Recovery of ammonia nitrogen from landfill leachate using a biopolar membrane equipped electrodialysis system
Cunkuan Zhang, Wenchuan Ding, Xiaolan Zeng and Xiaotang Xu

ABSTRACT
In this paper, a laboratory-scale electrodialysis reactor with five compartment cells separated by a bipolar membrane and ion exchange membrane was assembled to remove ammonia nitrogen from landfill leachate as a pretreatment process. The effects of humic acid, magnesium ions (Mg$^{2+}$) and calcium ions (Ca$^{2+}$) existing in leachate on the removal efficiency of ammonium (NH$_4^+$) were investigated by using simulated wastewater. The results indicate that humic acid has little impact on ammonium in the presence of an electric field. High concentrations of Mg$^{2+}$ and Ca$^{2+}$ in solution have a substantial impact on the removal efficiency of ammonium, but the average migration rate of the three ions is NH$_4^+$ > Mg$^{2+}$ > Ca$^{2+}$ under the same current intensity, and NH$_4^+$ plays a major role in electromigration for mixture electrodialysis. Therefore, ammonia nitrogen can be separated from leachate and accumulated effectively. Meanwhile, the bipolar membrane near the cathode produces alkali that is released into the base cell to promote ammonia nitrogen transformation from accumulated ammonium, which creates in-site alkaline condition for ammonia nitrogen recovery by a further stripping process. When the actual leachate collected from a local municipal sanitary landfill was employed, the reactor reached 86.17% of ammonia nitrogen removal after 3.0 h reaction. Analysis of membrane scale suggests the inhibitory effect of Mg$^{2+}$ on Ca$^{2+}$ migration during the initial working period of the reaction can potentially slow down the membrane scaling of the cation exchange membrane. This study provides a promising technology for the removal and recovery of ammonia nitrogen from landfill leachate.

Key words | ammonia nitrogen, bipolar membrane, electrodialysis, landfill leachate, membrane scale

HIGHLIGHTS
- Establishment of a bipolar membrane electrochemical membrane separation system.
- Humic acid, calcium and magnesium ions and ammonium ions interact in wastewater.
- The removal rate of ammonia nitrogen reaches 86.17%, and the acid liquid and alkali liquid are recovered with a concentration of 1 mol·L$^{-1}$.
- The inhibitory effect of Mg$^{2+}$ on Ca$^{2+}$ migration can effectively slow down membrane fouling.

INTRODUCTION
Landfill leachate is the primary noxious wastewater generated during the stabilization of municipal solid waste in municipal sanitary landfills (Damiano et al. 2014). Leachate containing a large amount of pollutants such as ammonia nitrogen, biodegradable and refractory organics, and heavy metals may cause serious environmental pollutions (Kjeldsen et al. 2002). Thus the landfill leachate needs to be treated strictly before being discharged into
the water body. Biological treatment is generally considered to be the preferred method for the cost-effective removal of organics and ammonia nitrogen from wastewater (Jokela et al. 2002). Unfortunately, the high concentration of ammonia nitrogen in landfill leachate significantly inhibits the activity of microorganisms in biological treatment systems resulting in decrease of the treatment efficiency (Su et al. 2019). In addition, high concentration of nitrogen pollutants in effluent from biological treatment systems will cause eutrophication in water, which can reduce water quality and destroy biodiversity (Ye et al. 2017). Therefore, it has been proposed to remove the ammonia nitrogen from leachate prior to the subsequent biological process to improve the leachate treatment performance. Many physical and chemical processes, such as breakpoint chlorination (Pressley et al. 1972), blowing off (Tao et al. 2018), ion exchange method (Yoshida & Kataoka 1986), and struvite precipitation (Kim et al. 2007), have been developed to remove ammonia nitrogen in water. Among these technologies, struvite precipitation and stripping can achieve ammonia nitrogen removal from solution as well as ammonia nitrogen recovery, which is valuable in practical application. Struvite precipitation occurred under Mg:N:P at a molar ratio of 3:1:1, and an ammonia removal rate of 85% was obtained (Huang et al. 2014). However, a high concentration of ammonia in leachate requires a large amount of magnesium and phosphate supplements to maintain the proper molar ratios of magnesium, ammonia, and phosphate for struvite precipitation formation, which limits its wide application. The ammonia recovery by vacuum steam stripping demonstrated 74.3–89.5% removal rate of ammonia nitrogen in leachate (Xiong et al. 2018). However, the pH in solution has to be adjusted at alkaline condition, which increases the treatment cost and introduces additional chemicals. Thus the development of new technology for ammonia nitrogen recovery from landfill leachate is still demanded.

Electrodialysis (ED) is an electrochemical membrane separation technology. In the ED reactor, the solution is desalinated and concentrated by using the transmission characteristics of the ion exchange membrane (Peraki et al. 2016). Mondor et al. (2008) presented the maximum ammonia nitrogen concentration of 16.02 g·L⁻¹ when he adopted ED to recover and concentrate ammonia nitrogen in pig manure. It was reported that the removal rates of ammonia nitrogen and phosphate in a sludge anaerobic digestion system reached 95.8–100% and 86.1–94.4%, respectively, when an ED and struvite precipitation combined process was fulfilled, and the concentrated nitrogen and phosphate could form struvite effectively (Wang et al. 2015). As the membrane is crucial to the performance of ED, some new types of ion exchange membranes such as monovalent selective ion membranes and bipolar membranes have been developed to remove and recover ammonia nitrogen and other substances in water. The bipolar membrane electrochemical membrane separation system that combines the bipolar membrane with other anion/cation exchange membranes is called the bipolar membrane electrodialysis method (BMED) (Ilhan et al. 2017). Ion transport will result in the formation of recoverable anions and cations during the BMED process. Similarly, the transfer of H⁺ to anionic species occurs in the acidic region, while the transfer of OH⁻ to cations occurs in the basic region (Raissouni et al. 2007). The BMED process has been used to recover phosphorus from the excess sludge in wastewater treatment plants (Wang et al. 2015). Shi et al. (2018) carried out a laboratory-scale BMED system to recover 52% of ammonia nitrogen, 98% of phosphate and 95% of volatile fatty acids in pig manure mixture, respectively. However, the research on the treatment of landfill leachate is still scarce. Therefore, in this study, a combined bipolar membrane and ion exchange membrane electrodialysis reactor was constructed to remove and recover ammonia nitrogen from landfill leachate. The removal rate of ammonia nitrogen, humic acid, and calcium and magnesium ions in leachate is still discussed. The selectivity of calcium and magnesium ions, and ammonium ions in the migration process and the effects on membrane fouling were analyzed.

MATERIALS AND METHODS

Experimental materials and devices

The experimental reactor is a rectangular reaction tank (effective size L × W × H = 10 cm × 10 cm × 12 cm) made of plexiglass. The reactor is composed of five compartment cells. The cells are separated by ion exchange membranes or bipolar membranes (Keka polymer Materials Technology Co., Ltd; the membrane parameters are given in Table 1) lined with waterproof rubber pads. There are generally two electrode cells, one raw water cell, one acid cell and one alkali cell. The anode and cathode are titanium-plated ruthenium-iridium electrodes (Jinbu Titanium Nickel Equipment Manufacturing Co., Ltd, L×H×W = 10.0 cm×10.0 cm ×0.1 cm). A voltage DC power supply (Maison Co., Ltd) outputs a constant current. The structure of the bipolar membrane electrochemical reactor is shown in Figure 1.
Experiment

According to preliminary experimental results, the operating current density of the system is 4 mA·cm$^{-2}$. There is 200 mL of simulated leachate ammonia nitrogen wastewater in the raw water chamber, and the concentration of NH$_3$-N is 2,000 ± 2 mg·L$^{-1}$. There is 150 mL deionized water in the acid and base compartments and 150 mL 0.3 mol·L$^{-1}$ sodium sulfate solution in the two electrode compartments. The experimental groups were established with different concentrations of humic acid, Ca$^{2+}$ and Mg$^{2+}$. This method treats the leachate from the Chongqing Changshengqiao municipal solid waste landfill (for water quality indicators, see Table 1). X-ray diffraction (XRD) and scanning electron microscopy (SEM) detection and analysis are performed on the side of the alkali chamber of the cation exchange membrane.

Test analysis

The pH value of the solution was measured with a PHS-3C pH meter (Shanghai Leici). NH$_3$-N, PO$_4^{3-}$-P and other concentrations were measured using standard methods such as the Nessler’s reagent spectrophotometry (HJ535-2009) and ammonium molybdate spectrophotometry. Ca$^{2+}$ and Mg$^{2+}$ concentrations were determined by EDTA complexometric titration. The humic acid concentration was measured by UV spectrophotometry (T6UV-VIS, Beijing Purchase Corporation). The XRD pattern of the cation exchange membrane after the operation was measured using a Thermo Fisher X-ray diffractometer (CuK$\alpha$ radiation, $\lambda$ = 1.5406 Å, continuous scanning spectrum, scanning start angle is 5°, end angle is 70°, scanning speed 3’min$^{-1}$), compared with the standard spectrum of the database, and analyzed for the scale components. The surface morphology and structure of the cation exchange membrane were analyzed by a VEGA 3 LMH scanning electron microscope. At the same time, an X-ray energy spectrum analyzer equipped with the scanning electron microscope was used to perform element determination and analysis of the film scale.

Data analysis

The recovery rate in the ammonia nitrogen liquid phase was determined by Equation (1).

$$R_N = \frac{C_{aN,t} \times V_a}{C_{aN,0} - C_{aN,t}} \times 100\%$$

where $R_N$ is the recovery rate of ammonia nitrogen in the liquid phase at time $t$ in the experiment; $C_{aN,t}$ and $C_{aN}$ are the ammonia nitrogen mass concentration (mg·L$^{-1}$) measured in the alkali and raw water chamber solutions at
time $t$; $C_{\text{N,0}}$ is the mass concentration of ammonia nitrogen (mg·L$^{-1}$) in the raw water chamber solution measured at the initial time; $V_a$ and $V_r$ are the volume of the reaction solution in the alkali and raw water chambers, respectively.

The average migration rate of an ion in a certain period was determined by Equation (2).

$$M_X = \frac{C_{X,t_n} - C_{X,t_{n+1}}}{\Delta t}$$

where $M_X$ is the average migration rate (mg·min$^{-1}$) of an ion in a certain period in the experiment; $C_{X,t_n}$ and $C_{X,t_{n+1}}$ are the measured mass concentration of an ion in the solution at time $t_n$ and time $t_{n+1}$, respectively (mg·L$^{-1}$); $\Delta t$ is the time interval (min).

The power consumption was determined by Equation (3).

$$W = \int UIdt$$

where $W$ is the electric energy consumption of the bipolar membrane electrochemical membrane separation system (J); $U$ is the voltage value (V) between the cathode and anode stages; $I$ is the current value (A); $t$ is the reaction time (s).

The current efficiency calculation was determined by Equation (4).

$$C_E = \frac{F \cdot z \cdot V \cdot \Delta C_X}{I \cdot \Delta t} \times 100\%$$

where $C_E$ is the current efficiency of an ion in a bipolar membrane electrochemical membrane separation system (%); $F$ is the Faraday constant (96,485 C·mol$^{-1}$); $z$ is the valence of the ion; $V$ is the solution volume (L); $\Delta C_X$ is the molar concentration difference (mol·L$^{-1}$) between adjacent time intervals of ions; $I$ is the current value (A); $\Delta t$ is the time interval (s).

**RESULTS AND DISCUSSION**

**Effect of humic acid on ammonia nitrogen recovery**

The humic acid-free system (group 1) is consistent with the change trend of ammonia nitrogen concentration when it contains 500 mg·L$^{-1}$ humic acid (group 2) (Figure 2). At the reaction time of 3.0 h, the ammonia nitrogen concentration in the raw water chamber (room) decreased to 0 mg·L$^{-1}$, indicating that the adsorption effect of humic acid on ammonia nitrogen could be ignored. The ammonia nitrogen could not be fixed in the raw water cell by overcoming electromigration. Thus the humic acid has slight effects on the migration of ammonia nitrogen particularly in the early stage of system operation. From 0 to 0.25 h, the average migration rates of ammonia nitrogen in the two experimental systems were 14.74 mg·min$^{-1}$ and 10.98 mg·min$^{-1}$, respectively. It is presumed that the macromolecular humic acid has an electrostatic adsorption effect on NH$_4^+$ (Ogata & Miura 2014). During the initial operation of the system, part of the electric field force acts to overcome the influence of the adsorption force, that is, to suppress the migration speed of ammonia nitrogen.

After 3.0 hours of reaction, the concentration of humic acid in the raw water chamber decreased to 429 mg·L$^{-1}$, which was about 14.2% (Figure 3). The carboxyl and phenolic groups in humic acid are negatively charged and move to the anion membrane under the action of an electric field. However, some studies have found that humic acid membrane pollution is more likely to occur in positive membranes than negative membranes (Lee et al. 2002). The concentration of humic acid in the acid chamber...
increased from 0 mg·L\(^{-1}\) to 52 mg·L\(^{-1}\), and there was almost no humic acid in the alkali chamber. From the point of view of the mass balance of humic acid, the mass of humic acid in the original water chamber solution decreased by 14.2 mg, while that in the acid and base chamber solutions increased by 8.25 mg. According to the analysis of pH changes in the three chambers, the pH value of the raw water chamber decreased to 5.22 at the end of the reaction, while that of acid chamber decreased to 0.07 at the end of the reaction. The solubility of humic acids in acidic solution decreased, and some humic acids began to precipitate in the form of precipitates.

### Calcium and magnesium ions and ammonia nitrogen migration

Under this system, the cations in the solution migrate to the alkaline chamber, and high-valent cations (more than divalent or higher) such as Ca\(^{2+}\) and Mg\(^{2+}\) will form a precipitate in an alkaline environment (Wang et al. 2011). The presence of a large number of magnesium ions and calcium ions in the leachate may cause competition between ammonia nitrogen migration and membrane pollution. However, it is necessary to reveal the migration law in this system.

### Effect of magnesium ion on ammonia nitrogen migration

Three groups of different Mg\(^{2+}\) concentrations (0 mg·L\(^{-1}\), 500 mg·L\(^{-1}\), 1,000 mg·L\(^{-1}\)) were selected and recorded as groups 1, 2, and 3. The ammonia nitrogen (1), ammonia nitrogen (2), and ammonia nitrogen (3) curves of Figure 4 represent the average migration rates of ammonia nitrogen adjacent to the raw water compartments at adjacent time intervals in groups 1, 2, and 3, respectively. The Mg\(^{2+}\) (2) and Mg\(^{2+}\) (3) curves represent the average migration rates of adjacent time intervals of the raw water chamber Mg\(^{2+}\) in groups 2 and 3.

When there is no Mg\(^{2+}\) in the solution, the concentration of ammonia nitrogen in the raw water chamber is reduced to 0 mg·L\(^{-1}\) at 2.75 h (Figure 4). However, in the experimental groups with Mg\(^{2+}\) concentration of 500 mg·L\(^{-1}\) and 1,000 mg·L\(^{-1}\), ammonia nitrogen in the raw water chamber also existed, 41.57 mg·L\(^{-1}\) and 61.63 mg·L\(^{-1}\) at 3.0 h, respectively. The existence of Mg\(^{2+}\) has a great influence on the recovery of ammonia nitrogen, and the change curve of ammonia nitrogen concentration in the second and third groups is more consistent. At this concentration level, the migration effect of ammonia nitrogen is not sensitive to the change of Mg\(^{2+}\) concentration. When there is no Mg\(^{2+}\) in the system, the migration rate of ammonia nitrogen reaches the maximum at the initial time and decreases gradually with time. In the presence of Mg\(^{2+}\), the migration rate of ammonia nitrogen at the beginning decreased more than that in the absence of Mg\(^{2+}\). The migration rate of ammonia nitrogen was relatively stable in

![Figure 3](http://iwaponline.com/wst/article-pdf/82/9/1758/781218/wst082091758.pdf)

**Figure 3** Changes of humic acid (HA) concentration in different compartments with 500 mg·L\(^{-1}\) HA.

![Figure 4](http://iwaponline.com/wst/article-pdf/82/9/1758/781218/wst082091758.pdf)

**Figure 4** (a) Changes of ammonia nitrogen concentration; (b) changes of ammonia nitrogen and Mg\(^{2+}\) average transport rates with different Mg\(^{2+}\) concentrations.
the whole process and increased slightly before 1.25 h. The reason may be that the Mg$^{2+}$ competes with the currently used ammonia nitrogen, and its presence makes up for the problem that the ammonia nitrogen cannot move to the membrane surface in time, thereby reducing the polarization during the concentration reaction. Also, the migration rate of Mg$^{2+}$ in Experiment 2 and Experiment 3 was similar.

The main difference is that Mg$^{2+}$ completely migrated at the end of the reaction in Experiment 2, and the migration rate decreased. In Experiment 3, as the concentration of ammonia nitrogen decreases, the migration rate of Mg$^{2+}$ increases due to the advantage of the Mg$^{2+}$ concentration. From the 2.5 h overall average migration rate, the second group is 3.15 mg·min$^{-1}$, and the third group is 3.38 mg·min$^{-1}$. The increase in Mg$^{2+}$ concentration increases average migration rate by about 8%, and the Mg$^{2+}$ concentration in this system has little effect on its migration rate.

**Effect of calcium ion on ammonia nitrogen migration**

Different concentrations of Ca$^{2+}$ (0 mg·L$^{-1}$, 250 mg·L$^{-1}$, 500 mg·L$^{-1}$) were selected and recorded as the first, second and third groups. Ammonia nitrogen (1), ammonia nitrogen (2) and the ammonia nitrogen (3) curves of Figure 5 represent the average mobility of ammonia nitrogen in adjacent raw water compartments in groups 1, 2 and 3, respectively.

The Ca$^{2+}$ (2) and Ca$^{2+}$ (3) curves represent the average mobility of Ca$^{2+}$ in adjacent time intervals in the raw water chambers of the second and third groups. In the absence of Ca$^{2+}$, the ammonia nitrogen concentration in the raw water chamber dropped to 0 mg·L$^{-1}$ at 2.75 h, while the ammonia nitrogen concentration in the experimental group was 250 mg·L$^{-1}$. The ammonia nitrogen concentration in the raw water chamber was 5.42 mg·L$^{-1}$ and 7.27 mg·L$^{-1}$, respectively, in 3 h under Ca$^{2+}$ concentration of 250 mg·L$^{-1}$ and 500 mg·L$^{-1}$ (experimental groups Ca$^{2+}$(2) and Ca$^{2+}$(3)) (Figure 5). The presence of Ca$^{2+}$ affects the recovery rate of ammonia nitrogen, but it is less than the effect of the same concentration of Mg$^{2+}$. The ammonia nitrogen concentration curves of the second group and the third group are more consistent, and the difference is small. At this concentration level, the migration effect of ammonia nitrogen is not sensitive to changes in Ca$^{2+}$ concentration but is higher than that of Mg$^{2+}$ concentration. According to the average migration rate over 2.5 h, group 2 is 1.61 mg·min$^{-1}$, and group 3 is 2.06 mg·min$^{-1}$. The increase of Ca$^{2+}$ concentration has a relatively large impact on its migration rate. Comparing the 500 mg·L$^{-1}$ Mg$^{2+}$ and 500 mg·L$^{-1}$ Ca$^{2+}$, the average migration rate of Mg$^{2+}$ is higher than that of Ca$^{2+}$, which leads to the little contribution of Ca$^{2+}$ to the reduction of concentration polarization.

**Migration of each ion in the presence of magnesium and calcium ions**

To investigate the migration changes of Ca$^{2+}$, Mg$^{2+}$, and NH$_4^+$ in the system under the coexistence of calcium and magnesium ions, the concentrations of Mg$^{2+}$ and Ca$^{2+}$ were 1,000 mg·L$^{-1}$ and 500 mg·L$^{-1}$, respectively.

Under the conditions of a current density of 4 mA·cm$^{-2}$ and an initial pH of 7, the ammonia nitrogen concentration in the raw water room reached 0 mg·L$^{-1}$ within 3.25 hours of system operation (Figure 6). Compared with the 2.75 h without the influence of other cations, there is a lag. It indicates that the presence of calcium and magnesium ions has a significant impact on the migration of ammonia nitrogen, and the concentration of ammonia nitrogen in the raw water chamber at 3.0 h is close to the concentration in the experiment with 1,000 mg·L$^{-1}$ Mg$^{2+}$ alone. Preliminarily judged, compared with Ca$^{2+}$, Mg$^{2+}$ plays a leading role in the migration of ammonia nitrogen. The Mg$^{2+}$ in the alkali

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![Figure 5](http://iwaponline.com/wst/article-pdf/82/9/1758/781218/wst082091758.pdf)  
(a) Changes of ammonia nitrogen concentration; (b) changes of ammonia nitrogen and Ca$^{2+}$ average transport rates with different Ca$^{2+}$ concentrations.
chamber dropped rapidly after reaching the peak value at 1.0 h and then dropped to 0 mg·L⁻¹ after 3.0 h. There is no soluble magnesium in the alkali chamber and all the magnesium has precipitated. The Ca²⁺ ion in the alkali chamber increased gradually, reached the maximum value of 92.3 mg·L⁻¹ at 1.75 h, and then stabilized at this value. The solubility of calcium hydroxide at 10°C is about 0.176 g, and the theoretically dissolved Ca²⁺ content is 95.14 mg·L⁻¹, which is consistent with the experimental results. That is, the Ca²⁺ ions in the alkali chamber produce calcium hydroxide. After reaching saturation in the solution, excess calcium ions will form a precipitate.

Except for the decrease in the calculated migration rate caused by the exhaustion of the three ions at the end of their migration, the three average migration rates during system operation at this concentration level are NH₄⁺ > Mg²⁺ > Ca²⁺ (Figure 7). When the system runs for 0–1.25 h, the overall current efficiency of the system is on the rise, and the migration of NH₄⁺ makes the main contribution. Compared with the other two ions, the current efficiency of NH₄⁺ increased more obviously and reached the maximum value at 1.25 h. During the operation period of 1.25–2.5 h, NH₄⁺ current efficiency began to decrease slowly, Mg²⁺ current efficiency increased slowly, and the overall current efficiency increased slightly, reaching the maximum value overall the operation at 2.0 h. When the NH₄⁺ concentration in the raw water chamber is close to 0 (starting from 3.0 h), the current efficiency of Mg²⁺ and Ca²⁺ increases sharply, leading to current transmission. When the Mg²⁺ concentration in the raw water chamber approaches 3.5 (starting from 3.5 h), the Ca²⁺ current efficiency continues to increase.

Based on the above results, the movement of cations to the alkali chamber under the system is analyzed. The main driving force for the migration of cations in the system medium is the electric field force. The reason may be that cations with low molecular weight will have a higher migration rate. In other words, NH₄⁺ will dominate the electron transfer. As for Mg²⁺ and Ca²⁺ in the same valence state, due to the low relative molecular mass of Mg²⁺, the migration rate is higher at the same concentration level, which is consistent with the experimental results. The transmembrane process of cations is also an important part of their migration. There is a mutual attraction between cations and the fixed groups in cation exchange membranes, and the force is related to the ionic radius and hydrated ion radius. Generally speaking, the smaller the ion radius, the higher the valence and the greater the force. The introduction of an electric field may destroy the electrostatic interaction between cations and water molecules, so most of them exist in the form of bare ions. Table S2 (Supplementary Information) shows the ionic radius and hydrated ionic radius of NH₄⁺, Mg²⁺ and Ca²⁺ (Volkov et al. 1997;
The introduction of an electric field may destroy the electrostatic interaction between cations and water molecules, so most of them exist in the form of bare ions. The radius of Mg$^{2+}$ is about 0.072 nm, and the radius of Ca$^{2+}$ of the same charge is about 0.100 nm. This may make Mg$^{2+}$ have a stronger affinity for the exchange group. Mg$^{2+}$ has the advantage of having a high affinity for the negatively charged fixing groups of the membrane. Mg$^{2+}$ occupies more exchange sites than Ca$^{2+}$, which indicates that Mg$^{2+}$ has a stronger inhibitory effect on NH$_4^+$ migration than Ca$^{2+}$ at the same concentration. In the experiment of the coexistence system of Mg$^{2+}$ and Ca$^{2+}$, the mobility of Ca$^{2+}$ is much lower than in the experiment where Ca$^{2+}$ exists alone. The system runs for 1.25 h. The advantage of Mg$^{2+}$ and Ca$^{2+}$ competing for negatively charged fixed groups is that the system is more obvious in the initial working stage and inhibits the migration of Ca$^{2+}$.

The selective permeability of ion exchange membranes is usually explained by the electric double layer theory and the Donnan equilibrium theory. However, the essence of the two is the transmembrane effect of ions without the action of an electric field, and the actual equilibrium situation is different when there is an electric field. Some experiments based on Donnan theory have shown that the smaller the hydrated ion radius of heavy metal ions, the faster the ion migration speed, and the stronger the removal capacity of the ion exchange membrane (Vasil’eva et al. 2019). The difference from the results of this study is that the electric field affects the destruction of the ion hydration shell, and no conclusion can be drawn based on the hydration ion radius. Besides, in this system, the migration rate of Ca$^{2+}$ and Mg$^{2+}$ is less sensitive to its concentration. This is because electromigration mass transfer is dominant compared to slower concentration diffusion mass transfer. When the NH$_4^+$ in the raw water chamber is exhausted, the migration rate of Ca$^{2+}$ and Mg$^{2+}$ increases significantly, and the response of Mg$^{2+}$ takes priority over Ca$^{2+}$. Referring to the new theory of ion ‘hole’ transfer under a DC electric field (Liang & Newton 1992), more cation holes are released due to the decrease of NH$_4^+$ in the membrane channel, which makes more Ca$^{2+}$ and Mg$^{2+}$ migrating to the solution membrane interface enter into the membrane channel to compensate for the holes.

**Treatment effect of actual leachate**

The experimental landfill leachate was collected from the Chongqing No. 1 Leachate Treatment Station. The Chang-shengqiao landfill serviced by the treatment station was put into use in 2003 and closed in 2016. Its landfill leachate is an aging (mature) landfill leachate. The system works for 3.0 h, and the concentration of the acid/alkali solution in the acid chamber and the alkali chamber reaches about 1 mol·L$^{-1}$. It can be seen in Figure 8 that there is a difference between the actual leachate treatment experiment and the simulated wastewater experiment in the change of pH value. In the simulated experiment, the pH value of the original water chamber showed a downward trend. In the actual percolate experiment, the pH value of the original water chamber rose slowly, and the pH value of the alkali chamber rose faster. At the end of the reaction, it was about 14. The reason may be that the actual leachate also contains a large amount of Na$^+$ and K$^+$ compared with the simulated wastewater in this study. The strong alkali formed after migration to the alkali chamber has high alkalinity, which causes the pH of the alkali chamber to rise rapidly. Since the H$^+$ concentration in the acid chamber is higher than the OH$^-$ concentration in the alkali chamber in the simulated wastewater experiment, the H$^+$ back-diffusion in the acid chamber dominates, causing the pH of the raw water chamber to drop. In actual landfill leachate experiments, H$^+$ back-diffusion in the acid chamber is relatively balanced with OH$^-$ back-diffusion in the alkali chamber, and the migration of NH$_4^+$ to the alkali chamber reduces the NH$_4^+$ hydrolysis, resulting in a slow rise in the pH of the raw water chamber.

In the actual leachate treatment experiment, the concentration changes of ammonia nitrogen, Ca$^{2+}$, Mg$^{2+}$, and humus (characterized by UV254) in the raw water room, alkali room and acid room are basically consistent with the previous conclusions (Figure 9). The separation effect of ammonia nitrogen was better. The ammonia nitrogen concentration in the raw water chamber was reduced by
1,972.55 mg·L$^{-1}$ within 3.0 h, and the removal rate was about 86.17%. However, the ammonia nitrogen concentration in the alkali chamber is lower than that in the simulated wastewater; that is, the recovery rate of ammonia nitrogen in the liquid phase is reduced, and is 72.55% when the system is operated for 3.0 h. This shows that during the actual leachate treatment, the pH of the alkali chamber was higher than that in the simulated wastewater experiment, which resulted in more free ammonia volatilization in the open system.

In addition, by comparing the conductivity before and after treatment, the system can reduce the conductivity of raw water by about 2,280 μS·cm$^{-1}$ after working for 3.0 h, indicating that it has a better desalination effect, which is beneficial to subsequent biological or other processes.

Membrane fouling analysis

The system has been used to treat the leachate from the actual landfill for five times, each for 3 hours. The cation exchange membrane after the operation is termed CEM-1, and the original unused cation exchange membrane is termed CEM-0. An XRD test was performed on one side of the alkali chamber to analyze the composition of membrane fouling. CEM-2 represents the XRD spectrum of calcite-CaCO$_3$ (Figure 10).

Comparing the XRD patterns of the cation exchange membrane before and after the operation, CEM-1 showed obvious calcite peaks. The crystalline component of the cation exchange membrane scale is mainly CaCO$_3$. This is because Ca$^{2+}$ attached to the alkali compartment side of the cation exchange membrane combines with OH$^-$ to form Ca(OH)$_2$ and then contacts with CO$_2$ in the liquid phase and air to form CaCO$_3$. Compared with Ca$^{2+}$, the membrane fouling caused by Mg$^{2+}$ has little effect on the voltage of the electrodialysis cell. The formation of membrane fouling with the same concentration of Mg$^{2+}$ has little effect on the resistance of the cation exchange membrane and less pollution. The coexisting ions in the solution will also affect the formation of membrane fouling and the morphology of precipitated crystals. The nature of cation membrane fouling will change under different Mg/Ca concentration ratios (Banasiak & Schafer 2009). The inhibitory effect of Mg$^{2+}$ on the migration of Ca$^{2+}$ affects the formation of membrane fouling. This research system treats 15 actual landfill leachates, each working 1.0 h (the same as the total working time of CEM-1). The cation exchange membrane after five runs is denoted as CEM-2. SEM tests and energy dispersive spectroscopy (EDS) analyses were performed on CEM-0, CEM-1 (alkaline chamber side), and CEM-2 (alkaline chamber side) (Figures 10 and 11).

Comparing the SEM images, it can be seen that after running for a certain time, there is scaling on the alkali
chamber side of the cation exchange membrane, and the scaling covers the membrane. Combined with the results of EDS, it was determined that CaCO$_3$ is the main component in the CEM-1 scale, which is consistent with the XRD results. The atomic percentage of Ca element is 17.79%. The atomic percentage of Mg in the CEM-1 scale is 1.43%, which is smaller than that of Ca. There was no obvious peak in the XRD pattern, which suggested that the morphology of Mg(OH)$_2$ was amorphous. The results show that the main component of membrane fouling is a calcium compound, and the contribution of Ca ion to membrane fouling is the largest in this system. This is consistent with the results of previous studies (Ren et al. 2008). The main reason may be that amorphous Mg(OH)$_2$ is not easy to adhere to the film surface. In contrast, after Ca$^{2+}$ forms calcite seeds on the membrane surface, the crystals grow on the membrane surface and become the main component of membrane fouling. Compared with CEM-1 membrane fouling, the membrane fouling of CEM-2 has greatly reduced membrane fouling thickness and membrane fouling area, and crystal growth is poor. The EDS analysis of CEM-2 shows that the atomic percentages of Ca and Mg are 3.39% and 0.84%, respectively. Compared with CEM-1, the content of Ca is significantly reduced. It shows that Mg$^{2+}$ inhibition of Ca$^{2+}$ migration at the beginning of the system is beneficial to reduce membrane fouling. There are two main reasons for this analysis: one is that the inhibition of Ca$^{2+}$ migration leads to a smaller concentration of CaCO$_3$ produced; the second is, compared with Ca$^{2+}$, the amount of Mg$^{2+}$ occupies a major position in the alkali chamber (Mg/Ca larger), and Mg$^{2+}$ will enter calcite seed crystals and form a new crystal surface, inhibiting the growth of calcite crystals. (Zhang & Dawe 2000).

In conclusion, the system is more suitable for landfill leachate with high Mg/Ca content if the influent does not require hardness removal. Landfill leachate with relatively low Mg/Ca can reduce membrane fouling and control the working time of the system before the mass migration of Ca$^{2+}$. Taking the actual leachate in this study as an example,
the control of a single working time is 1.0 h, which can slow down the membrane pollution under the same total operation time.

**CONCLUSION**

1. Humic acid slightly affects the migration of ammonia nitrogen in the system, which is mainly manifested in the adsorption of $\text{NH}_4^+$ by the macromolecular humic acid at the beginning of the system’s work, which reduces its migration rate. And during the operation of the system, the overall humic acid mobility is not high, and due to the low pH of the acid chamber and the drop in the pH of the raw water chamber, a small part of the humic acid precipitates out.

2. The presence of $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ affects the recovery of ammonia nitrogen, but the effect of $\text{Ca}^{2+}$ was less than that of $\text{Mg}^{2+}$ at the same concentration. In the three ionic coexistence systems, the average migration rate of the three ions is $\text{NH}_4^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$. $\text{NH}_4^+$ plays a major role in electromigration. The effect of $\text{Mg}^{2+}$ on the migration effect of $\text{NH}_4^+$ is greater than that of $\text{Ca}^{2+}$ at the same concentration. Low molecular weight cations will have a higher electromigration rate. In the transmembrane process, $\text{Mg}^{2+}$ with a smaller ionic radius has a stronger affinity for the exchange group, which has an advantage over $\text{Ca}^{2+}$ in the competition.

3. The ion migration law in the process of using the system to treat actual landfill leachate is similar to the conclusion for the simulated wastewater experiment, but the pH of the alkali chamber is high. Treatment of 1 volume of actual leachate can remove 86.17% of ammonia nitrogen in the raw water chamber in 3.0 hours, and recover 0.75 volumes of the acid solution and alkali solution in the acid chamber and alkali chamber.
respectively. The recovery rate of ammonia nitrogen in the alkali solution is about 72.55%.

4. The calcium and magnesium ions in the system will scale on the membrane. The components of the scale are mainly calcite (CaCO₃) and amorphous Mg(OH)₂. Ca²⁺ has the largest contribution to membrane fouling. Based on this, the inhibition of Ca²⁺ migration by Mg²⁺ in the initial stage of the reaction system can effectively reduce membrane fouling.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


Wang, X. L., Wang, Y. M., Zhang, X., Feng, H. Y., Li, C. R. & Xu, T. W. 2015 Phosphate recovery from excess sludge by conventional electrodialysis (CED) and electrodialysis with


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