

Electrocatalytic reduction of nitrate using Pd-Cu modified carbon nanotube membranes

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HIGHLIGHTS

- Pd-Cu modified CNT membranes were prepared successfully by electrodeposition method.
- The deposition voltage and deposition time were optimized for Pd-Cu co-deposition.
- NO_3^- -N was removed efficiently from water by Pd-Cu modified CNT membranes.
- The presence of dissolved oxygen did not affect the nitrate reduction performance.
- Mass transfer rate was promoted significantly with the increase in membrane flux.

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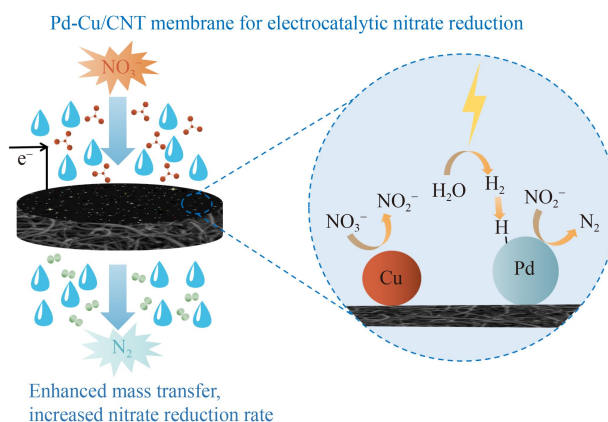
Nitrate reduction

Flow-through

Electrodeposition

Electrocatalytic reduction

GRAPHIC ABSTRACT



ABSTRACT

Excessive nitrate in water is harmful to the ecological environment and human health. Electrocatalytic reduction is a promising technology for nitrate removal. Herein, a Pd-Cu modified carbon nanotube membrane was fabricated with an electrodeposition method and used to reduce nitrate in a flow-through electrochemical reactor. The optimal potential and duration for codeposition of Pd and Cu were -0.7 V and 5 min, respectively, according to linear scan voltammetry results. The membrane obtained with a Pd:Cu ratio of 1:1 exhibited a relatively high nitrate removal efficiency and N_2 selectivity. Nitrate was almost completely reduced ($\sim 99\%$) by the membrane at potentials lower than -1.2 V. However, -0.8 V was the optimal potential for nitrate reduction in terms of both nitrate removal efficiency and product selectivity. The nitrate removal efficiency was 56.2% , and the N_2 selectivity was 23.8% for the Pd:Cu=1:1 membrane operated at -0.8 V. Nitrate removal was enhanced under acidic conditions, while N_2 selectivity was decreased. The concentrations of Cl^- ions and dissolved oxygen showed little effect on nitrate reduction. The mass transfer rate constant was greatly improved by 6.6 times from 1.14×10^{-3} m/h at a membrane flux of $1 \text{ L}/(\text{m}^2 \cdot \text{h})$ to 8.71×10^{-3} m/h at a membrane flux of $15 \text{ L}/(\text{m}^2 \cdot \text{h})$, which resulted in a significant increase in the nitrate removal rate from 13.6 to $133.5 \text{ mg}/(\text{m}^2 \cdot \text{h})$. These findings show that the Pd-Cu modified CNT membrane is an efficient material for nitrate reduction.

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1 Introduction

Nitrate pollution in water has attracted increasing

attention due to the discharge of industrial wastewater and the overuse of farmland fertilizers (Abascal et al., 2022). Excessive nitrate in water has a great impact on the productivity and lives of humans, as with eutrophication and “blue baby syndrome”, and increases the risk of cancer (Liu et al., 2022). Therefore, efficient removal of nitrate is a significant need and challenge.

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Several techniques have been used to eliminate nitrate from water, including reverse osmosis filtration (Lejarazu-Larrañaga et al., 2022), chemical reduction (Liu and Wang, 2019), biological denitrification (Fan et al., 2022; Li et al., 2022), and electrocatalytic reduction (Su et al., 2020). Among them, biological denitrification is technologically mature, cost-effective, and widely used (Xu et al., 2021; Luo et al., 2022). However, biological processes are often sluggish and easily affected by variable environmental conditions, such as temperature and the availability of carbon supplies (Saha et al., 2022). Limits on carbon supplies often prevent full implementation of denitrification, so the concentrations of nitrate in secondary effluents exceed the discharge standard (Tang et al., 2021; Zhou et al., 2022). Compared with biological denitrification, electrocatalytic technology is a promising method for nitrate removal because no chemicals are needed, no sludge is produced, and implementation of the methodology is convenient.

Great effort has been expended in providing catalysts with high activity and selectivity toward nitrate reduction. The catalysts commonly used for nitrate reduction include monometallic catalysts such as Cu, Fe, and Ni and bimetallic catalysts such as Cu-Sn, Cu-Ni, and Pd-Cu (Duan et al., 2019). Among these materials, Pd-Cu bimetallic catalysts exhibit appreciable activity for nitrate reduction (Ma et al., 2022). In the Pd-Cu bimetal system, Cu functions as the promoter metal that provides active sites for transformation of NO_3^- to NO_2^- , which is the rate-limiting step in nitrate reduction, and Pd functions as the catalyst for the further transformation of NO_2^- to N_2 or NH_4^+ (Martínez et al., 2017; Sanchis et al., 2022).

However, mass transfer still provides challenges in the field of electrocatalytic nitrate reduction. Electrocatalytic reduction of nitrate requires initial adsorption of nitrate onto the cathode surface, which can be inhibited by ions coadsorbed from the solution (García-Segura et al., 2018). In addition, most of the electrodes currently used are conventional plate cathodes implemented in parallel plate reactors, in which mass transfer is strongly limited. Consequently, the overall electrocatalytic nitrate reduction rate decreases (Trellu et al., 2018). It has been shown that using porous electrodes in a flow-through configuration can significantly alleviate mass transfer limitations (Li et al., 2021). Recent studies have demonstrated that reactive electrochemical membranes (REMs) constitute a breakthrough technology for nitrate reduction during water treatment (Gao and Vecitis, 2012). By combining the membrane filtration process with electrocatalytic reactions, the limits of mass transfer on the electrode surface can be overcome (Jiang et al., 2018). Novel REM materials such as MXene (Li et al., 2021) and Pd-modified Magnéli phase TiO_2 (Gayen et al., 2018) were previously reported for nitrate reduction, but the synthetic processes for these proposed materials are complicated. Acid/alkaline solutions and organic solvents

are commonly used, and a fabrication temperature as high as 1000 °C is sometimes needed, which increases the preparation cost and hinders practical application of REMs. Instead of complex membrane fabrication processes, there is a great need for development of nitrate-reducing REMs by a simpler and more reliable method using easily accessible materials. Carbon nanotube (CNT) conductive membranes are prospective materials that have been demonstrated to be excellent supports for electrochemical catalysts due to their ultrahigh mechanical strengths, excellent electrical properties, large specific surface areas, and high aspect ratios (Huang et al., 2009; Li et al., 2013). CNT membranes doped with catalysts were previously used as anodes for organic oxidations, and mass transfer was effectively enhanced during filtration (Gao and Vecitis, 2012).

In this study, a novel Pd-Cu modified CNT membrane cathode was fabricated on a polyvinylidene difluoride (PVDF) substrate and used to overcome mass transfer issues during nitrate reduction. The electrodeposition method was applied to dope Pd-Cu bimetallic particles onto the CNT fibers. The optimum conditions for Pd-Cu codeposition were determined based on linear scan voltammetry (LSV) tests. The effects of the Pd-Cu molar ratio and electrode potential on nitrate removal were explored. The influence of solution conditions, such as the presence of chloride, solution pH, and dissolved oxygen (DO), were also investigated. To illustrate the effect of flow-through operation on mass transfer, the performance for nitrate reduction was evaluated, and mass transfer rate constants were calculated for different membrane fluxes.

2 Materials and methods

2.1 Fabrication of Pd-Cu modified CNT membranes

The Pd-Cu modified CNT membranes were prepared by the following steps. First, CNT membranes were prepared by a positive pressure filtration method with a PVDF microfiltration membrane (0.22 μm , MV020T, Deliyuan, China), which was kept in a 25 % isopropanol solution before use as the substrate. Multiwalled carbon nanotubes (MWCNTs, 10–20 nm in diameter and 10–30 μm in length, XFNANO, China) were evenly dispersed in deionized (DI) water with an ultrasound cell disruption apparatus (Scientz-IIID, Scientz, China), and 5.0 mg/L dodecylbenzenesulfonic acid (DDBS) was used as the surfactant. The dispersed MWCNTs with a concentration of 0.5 g/L were preserved in a volumetric flask for use. Then, different volumes of the MWCNT suspension were filtered onto the PVDF membrane to form a conductive layer at 1.5 bar, followed by immediate filtering with an equal volume of DI water to wash the surfactant off. After

that, the PVDF-supported CNT membrane was dried in an oven at 80 °C for 2 h. The water permeabilities and sheet resistances with different CNT dosages were tested (Fig. S1). For economic reasons, a CNT dosage of 0.8 mg/cm² was chosen in the following experiments.

The Pd-Cu bimetallic catalysts were loaded onto PVDF-supported CNT membranes by the electrodeposition method (Zhang et al., 2014). The electrodeposition experiment was performed in a dead-end filtration cell with an effective membrane area of 16 cm² (4.5 cm in diameter). The CNT membrane was precisely installed into the dead-end cell, while a Pt plate (0.5 cm × 0.5 cm) and a saturated calomel electrode (SCE, 242 mV vs. standard hydrogen electrode; Leici, China) were also inserted into the cell. For Pd-Cu deposition, the membrane potential was controlled by a potentiostat (DJS-292B, Xinrui Instruments, China) with the CNT membrane as the working electrode, the Pt plate as the counter electrode and the SCE as the reference electrode. During electrodeposition, a constant flux of 50 L/(m²·h) was produced by a digital pump (YZ1515x, Longer Pump, China) to promote Pd-Cu deposition. All potentials in this study were referenced to the SCE electrode. Potentiostatic depositions of Pd-Cu bimetallic catalysts were performed at −0.7 V with a 0.5 mol/L NaCl solution containing x mmol/L PdCl₂ (99.0 %, Picasso.com, China) and (10− x) mmol/L Cu(NO₃)₂·3H₂O (99.0 %, Maclin, China), where x = 0, 2.5, 5, 7.5 or 10. The resulting samples were denoted Pd:Cu = x :(10− x). For example, Pd:Cu=1:3 was a Pd-Cu modified CNT membrane fabricated in a deposition bath containing 2.5 mmol/L PdCl₂ and 7.5 mmol/L Cu(NO₃)₂·3H₂O. The sample obtained with 10 mmol/L PdCl₂ was denoted Pd = 10, and that with 10 mmol/L Cu(NO₃)₂·3H₂O was denoted Cu = 10. Further, the durations for electrodeposition (0, 5, 7.5 and 10 min) were evaluated to determine the optimal deposition conditions.

2.2 Electrocatalytic reduction of nitrate by Pd-Cu modified CNT membranes

The electrocatalytic nitrate reduction experiments were performed in a three-electrode filtration cell with an effective solution volume of 250 mL (Fig. S2). A single filtration form was used in the experiments. Electrocatalytic nitrate reduction was conducted with the Pd-Cu modified CNT membrane as the cathode, a 0.5 cm × 0.5 cm Pt plate as the anode and an SCE as the reference electrode. The Pd-Cu modified CNT membrane was installed in a membrane module, and the membrane module was inserted into the reactor. The effective area of the prepared Pd-Cu modified CNT membranes for nitrate reduction was 7 cm² (3.0 cm in diameter), and the distance between the Pt anode and the membrane cathode was set as 1 cm. Electrocatalytic nitrate reduction was performed in flow-through mode by continuously pumping the solution out of the reactor through the

membrane module. Fresh feed solution containing nitrate was added into the reactor with another pump providing the same flow rate as the membrane effluent. The feed solution contained 50 mmol/L Na₂SO₄, 20 mg/L NO₃[−]-N and 200 mg/L NaHCO₃, with an initial pH of approximately 8. The nitrate concentration of this feed solution is typical of the secondary effluent from municipal wastewater treatment plants. The solution was purged with Ar gas at a flow rate of 30 mL/min to achieve oxygen-free conditions during the experiment.

To determine the optimal potential for electrocatalytic nitrate reduction in flow-through mode, nitrate reduction was conducted with Pd-Cu modified CNT membranes with different potentials ranging from −2.0 to −0.4 V and a constant membrane flux of 10 L/(m²·h). To determine the effect of solution pH, the nitrate reduction performance was examined for solution pH values of 4, 8 and 12. The pH was adjusted with 1 mol/L HCl and 1 mol/L NaOH. The effect of Cl[−] was determined by adding NaCl into the feed solution, and Cl[−] concentrations of 0, 0.5, 1.0 and 1.5 g/L were tested. The effect of DO was investigated by comparing nitrate reduction reactions with and without Ar purging. The DO of the feed solution without Ar purging was determined to be 7.5 mg/L. To further illustrate the effect of mass transfer, nitrate reduction experiments were performed with different membrane fluxes ranging from 1 to 15 L/(m²·h).

2.3 Analyses

The morphology of the membrane surface was observed with a scanning electron microscope (SEM, S-3400 N II, Hitachi, Tokyo, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDX) analyzer for elemental analyses.

To identify a suitable potential for Pd and Cu deposition, LSV tests of new CNT membranes in 50 mmol/L NaCl, 50 mmol/L NaCl with 10 mmol/L PdCl₂, and 50 mmol/L NaCl with 10 mmol/L Cu(NO₃)₂·3H₂O were carried out with an electrochemical workstation (CHI 1140C, Shanghai Chenhua, China). The CNT membranes were immersed in the solutions for 20 min to obtain the open circuit potentials, and then the potential was varied from the open circuit potential to −0.9 V with a 10 mV/s scanning rate. To determine the optimum time for Pd-Cu codeposition, LSV tests of Pd:Cu = 1:1 membranes obtained with different electrodeposition times (0, 2.5, 5, 7.5 min) were also conducted. Tests were carried out in a solution containing 50 mmol/L Na₂SO₄ and 50 mg/L NO₃[−]-N by scanning the potential from the open circuit potential to −1.0 V at 10 mV/s. The electrochemical activities of Pd-Cu modified CNT membranes prepared with different Pd:Cu ratios were also characterized by LSV by scanning from the open circuit potential to −1.2 V at 10 mV/s in a solution containing 50 mmol/L Na₂SO₄ and 50 mg/L NO₃[−]-N. All the solutions during LSV tests were continuously purged with Ar gas to

achieve oxygen-free conditions.

The concentrations of NO_3^- , NO_2^- and NH_4^+ were detected with UV-Vis spectroscopy methods (T6 new century, PERSEE, China). DO was measured with a portable DO meter (Hach HQ 30d).

The nitrate removal efficiency, product selectivity, current efficiency and energy consumption were calculated with the following formulas.

The NO_3^- -N removal efficiency was defined as $\frac{C_0 - C_t}{C_0} \times 100\%$, where C_0 and C_t are the influent and effluent concentrations of NO_3^- -N (mol/L), respectively.

The product selectivity (S_i) was calculated with Eq. (1). It is worth noting that this involved an approximate evaluation of the products based on the hypothesis that NO_2^- , N_2 and NH_4^+ were the reaction products.

$$S_i = \frac{C_i}{C_0 - C_t} \times 100\%, \quad (1)$$

where C_i indicates the concentration of NO_2^- , NH_4^+ or N_2 (mol/L).

The NO_3^- -N removal rate in flow-through mode was defined as $J \times (C_0 - C_t)$, where J is the membrane flux ($\text{L}/(\text{m}^2 \cdot \text{h})$).

The mass transfer rate constant (k_t) was calculated according to Eq. (2) (Zhu et al., 2002):

$$\ln \frac{C_0}{C_t} = \frac{k_t \times t \times A}{V}, \quad (2)$$

where C_0 and C_t are the influent and effluent concentrations of NO_3^- -N (mol/L), t is the operating time (s), A is the effective surface area of the membrane electrode (m^2), and V is the volume of filtered electrolyte solution (L; $V = J \times t$).

The current efficiency (CE) was defined as in Eq. (3).

$$CE(\%) = \frac{z \times J \times F \times (C_0 - C_t)}{j} \times 100\%, \quad (3)$$

where z is the moles of electrons transferred per mole of reactant, F is the Faraday constant (96485 C/mol), J is the membrane flux ($\text{L}/(\text{m}^2 \cdot \text{s})$), and j is the current density (A/m^2).

The electrical energy per order (E_{EO}) metric was calculated according to Eq. (4), which provided a measurement of the electric energy (kWh/m^3) needed to reduce the nitrate concentration by 1 order of magnitude.

$$E_{EO} = 10^{-3} \times \frac{U \times I}{Q \times \log \frac{C_0}{C_t}}. \quad (4)$$

3 Results and discussion

3.1 Pd-Cu electrodeposition for Pd-Cu modified CNT membranes

The optimal potential for both Pd and Cu deposition was

determined according to the LSV results for CNT membranes in different solutions (Fig. 1(a)). In 0.5 mol/L NaCl solution, no distinct reduction peak was observed, and the current was relatively low. However, the currents for CNT membranes in solutions containing PdCl_2 or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were much more negative, indicating that reduction reactions occurred on the CNT membrane when Pd^{2+} or Cu^{2+} ions were present in the electrolyte. The LSV curve for the CNT membrane in the solution with PdCl_2 showed a broad reduction peak that ranged from 0.1 to -0.25 V, corresponding to the reduction of Pd^{2+} to Pd (Safavi et al., 2007). In the solution containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, two obvious reduction peaks were observed. The first reduction peak with a peak potential of 0.07 V represented the conversion of Cu^{2+} to Cu^+ (Mattarozzi et al., 2017), and the other peak at -0.33 V represented the conversion of Cu^+ to Cu. Thus, a potential of -0.70 V was selected for codeposition of Pd and Cu on the CNT membranes used in this study.

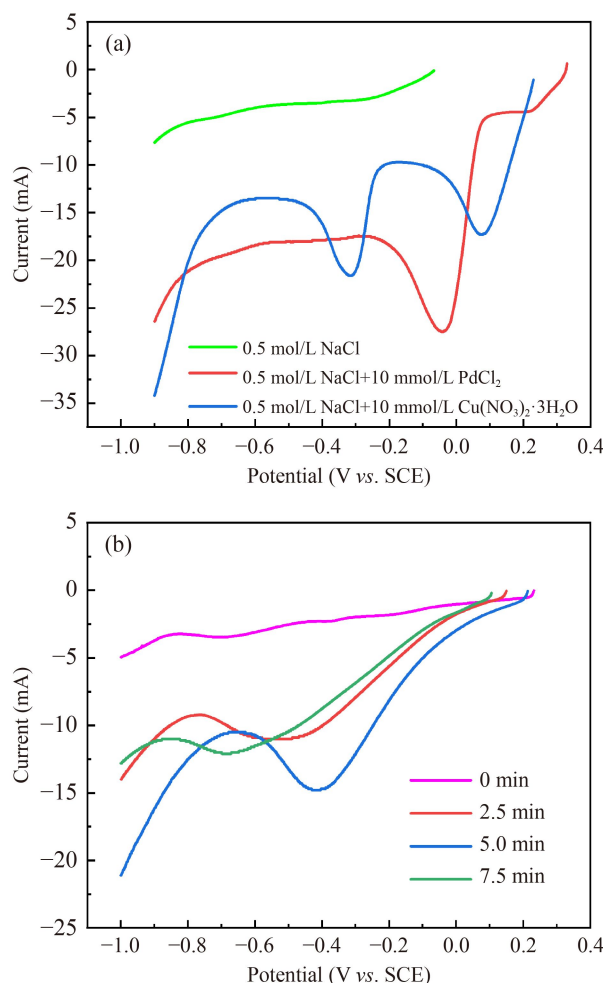


Fig. 1 LSV for (a) CNT membranes in 0.5 mol/L NaCl, 0.5 mol/L NaCl with 10 mmol/L PdCl_2 , and 0.5 mol/L NaCl with 10 mmol/L $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, (b) Pd-Cu modified CNT membranes (Pd:Cu = 1:1) obtained with different electrodeposition times (solution: 50 mmol/L Na_2SO_4 and 50 mg/L NO_3^- -N).

The electrocatalytic nitrate reduction results for Pd-Cu modified CNT membranes (Pd:Cu = 1:1) obtained with different electrodeposition times were also evaluated with LSV tests (Fig. 1(b)). All of the membranes with deposited Pd-Cu showed larger current responses in the NO_3^- -containing solution than the plain CNT membrane (0 min), which suggested that Pd-Cu bimetallic catalysts provided excellent performance in the reduction of nitrate. The current response increased significantly when the Pd-Cu deposition duration was increased from 0 to 5 min. However, further extending the Pd-Cu deposition duration to 7.5 min resulted in a reduction in the current response, indicating that the Pd-Cu modified CNT membrane obtained with an electrodeposition duration of 5 min had the highest catalytic activity for nitrate reduction. The weakened current response for long-time electrodeposition (7.5 min) was attributed to agglomeration of excess Pd-Cu particles and reduction in the real catalytic surface area (Chu et al., 2007). Hence, a deposition duration of 5 min was chosen for fabrication of the Pd-Cu modified CNT membranes.

3.2 Characterization of Pd-Cu modified CNT membranes

In view of the porous and relatively sparse surface structure of the PVDF membrane (Fig. 2(a)), a layer of MWCNTs was uniformly deposited onto the surface of the PVDF support (Fig. 2(b)). This CNT layer acted mainly as a conducting layer (Fig. S1) and was without electrocatalytic activity for nitrate reduction, since the current response of the plain CNT membrane (0 min) in Fig. 1(b) was relatively weak. After electrodeposition of Pd-Cu in the solution with a Pd:Cu ratio of 1:1, Pd and

Cu particles formed dense dendrites on the CNT fibers (Fig. 2(c)). EDX results showed that both Pd and Cu were successfully deposited and evenly dispersed on the membrane surface (Figs. 2(d)–2(f)). This provided the membrane with nitrate reduction activity (Fig. 1(b)).

It was previously reported that the catalytic activity and product selectivity for nitrate reduction are strongly influenced by the Pd:Cu ratio (Soares et al., 2012). To optimize the Pd:Cu ratio, the electrochemical properties of Pd-Cu modified CNT membranes with different Pd:Cu ratios were studied. The sheet resistance decreased gradually with increases in the proportion of Pd (Fig. S3), indicating that Pd-Cu modified CNT membranes with higher Pd:Cu ratios were more conductive. The current in the LSV tests increased when the Pd:Cu ratio was increased from 0 (Cu = 10) to 1:1 and then decreased with further increases in the Pd:Cu ratio (Fig. 3). The current of the Pd modified CNT membrane (Pd = 10) was much lower than those of the other tested membranes, and no obvious reduction peak was detected, which indicated that the catalytic activity of bare Pd was weak (Zhang et al., 2014). The membrane obtained from the Pd:Cu=1:1 solution exhibited the largest current, which indicated fast nitrate reduction. However, the product selectivity of these membranes still needed further quantitative analysis.

3.3 Electrocatalytic nitrate reduction by Pd-Cu modified CNT membranes in flow-through mode

3.3.1 Optimization of the Pd:Cu ratio and cathode potential for nitrate reduction

To further investigate the electrocatalytic nitrate reduc-

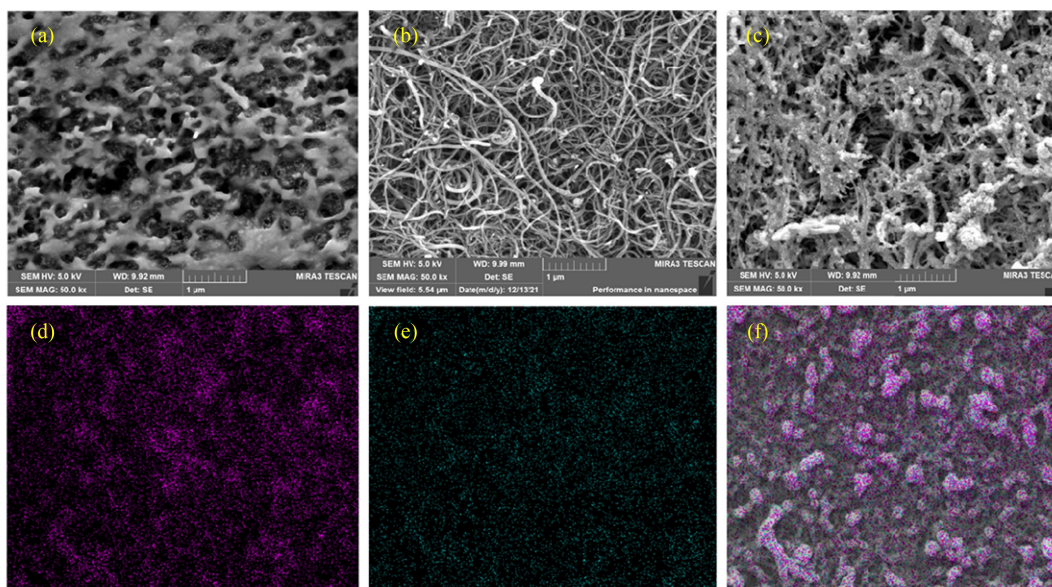


Fig. 2 SEM images of (a) PVDF membrane, (b) PVDF supported CNT membrane, (c) Pd-Cu modified CNT membrane (Pd:Cu=1:1), and EDX elemental maps for (d) Pd, (e) Cu, and (f) full coverage of both Cu and Pd on the Pd-Cu modified CNT membrane (Pd:Cu=1:1).

tion performance of Pd-Cu modified CNT membranes obtained with different Pd:Cu molar ratios, the NO_3^- -N removal efficiencies and final products were analyzed after application of various potentials ranging from -0.4 to -2.0 V. The results showed that potential played a critical role in nitrate reduction (Fig. 4). The nitrate removal efficiency was promoted by decreasing the cathode potential for all tested Pd-Cu modified CNT membranes (Fig. 4(a)). However, the membrane loaded with Pd alone (Pd = 10) exhibited a much lower nitrate removal efficiency than the other membranes, which was consistent with the LSV results (Fig. 3). The nitrate removal efficiency at potentials of approximately -0.6 to -0.8 V increased when the Pd:Cu ratio was increased from 0 (Cu = 10) to 1:1 and then decreased with further increases in the Pd:Cu ratio, which was also consistent with the catalytic activity illustrated in Fig. 3 for the same potentials. For the membranes deposited with Pd-Cu bimetallic catalysts and those with Cu alone, the nitrate removal efficiencies increased sharply when the potential was lower than -0.6 V. Nitrate was almost completely removed at a potential of -1.2 V. For the membranes deposited with Pd-Cu bimetallic catalysts, the nitrate

removal efficiencies remained constant at potentials lower than -1.2 V. The nitrate removal efficiency of the membrane deposited with Cu alone (Cu = 10) dropped slightly from $99.7\% \pm 0.1\%$ to $87.6\% \pm 0.8\%$ when the potential was decreased from -1.4 to -2.0 V. During this

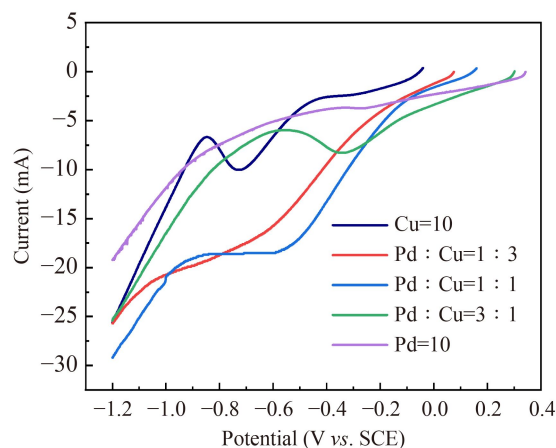


Fig. 3 LSV of Pd-Cu modified CNT membranes with different Pd:Cu ratios in a solution containing 50 mmol/L Na_2SO_4 and 50 mg/L NO_3^- -N.

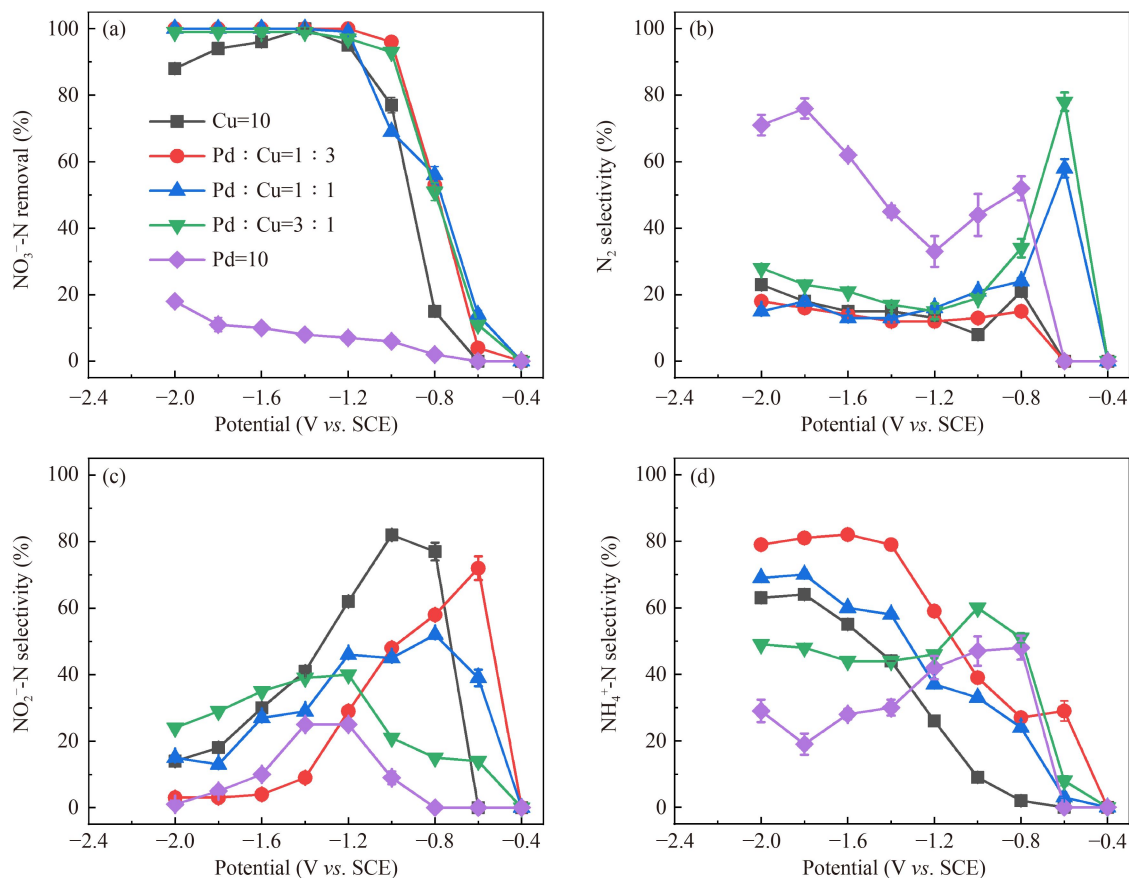


Fig. 4 (a) NO_3^- -N removal efficiency, (b) N_2 selectivity, (c) NO_2^- -N selectivity, and (d) NH_4^+ -N selectivity for Pd-Cu modified CNT membranes prepared with different Pd:Cu ratios (solution: 20 mg/L NO_3^- -N, 50 mmol/L Na_2SO_4 and 200 mg/L NaHCO_3 , pH=8.0; membrane flux: 10 L/($\text{m}^2 \cdot \text{h}$)).

experiment, small bubbles were observed on the membrane surface at potentials lower than -1.4 V, which was attributed to electrocatalytic production of H_2 . However, the effect of simultaneous hydrogen production on nitrate reduction is still controversial. Adsorption of molecular hydrogen (H_2) on the electrode surface was reported to block the active sites, thus weakening the nitrate reduction performance (Li et al., 2021). However, the hydrogen evolution reaction was also believed to represent a favorable side reaction that created a reductive environment for nitrate reduction (Chen et al., 2019). The results in Fig. 4(a) show that the reduction efficiency of nitrate did not decrease at potentials lower than -1.2 V, indicating that nitrate reduction by Pd-Cu modified CNT membranes was not negatively affected by hydrogen evolution.

Figs. 4(b)–4(d) illustrates the distributions of final products, including N_2 , NO_2^- -N and NH_4^+ -N. For the membranes deposited with Cu alone or Pb:Cu=1:3, N_2 was not detected at potentials higher than -0.6 V. Their N_2 selectivities increased slightly to 10 %–20 % at potentials lower than -0.8 V (Fig. 4(b)). In comparison, the proportion of N_2 reached its maximum at -0.6 V for membranes with Pd:Cu ratios of 1:1 ($58.0\% \pm 2.8\%$) and 3:1 ($77.9\% \pm 2.8\%$), and then dropped with decreases in potential and stabilized at approximately 15 %–30 % at potentials lower than -1.0 V. The N_2 selectivities of the Pd = 10 membrane at potentials lower than -0.8 V were much higher than those of the other membranes. However, due to its low nitrate removal efficiency, the membrane deposited with only Pd (Pd = 10) was not suitable for electrocatalytic nitrate reduction. The distribution patterns for NO_2^- -N and NH_4^+ -N can be divided into two types. One was for the Cu=10 membrane and the membranes with Pd:Cu ratios of 1:3 and 1:1, which revealed that NO_2^- -N was the main product at higher potentials, while NH_4^+ -N became the main product at lower potentials (Figs. 4(c) and 4(d)). These two products were in a state of counterbalance. For example, the nitrate reduction products of the Pd:Cu = 1:3 membrane were dominated by NO_2^- -N ($71.5\% \pm 3.5\%$) at -0.6 V, while at potentials lower than -1.4 V, the NO_2^- -N selectivity was lower than 10%, and the NH_4^+ -N selectivity was as high as 80 %. The reason was that hydrogen production was accelerated at lower potentials, and excessive H_2 promoted the formation of N-H bonds (Lan et al., 2015), which led to the formation of more NH_4^+ -N. The other type of NO_2^- -N and NH_4^+ -N distribution was for the membranes with more Pd (Pd:Cu=3:1 and Pb = 10). The proportions of NO_2^- -N for these two membranes continued to grow slightly as the potential dropped and reached their maxima at -1.2 V; this was followed by slow decreases at lower potentials. Their NH_4^+ -N selectivities also showed similar trends but reached their maxima at -0.8 to -1.0 V. The product distribution diagrams showed that higher N_2

proportions were obtained at relatively high potentials (-0.8 to -0.6 V). This was because more positive potentials effectively promoted N–N bonding, thereby enhancing the selectivity for N_2 . For practical applications of electrocatalytic nitrate reduction, the nitrate removal efficiency and the distribution of reduction products should be considered comprehensively, although lower potentials resulted in higher removal rates. Due to the relatively high nitrate removal efficiency and high selectivity for N_2 at -0.8 V, the Pd-Cu modified CNT membrane with a Pd:Cu ratio of 1:1 was considered the ideal material for nitrate reduction. The Pd:Cu=1:1 membrane was employed in the following experiments run at -0.8 V.

3.3.2 Optimization of the solution conditions for nitrate reduction

To develop an in-depth understanding of the membrane-electrocatalytic system, the influences of solution pH, Cl^- , and DO on nitrate reduction were studied.

The efficiency for removal of nitrate by the Pd-Cu modified CNT membrane decreased by 33 % from $67.3\% \pm 0.4\%$ to $44.7\% \pm 0.2\%$ upon increasing the pH from 4 to 12 (Fig. 5(a)). In contrast, the N_2 selectivity increased significantly from $10.8\% \pm 1.1\%$ at pH 4 to $33.7\% \pm 1.7\%$ at pH 12, while the NH_4^+ -N selectivity decreased from $47.9\% \pm 0.5\%$ to $21.5\% \pm 1.9\%$, and the NO_2^- -N selectivity remained constant at approximately 30 %. The nitrate removal efficiency was $57.9\% \pm 0.4\%$ and the N_2 selectivity was $23.2\% \pm 1.0\%$ at near neutral pH. Since nitrate reduction is a proton consuming process (e.g., $NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$, $2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4H_2O$, $NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O$), acidic conditions with higher proton concentrations are beneficial for nitrate reduction. Because nitrate reduction to NH_4^+ consumes more protons than reduction to N_2 , the inhibition of NH_4^+ production at higher pH would be much more obvious than that of N_2 production. Therefore, the selectivity for NH_4^+ decreased at higher pH values, leading to an increase in the N_2 proportion.

The addition of Cl^- showed no obvious effects on nitrate removal and product distribution in the flow-through mode (Fig. 5(b)). This differed significantly from the results obtained with a conventional electrochemical cell, in which case the reactor was operated in batch-fed mode and an appropriate concentration of Cl^- in the electrolyte increased the N_2 selectivity (Zhou et al., 2021). This occurred because Cl^- was oxidized on the anode to ClO^- , which then migrated to the cathode side and oxidized NH_4^+ -N into N_2 , thus increasing the N_2 selectivity. However, in flow-through mode, the contact time between nitrate and the membrane was short, and NH_4^+ -N produced on the membrane was immediately washed out of the reactor. Therefore, NH_4^+ -N could not be oxidized by ClO^- in this mode, and the product

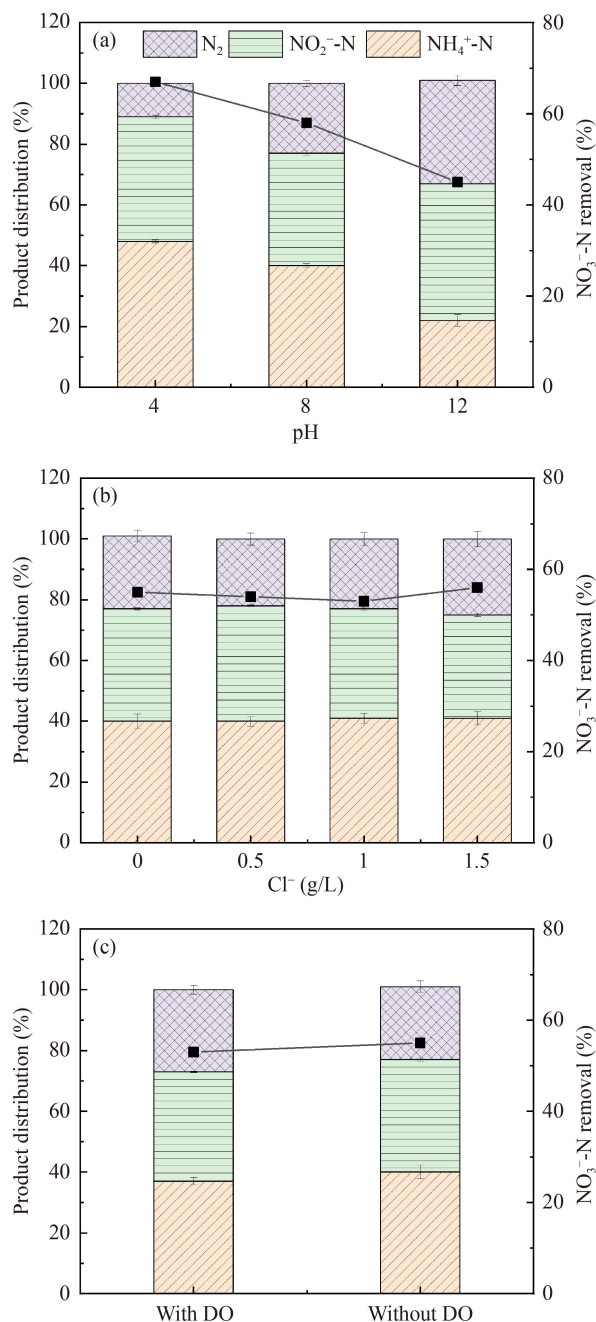


Fig. 5 Nitrate removal efficiencies and product distributions at (a) different pH values, (b) different concentrations of Cl⁻, and (c) different levels of DO. (Solution: 20 mg/L NO₃⁻-N, 50 mmol/L Na₂SO₄ and 200 mg/L NaHCO₃; Potential: -0.8 V; Pd:Cu=1:1; Membrane flux: 10 L/(m²·h))

selectivity did not change.

In the presence of DO (~7.5 mg/L), the nitrate removal efficiency was 53.3 % ± 0.4 %, which was essentially the same as that seen in the absence of DO (55.1 % ± 0.6 %) (Fig. 5(c)). The product distributions with and without DO were also similar. These results indicated that the oxygen reduction reaction (ORR) did not compete with nitrate reduction on the Pd-Cu modified CNT membrane.

These results may be attributed to the low ORR activities of both the MWCNTs and the Pd-Cu bimetal particles. Compared to other electrocatalytic NO₃⁻ reduction processes that require anoxic solution conditions (Rajic et al., 2015), the Pd-Cu modified CNT membrane had no requirement for elimination of DO, which is a prominent advantage over other catalytic systems. After continuous operation in the presence of DO for 15 hours, the nitrate removal efficiency and product distribution were essentially the same as those tested at the beginning of the experiment. Changes in the color of the effluent and the membrane surface were not observed. These results indicated that even in the presence of DO, Pd-Cu did not leach from the membrane surface, or the amount of leaching was very limited.

3.4 Mass transfer characterization

Membrane flux can affect the flow pattern of the electrolyte and thus affect the mass transfer process (Yang et al., 2009). Therefore, the performance of the Pd-Cu modified CNT membrane for electrocatalytic reduction of nitrate was investigated at different membrane fluxes. The nitrate removal efficiencies at membrane fluxes of 1 L/(m²·h) (67.7 % ± 0.2 %) and 5 L/(m²·h) (67.4 % ± 0.3 %) were almost the same (Fig. 6(a)). A further increase in membrane flux resulted in a decrease in nitrate removal efficiency, which decreased from 67.4 % ± 0.3 % at a flux of 5 L/(m²·h) to 44.3 % ± 0.4 % at a flux of 15 L/(m²·h). The N₂ selectivity decreased slightly from 26.1 % ± 0.9 % to 18.0 % ± 1.2 %, and the NH₄⁺-N selectivity also decreased from 46.4 % ± 0.6 % to 32.6 % ± 1.6 % when the flux was increased from 1 to 15 L/(m²·h). In contrast, the proportion of NO₂⁻-N increased from 28.0 % ± 0.3 % to 48.9 % ± 0.1 % with the increase in membrane flux. These results could be attributed to the shorter response times available for nitrate reduction with higher membrane fluxes. As described in Section 1, the mechanism for electrochemical nitrate reduction consists of several steps, such as NO₃⁻ reduction to NO₂⁻, NO₂⁻ reduction to N₂ and NO₂⁻ reduction to NH₄⁺ (Martínez et al., 2017; Sanchis et al., 2022). Therefore, NO₂⁻ could be an intermediate during nitrate reduction and then undergo further reduction to N₂ or NH₄⁺. With the increase in membrane flux, the contact time between the reactants and catalysts was shortened, and the NO₂⁻ produced from nitrate reduction could not be further reduced to N₂ or NH₄⁺, leading to accumulation of NO₂⁻ and the decreased proportions of N₂ and NH₄⁺.

To further illustrate the effects of flow-through operation on mass transfer, the nitrate removal rates and mass transfer rate constants were estimated at different fluxes. The nitrate removal rate was significantly increased, from 13.6 ± 0.0 to 133.5 ± 2.1 mg/(m²·h), by increasing the membrane flux from 1 to 15 L/(m²·h)

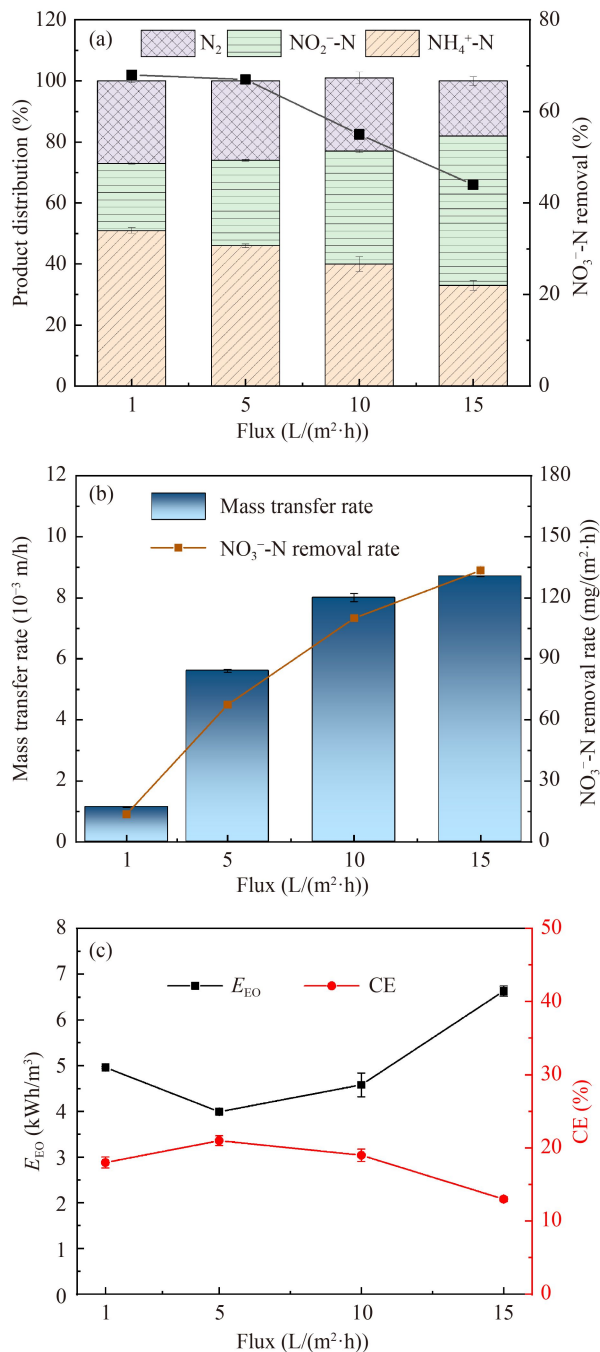


Fig. 6 (a) Nitrate removal efficiency and production distribution, (b) mass transfer rate constant and nitrate removal rate, and (c) electrical energy consumption per order nitrate reduction (E_{EO}) and current efficiency (CE) at different membrane fluxes (Solution: 20 mg/L NO₃⁻-N, 50 mmol/L Na₂SO₄ and 200 mg/L NaHCO₃; Potential: -0.8 V; Pd:Cu=1:1).

(Fig. 6(b)). The mass transfer rate constant also increased substantially, from $(1.14 \pm 0.01) \times 10^{-3}$ m/h at a membrane flux of 1 L/(m²·h) to $(8.71 \pm 0.01) \times 10^{-3}$ m/h at a membrane flux of 15 L/(m²·h), which gave direct evidence for enhanced convective diffusion of reactants to the membrane surface. Both the increases in nitrate

reduction rate and the increase in the mass transfer rate constant slowed with higher fluxes. This might be because the reaction activity gradually became a limiting factor at higher fluxes.

The energy consumption per order nitrate reduction (E_{EO}) decreased from 4.96 ± 0.02 kWh/m³ at 1 L/(m²·h) to 3.99 ± 0.05 kWh/m³ at 5 L/(m²·h) (Fig. 6(c)), indicating that an appropriate membrane flux provided energy savings. Then, E_{EO} increased with a further increase in membrane flux due to the decreased nitrate removal efficiency. The E_{EO} values at 10 L/(m²·h) and 15 L/(m²·h) were 4.58 ± 0.26 kWh/m³ and 6.63 ± 0.11 kWh/m³, respectively. The current efficiency showed the opposite trend and increased slightly from 18.0 % $\pm$ 0.3 % to 21.0 % $\pm$ 0.3 % when the membrane flux was increased from 1 to 5 L/(m²·h), and then efficiency decreased with further increases in flux. This occurred because the current increased with increasing membrane flux (data not shown), while the nitrate removal efficiency decreased, thus reducing the current efficiency.

4 Conclusions

Pd-Cu modified CNT membranes were prepared via the electrodeposition method, and a flow-through electrocatalytic system was constructed to reduce nitrate in this study. Pd and Cu particles were successfully codeposited onto CNT membranes at a potential of -0.70 V. The optimum deposition time was determined to be 5 min, and a Pd:Cu ratio of 1:1 was considered to be optimal for membrane fabrication. Nitrate in solution was almost completely reduced by the membrane at potentials lower than -1.2 V. However, -0.8 V was considered to be optimal for nitrate reduction in terms of both nitrate removal efficiency and product selectivity. The nitrate removal efficiency was 56.2 % $\pm$ 2.6 %, and the N₂ selectivity was 23.8 % $\pm$ 1.0 % for the Pd:Cu=1:1 membrane operating at -0.8 V. Increasing the solution pH significantly improved the N₂ selectivity while reducing the nitrate removal efficiency. Cl⁻ ions and DO showed limited effects on nitrate reduction for the Pd-Cu modified CNT membrane. Mass transfer was enhanced effectively by increasing the membrane flux, while both the nitrate reduction rate and mass transfer rate constant increased significantly with increasing membrane flux. This technology has broad application prospects for effective nitrate reduction and is worthy of further modification in practice.

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