm^{-2}, respectively), starting from which the process of generation of H^+, OH^- ions at the bipolar boundary and their transfer through the cation- and anion-exchange layers becomes dominant [9] in the studied bipolar membranes. Operation of the BMED at current densities above i_{cr} makes it possible to maintain the pH of the feed solution at the inlet to the LLMC at a level of 9.2±0.3 and to extract from it ammonia nitrogen, the amount of which is comparable to that extracted using the reagent process. The closest values of $n^{NH_4^+)}$ for the LLMC and LLMC+BMED processes are achieved at a current density of 2 mA cm^{-2}, which is 2 times (Neosepta Bp-1) and 1.5 times (TWEDBp-1) higher than the i_{cr} values. Increasing the current density in the BMED leads to a decrease in the mass transfer characteristics of the LLMC+BMED process and is accompanied by an increase in energy consumption for the reagent-free generation of H^+ and OH^- ions by bipolar membranes. Apparently, an increase in current density causes an enhancement of the proton flux from the acidic chamber of the BMED. These are transferred through the Ralex CMH PES membrane into the alkaline chamber and recombine with the generated OH^- ions, reducing the pH of the feed solution.

4. Conclusion

The use of electrodialysis with bipolar membranes is an effective way to reduce reagent consumption for the selective recovery of ammonia nitrogen from wastewater. The transition from dosing concentrated alkali to its reagent-free generation via Neosepta Bp-1 and TWEDBp-1 bipolar membranes is feasible at a relatively low current density (2 mA cm^{-2}). This operating current density exceeds the critical current density of these membranes (1.0 and 1.3 mA cm^{-2}, respectively) by a factor of only 1.5–2.0, whereas previously reported studies utilized current

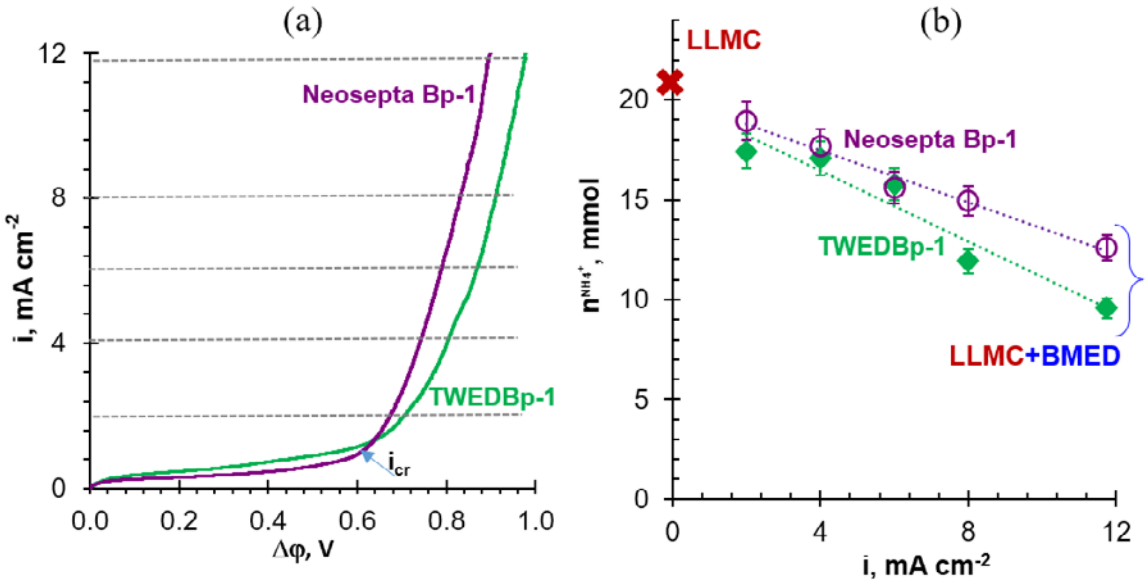

Fig. 2. Current-voltage curves of bipolar membranes (a) and the amount of ammonia nitrogen extracted from the feed solution and accumulated in the stripping solution vs the current density in the BMED (b). The dotted lines (a) correspond to the current densities during the implementation of the LLMC + BMED process (b)

densities exceeding 10 mA cm^{-2} for the same purpose. Furthermore, the amount of ammonium nitrogen recovered using the low-reagent hybrid membrane process is comparable to that achieved in the conventional reagent-assisted process.

At $i \leqslant 6$ mA cm^{-2}, both bipolar membranes yield similar pH values in the feed solution, thereby facilitating the recovery of equivalent amounts of NH_3. Conversely, at $i > 6$ mA cm^{-2}, the use of TWEDBp-1 results in feed solution pH values that are 0.30±0.05 units lower, leading to a reduction in the efficiency of the low-reagent process compared to the configuration utilizing Neosepta Bp-1. Further optimization of the BMED module operating conditions requires an investigation into the coupled process of H^+ and OH^- ion generation by bipolar membranes and competitive proton transport across cation-exchange membranes [6, 10].

Authors' declared contributions

K. V. Brizhan – experimental studies, writing of the original draft. V. V. Sarapulova – systematization of the material, scientific editing of the manuscript. V. V. Gulyaeva – experimental studies, processing of experimental data. N. D. Pismenskaya – research conceptualization, final conclusions.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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