

A Novel Electrochemical Reactor for Nitrogen and Phosphorus Recovery from Domestic Wastewater

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HIGHLIGHTS

- An electrochemical reactor with connected anode and cathode was designed.
- Phosphate and ammonia were concentrated 4–5 times continuously and selectively.
- Concentration differences between chambers were utilized to control the separation.
- Long-term operation with struvite formation was proved to be repeatable.

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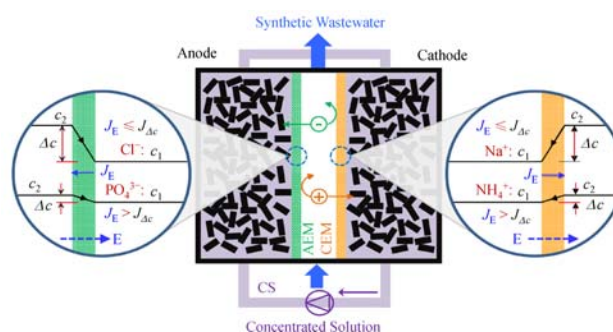
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GRAPHIC ABSTRACT



ABSTRACT

To separate and concentrate NH_4^{4+} and PO_4^{3-} from the synthetic wastewater to the concentrated solution through a novel electrochemical reactor with circulated anode and cathode using the difference of the concentration between electrode chamber and middle chamber. In recent years, the research on electrochemical processes have been focused on phosphate and ammonium removal and recovery. Among the wide range of possibilities with regards to electrochemical processes, capacitive deionization (CDI) saves the most energy while at the same time does not have continuity and selectivity. In this study, a new electrochemical reactor with electrolyte cyclic flowing in the electrode chambers was constructed to separate and concentrate phosphate and ammonium continuously and selectively from wastewater, based on the principle of CDI. At the concentration ratio of NaCl solution between the electrode chambers and the middle chamber (r) of 25 to 1, phosphate and ammonium in concentration level of domestic wastewater can be removed and recovered continuously and selectively as struvite. Long-term operation also indicated the ability to continuously repeat the reaction and verified sustained stability. Further, the selective recovery at the certain r could also be available to similar technologies for recovering other kinds of substances.

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1 Introduction

Nitrogen and phosphorus are both essential elements for all living organisms, which could cause serious eutrophication when introduced into surface waters [1,2]. Meanwhile, previous studies reported that the remaining accessible reserves of phosphate rock was estimated to be completely exhausted in 50–400 years, if the growth of demand remained at only 3% per year [3–5]. Yet the demand for

phosphorus has continued to increase over the past decade, while phosphorus cannot be synthesized and has no substitute in the field of production [6].

Therefore, a wide range of technologies have been adopted to remove and recover phosphate and ammonia from wastewater [7,8]. Among all of them, struvite crystallization has drawn great attention all over the world, which could remove and recover phosphate and ammonia simultaneously [9–11]. Different configurations such as stirred reactors, fluidized bed reactors, and air-agitated reactors have been designed to promote the benefit and efficiency of struvite recovery [12–16].

In recent years, electrochemical processes have also

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been used for phosphate and ammonia removal and recovery, including electrolytic process, electrodialysis (ED), and capacitive deionization (CDI) [17–21]. Electrolytic process was mainly used to treat wastewater with nutrients in high concentration. Electrodialysis (ED) configuration with monovalent selective anion exchange membranes (MVA) was adopted to improve the efficiency of phosphate recovery from a struvite reactor [17]. As an energy efficient and environmental friendly water treatment technology without electrode reaction, CDI has been proved to be effective in removing phosphate ($50\text{--}300\text{ mg}\cdot\text{L}^{-1}$) and ammonia ($400\text{ mg}\cdot\text{L}^{-1}$) from wastewater [19–23]. Based on calculation, the energy consumption for the phosphate treatment with CDI was $\sim 7.01\text{ kWh}\cdot\text{kg}^{-1}\text{ P}$, which was far less than that for the treatment with ED, $\sim 16.67\text{ kWh}\cdot\text{kg}^{-1}\text{ P}$. Nevertheless, CDI was still used to treat wastewater with nutrient in high concentration, while the researches did not show any continuity or selectivity [21,23].

In this study, a new kind of electrochemical reactor with electrolyte cyclic flowing in the electrode chambers, based

on the principle of CDI, was used to separate and concentrate phosphate and ammonium from wastewater. Operating conditions, such as circulating mode, concentration ratio and cycle length were optimized, while long-term operation was investigated to verify the stability and repeatability of the process.

2 Materials and methods

2.1 Reactor construction and material

The electrochemical reactor was constructed with three cubic chambers (Fig. 1(a)): one chamber in the middle with a thickness of 2 cm and a volume of 12 mL was used for flow channel; and two same chambers with thickness of 3 cm and volume of 26 mL on both sides were served as electrode chambers. Both of the electrode chambers were filled with granular activated carbon (1.5 mm, Gongyi Songshan Filter Activated Carbon Factory), while activated carbon cloths and titanium chips were used for

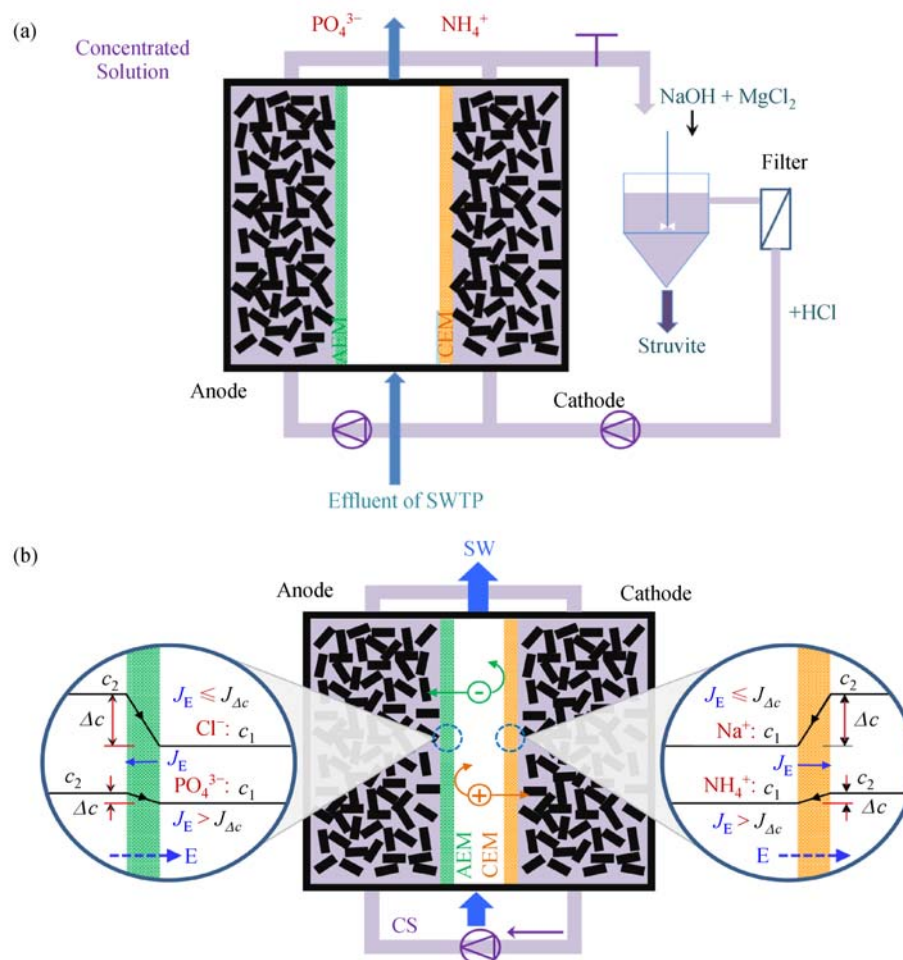


Fig. 1 (a) Schematic diagram of the laboratory-scale phosphate and ammonia recovery system based on electrochemical reactor. (b) The principle of separating and concentrating NH_4^+ and PO_4^{3-} from the synthetic wastewater (SW) to the concentrated solution (CS) using the difference of the concentration between electrode chamber and middle chamber.

current collecting. An anion exchange membrane (AEM) and a cation exchange membrane (CEM) (Shandong Tianwei Membrane Technology Co., Ltd) were used to separate the electrode chambers and the middle chamber.

The synthetic wastewater, as the inflow of middle chamber, was made similar to typical domestic wastewater in nutrient concentration levels, which contained (per liter): 0.02 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 0.02 g $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 0.1 g NH_4Cl , 0.3 g NaCl (approximately $1 \text{ mS} \cdot \text{cm}^{-1}$, phosphorus $5.7 \text{ mg} \cdot \text{L}^{-1}$, nitrogen $26 \text{ mg} \cdot \text{L}^{-1}$, $\text{pH} \approx 6.8$). The initial concentrated solution, as the inflow of electrode chambers, simply contained NaCl , at a concentration from $0.3 \text{ g} \cdot \text{L}^{-1}$ to $15 \text{ g} \cdot \text{L}^{-1}$ according to different r , and was finally determined to be $7.5 \text{ g} \cdot \text{L}^{-1}$ (as described by the experiment results in 3.1 Determination of r in batch operation).

2.2 Operation mode

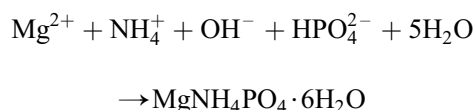
The pre-experiment demonstrated that the concentrating efficiency would be maximized when the anode chamber and cathode chamber were connected and circulated (Fig. S1 and Fig. S2 in Supporting materials). As a result, pH levels in electrode chambers would maintain neutral, which prevented its hindering on the deionizing process.

The electrode chambers were circulated with an external container of 50 mL liquid volume, and the middle chamber was self-circulated with an external container of 5 L liquid volume (Fig. 1(a)). According to the pre-experiment, a voltage of 1 V was applied to the reactor, and the flow rate for each chamber was set up to be $6 \text{ mL} \cdot \text{min}^{-1}$.

To promote the enriching efficiency of phosphate and ammonium, the appropriate concentration ratio of NaCl solution between the electrode chambers and the middle chamber (r) was explored in batch mode operation. Two steps of the test were carried out to obtain the optimal ratio for long-term operation. The pre-test would roughly determine the range of the appropriate ratio, while the final test would determine the optimal ratio for the operation.

In long-term operation, the synthetic wastewater was replaced every 6 days, when the operation of reactor paused. Meanwhile, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (1.8 mg) was added in the extracted water with concentrated ammonium and phosphate.

The pH of the concentrated solution was adjusted to 9.5 with sodium hydroxide solution, with the expectation of a reaction according to the following equation:



After filtration with the filter paper, the struvite can be obtained and the concentrated solution would be adjusted

to neutral and injected back into the electrode chambers (Fig. 1(a)).

2.3 Measurement method

The conductivity meter was used to detect the conductivity of the concentrated solution in the electrode chambers in real-time. (S700, Mettler Toledo, SWISS)

Phosphate was detected by a molybdenum antimony anti spectrophotometric method, while ammonium was detected by water quality determination of ammonium spectrophotometry with salicylic acid. (5B-6C, Lian-hua Tech. Co., Ltd, China)

The precipitate on the filter paper was scanned and analyzed with a scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS). (S-4800, Hitachi, Japan)

3 Results and discussion

3.1 Determination of r in batch operation

The curves of conductivity of the solution in electrode chamber are shown when r changed from 1 to 1, 20 to 1 to 50 to 1 (Fig. 2(a)). When r was set at 20 to 1 and 50 to 1, the slope of the curve obviously decreased, while the slope even turned to be negative at the r of 50 to 1. Meanwhile, the concentrations of phosphate and ammonium were tested every 12 h (Fig. 2(b)). The enriching rate increased obviously when r increased to 20 to 1 in comparison with that of 1 to 1, while it seemed not to change significantly with further increases to 50 to 1.

Furthermore, the changing curves of conductivity at final test were shown under r of 15 to 1, 20 to 1, 25 to 1, and 30 to 1 (Fig. 2(c)). According to the results of the linear regression as the formula:

$$G = kt + b$$

where G is the conductivity of the solution, k is the slope of the line, t is the period of the reaction, and b is the intercept of the line. The slopes of four lines under different ratios were presented to be $0.022 \text{ mS} \cdot \text{h}^{-1}$, $0.0054 \text{ mS} \cdot \text{h}^{-1}$, $-0.0050 \text{ mS} \cdot \text{h}^{-1}$ and $-0.022 \text{ mS} \cdot \text{h}^{-1}$. The absolute value of k was the minimum when r was 25:1, according to the results of the linear regression shown in the figure.

Additionally, the average current through the electrochemical reactor at the r of 25 to 1 was the lowest among four sets of tests, which was only $\sim 0.78 \text{ mA}$ (Fig. 2(d)).

According to Figs. 2(a) and 2(b), when r increased, the electrical conductivity of solution in the electrode chambers increased gradually, while the enriching efficiency of phosphate and ammonia was obviously enhanced. However, when r was 50 to 1, the conductivity of solution in the electrode chambers even decreased,

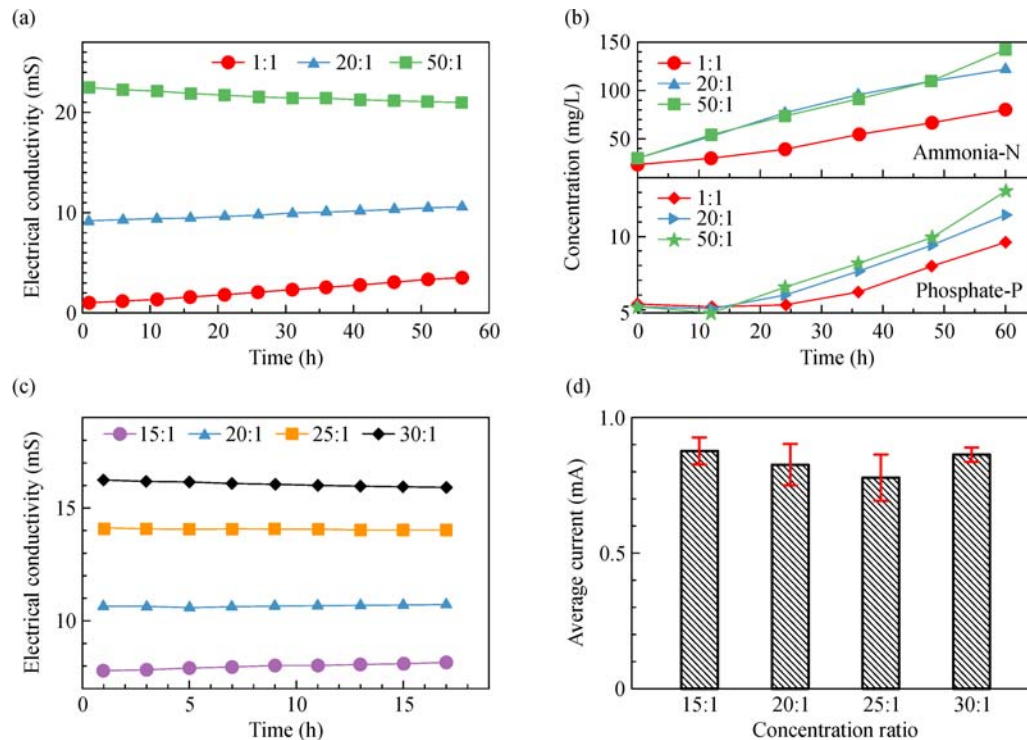


Fig. 2 The changing curves of (a) electrical conductivity at pre-test; (b) concentration of phosphate and ammonia at pre-test; (c) electrical conductivity at final test; (d) average current at final test according to different r_{em} .

which indicated that the ions mostly migrated from electrode chambers to the middle chamber. The enhancement of enriching efficiency was also limited when r was high enough, since no obvious enhancement was observed when r was between the 20 to 1 and 50 to 1. From the above, it could be inferred that there would be an optimal r of around 20 to 1, at which Na^+ and Cl^- were exactly prevented from moving between chambers, and the enriching efficiency of phosphate and ammonia was sufficiently enhanced.

According to Fig. 2(c), the conductivity of concentrated solution maintained stably when the r was 25 to 1, which indicated that Na^+ and Cl^- were precisely prevented from moving between chambers. Meanwhile, the average current proved that the electric energy mainly contributed to the migration of phosphate and ammonium at the r of 25 to 1, with the least energy waste on the migration of Na^+ and Cl^- . In summary, the ratio of 25 to 1 could be chosen as the optimal condition in this experiment, which indicated that the concentration of NaCl in electrode chamber was 25 times of that in the middle chamber ($7.5 \text{ g} \cdot \text{L}^{-1}$).

3.2 Long-term operation and struvite formation

To obtain the appropriate cycle-time-setting for long-term operation, the optimal changes of phosphate and ammonium concentrations in the concentrated solution were detected (Fig. 3(a)). After a nine-day concentrating

process, the curves became gentle and smooth, while the concentration of ammonium-N was $129 \text{ mg} \cdot \text{L}^{-1}$, about five times that of the synthetic wastewater; and the concentration of phosphate-P was $23 \text{ mg} \cdot \text{L}^{-1}$, about four times of the synthetic wastewater. Figure 3(a) also presented that in the concentrating process, the accumulation rates of phosphate and ammonium were both considerable within the first 6 days, thus the cycle time was chosen to be 6 days.

In the long term operation, the synthetic wastewater was replaced every 6 days in order to simulate a continuous operation feed with constant concentration wastewater. With $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ added to the concentrated solution and the pH adjusted to 9.5, white flocculent precipitate clearly appeared in the concentrated solution. The recovery curves presented stable periodicity from the second cycle, especially for phosphate recovery (Fig. 3(b)). The phosphate-P accumulated to $22\text{--}28 \text{ mg} \cdot \text{L}^{-1}$, which was 4–5 times of the initial wastewater for every cycle and could be almost completely removed after struvite formation. However, ammonium was accumulating throughout the entire experiment, since it could not be used in the struvite formation process due to its high initial concentration. Further study should be done to develop an appropriate method to determine what should be done with the residual ammonium.

The precipitate was scanned with SEM (Fig. S3), with a surface morphology that clearly presented itself against the filter paper. In a magnified image of 6000 times, the

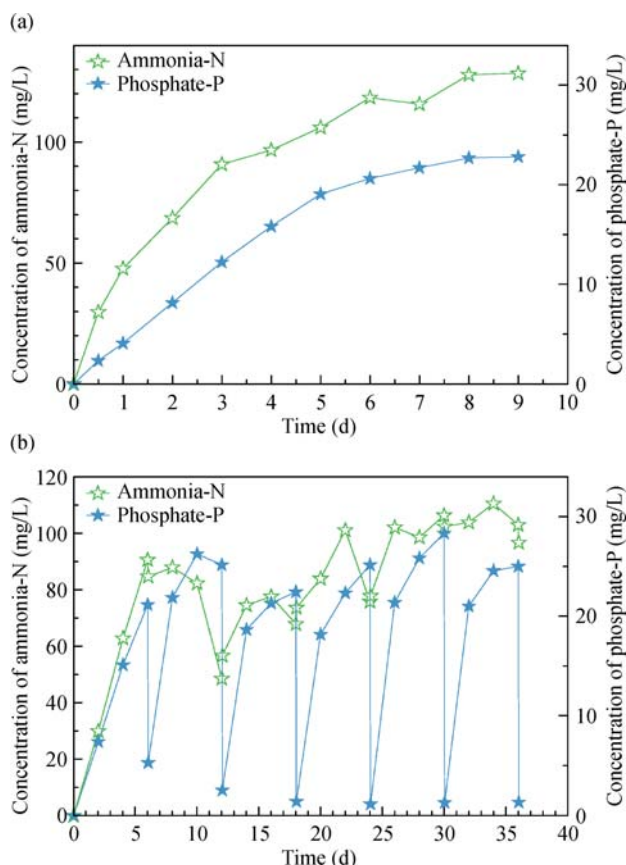


Fig. 3 (a) The phosphate and ammonia concentrating curves in 10 days; (b) The phosphate and ammonia recovery curves in a long-term operation.

precipitate showed dense microstructure. As a semiquantitative detection method, EDS analysis approximately showed the mole ratio of phosphorus, nitrogen, and magnesium (1 to 1 to 1), which conformed with the composition of $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$. However, due to some carbon impurities mixed in the small amount of precipitate, struvite did not present a crystalloid structure. This may be the influence of the fragment from the granular activated carbon or activated carbon cloth.

3.3 Discussion on the principle of separating and concentrating specific ions

According to the above results, it was proved that separating and concentrating phosphate and ammonium by enhancing r was a practical approach. In this experiment, two types of driving forces were used to construct an equilibrium state. When the concentration of NaCl in the electrode chambers increased, Na^+ or Cl^- ions would be driven by both the electric field force and the force against the direction of electric field, which came from the concentration differences. Under the input voltage of 1 V and the ratio of 25 to 1, the two kinds of forces came

to a balance exactly, so that the Na^+ and Cl^- ions would stop moving between chambers. Meanwhile, the reversible Faradaic formations of H^+ and OH^- ions would also occur in the electrode chambers, which would also consume some electricity [24]. However, the free H^+ and OH^- ions in the solution would neutralize into H_2O due to the circulated electrode design.

In this experiment, the r of 25 to 1 was set up to be the initial condition in long-term operation, considering time costs and experiment effects. Actually, this equilibrium state could be attained naturally after long-term running, since NaCl would accumulate in electrode chambers all along.

In particular, according to the results of the experiment, as for a specific kind of ions, the equilibrium state mainly related to the input voltage, the size of the reactor, and r , while electrode modification might also improve the system performance [25]. Further studies would focus on optimizing these four parameters in order to achieve the equilibrium state more easily and quickly.

4 Conclusions

The electrochemical reactor with electrolyte cyclic flowing in the electrode chambers was proved to be available for phosphate and ammonium removal and recovery. An appropriate r was set up to separate and concentrate the nutrients from wastewater selectively and continuously. The phosphate and ammonium was detected to be recovered in the form of struvite, while in the long term operation, the separation and recovery both showed great repeatability. In addition, this kind of electrochemical reactor and the adoption of r can be generalized to separation and recovery techniques for other matters, such as Zn^{2+} , Cu^{2+} from industrial effluent and so on.

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