Removal of Nitrate from Wastewater with Polymer-Enhanced Ultrafiltration (PEUF)

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Abstract. Polymer-enhanced ultrafiltration (PEUF) is an advanced technology for the efficient separation of heavy metal ions and organic matter from outlet water. The removal of nitrate ions from wastewater via PEUF was investigated using polyethyleneimine (PEI) and cationic polyacrylamide (CPAM). When the concentration of NO₃⁻ was 20 mg/L, the dosage of PEI/CPAM was 0.1 wt%, the best rejection were obtained, rejection of NO₃⁻ were 92.8% and 80.2%, respectively, and rejection of PEI and CPAM were 92.3% and 83.3%, respectively. Effect of pH value on NO₃⁻ rejection was obvious, rejection of NO₃⁻ decreased sharply with the increase of pH value. However, there was no obvious changes on the PEI rejection. The PEUF process was considered to be more suitable for nitrate rejection using PEI as a polymer reagent.

1. Introduction

Nitrate pollution of surface water and groundwater has become an increasingly serious environmental problem in both industrialized and developing countries. Therefore, nitrate removal is becoming one of the most critical problems in drinking water treatment. A large number of literatures have introduced a variety of nitrate removal methods, including physical methods, chemical methods, physicochemical methods and biochemical methods, such as ion exchange method, anaerobic-aerobic combination, precipitation, coagulation, membrane separation, etc. [1-4].

One of the methods in which it's worth paying attention is polymer-enhanced ultrafiltration (PEUF). This process has been widely studied and applied in the separation and concentration of wastewater containing metal ions to achieve the purpose of recycling heavy metals [5, 6]. Different from traditional membrane separation technology, PEUF has the advantage of separating low-molecular weight substances (heavy metals, dissolved organic compounds) and even ions from aqueous solution, which is difficult to achieve due to the loose membrane pores of traditional ultrafiltration[7-10].

Our main purpose is to study the process performance of PEUF for treating synthetic effluent containing nitrate. The differential rejection of nitrate and polymer as well as membrane fouling in polyacrylamide (CPAM)/ polyethyleneimine (PEI) system were also comparatively evaluated.
2. Methods and materials

2.1. Chemicals and membrane
Polyethyleneimine (PEI) with a molecule weight (MW) 60000 (50 wt.% aqueous solution) and cationic polyacrylamide (CPAM) with 150000 were purchased from Sigma-Aldrich Chemical Co. Inc. as polymers for removing NO$_3^-$, NaNO$_3$ as NO$_3^-$ was obtained from Tianjin Kermel chemical factory. The characteristics of the used hollow fiber ultrafiltration membrane were as follow: material was polysulfone, MWCO was 6K, max operating pressure was 0.25MPa, pH operating range was 1-14, operating temperature range was 5-50℃, max power of pump was 40W. UF membrane was offered from Yidong Membrane Engineering Equipment Ltd., Dalian, China.

2.2. Procedure
Firstly, NaNO$_3$ solution with a concentration of 20mg/L was prepared. A predetermined concentration of the polymer was then added to the synthetic wastewater. After adequately mixed, the prepared solution was subjected to ultrafiltration membrane. A small laboratory ultrafiltration system was shown in Figure 1. Ultrafiltration experiments were all carried out at room temperature. The operating pressure of all experiments were 30 kPa and the initial volume of synthetic wastewater were all 3.0 L. Circulating filtration method was adopted in the experiment, that is, the retentate solution was reflux to the feed tank, and the permeate flowed into the permeate tank.

After each run, the ultrafiltration membrane was cleaned successively with a certain concentration of acid, alkali and distilled water. After then, deionized water was filtered to determine the permeate flux in order to check the permeability of membrane. When the permeate flux returned to the flux at the beginning of the experiment, the ultrafiltration membrane was cleaned thoroughly.

2.3. Analysis
The concentration of nitrate was measured at 275nm by ultraviolet spectrophotometer[6]. The concentration of the polymer was determined using a TOC meter [2].

2.4. Calculations
Removal efficiency of nitrate/polymer R was defined as:

\[
R(\%) = \left(1 - \frac{c_P}{c_f}\right) \times 100\%
\]

Where $c_P$ (mg/L) is the concentration of NO$_3^-$ or PEI/CPAM in the permeate solution; $c_f$ (mg/L) is the concentration of NO$_3^-$ or PEI/CPAM in the feed solution.
3. Results and Discussion

3.1. Removal of nitrate with PEI

3.1.1. Effect of PEI concentration. The electrostatic interaction between nitrate ions in the solution and the electrical groups in the polymer molecular chain was the primary attribute of polymer for adding in ultrafiltration.

Treatment capacity of proposed process depends on polymer concentration. The influence of PEI concentration on NO_3^- removal rate was presented in Fig. 2. When the concentration of PEI in feed solution increased from 0 wt% to 0.10 wt%, the NO_3^- removal rate immediately increased from 18.7% to 92.8%. It is demonstrated that PEI is an effective polyelectrolyte for removing NO_3^- from aqueous solution.

It is interesting to note that 18.7% NO_3^- is removed in the absence of PEI. This means that in the ultrafiltration process, part of NO_3^- was directly adsorbed on the membrane surface and in membrane pores. The removal rate of NO_3^- remained constant as the concentration of PEI >0.1 wt%. Under the condition of low concentration of PEI, the amount of NO_3^- exceeded the ability of the polymer to bind ions effectively, and free NO_3^- could pass through the membrane pore freely, resulting in poor NO_3^- rejection rate. Obviously, with the increment of the PEI concentration, the sites available for binding NO_3^- increased, which resulted in more ions absorbed by functional groups into retentate[11,12].

![Fig. 2](image_url)  
**Fig. 2** Effect of initial PEI concentration on the rejection of NO_3^- and PEI. (Initial NO_3^- concentration=20 mg/L, pH=3, operating pressure=0.03 MPa)

Rejection of PEI increased first and then decreased slightly when the concentration rose which was higher than that of NO_3^- when PEI<0.1 wt%. This is because the MW of the membrane was smaller than that of the polymer, which enables the polymer to be intercepted. Most polymers larger than the membrane pores were retained on the surface of the membrane and then penetrate into the pores while forming a polymer layer on the surface of the membrane[13]. The lower polymer rejection may be due to the passage of many small polymer monomers through the pores in a high concentration polymer solution [2].

3.1.2. Effect of pH.

Effect of pH on the rejection of NO3- and PEI was shown in Fig.3. The nitrate rejection was substantially reduced with a rise of pH rate. The adding of PEI to an aqueous solution has a positive effect on the NO3- rejection at the pH<4. Under acidic conditions, because the amino group was protonated, the amino groups on the PEI chain would become positively charged, which is good for the
combination of PEI and NO3-. However, the PEI rejection was not significant changed, remained above 88%.

![Effect of pH on the rejection of NO3 and PEI](image1)

**Fig. 3** Effect of pH on the rejection of NO3 and PEI. (Initial NO3 concentration=20 mg/L, initial PEI concentration=0.10 wt%, operating pressure=0.03 MPa)

3.2. Removal of nitrate with CPAM

3.2.1. Effect of CPAM concentration.

As shown in Fig.4, increasing trend of NO3- and CPAM rejection were same as PEI experimental groups. However, the removal efficiency of them were both not as good as that of PEI experimental group. The highest rejection of NO3- and CPAM were 81.7% and 83.5% when CPAM concentration was 0.15 wt%, respectively, which was lower than that of NO3- and PEI 11.1% and 8.8% when PEI concentration was 0.10 wt%, respectively. It is noteworthy that, some flocs were present in the solution when CPAM concentration exceed 0.15%. Although it had no effect on the rejection, membrane hole was blocked and the flux was reduced [14].

![Effect of initial CPAM concentration on the rejection of NO3 and CPAM](image2)

**Fig. 4** Effect of initial CPAM concentration on the rejection of NO3 and CPAM. (Initial NO3 concentration=20 mg/L, pH=4, operating pressure=0.03 MPa)
Fig. 5 Effect of pH on the rejection of NO$_3^-$ and CPAM. (Initial NO$_3^-$ concentration=20 mg/L, initial CPAM concentration=0.10 wt%, operating pressure=0.03 MPa)

As observed in Fig.5, NO$_3^-$ rejection was sharply reduced when pH$>$4.0. This trend was similar to that of PEI group, but the inflection point was different. Compared with PEI group, the removal of NO$_3^-$ by CPAM was not sensitive to pH change. Under pH neutral condition, the NO$_3^-$ removal rate of PEI group was only 49.1%, while that of CPAM group was still 61%. However, when pH$>$4.0, the decline of CPAM rejection was more serious than that of PEI.

4. Conclusion

In this study, nitrate ions were effectively removed from synthetic laboratory wastewater by ultrafiltration membrane combined with two polymers. The influence of types and concentration of polymers and pH values on nitrate removal rate were investigated. Conclusions drawn from the experimental results as follows:

1) Higher nitrate rejection was obtained with larger dosages of polymer introduced into the UF system. For the same dosage, nitrate rejection using PEI was higher than that of CPAM. Polymer rejection was generally higher than that of NO$_3^-$ when the adding dosage $<$0.1 wt%.

2) With the increase in pH values the nitrate rejection was found to be reducing which was more obvious for PEI groups. The effect of pH on rejection of PEI was slighter than that of CPAM.

Overall, the PEUF process was found to be more suitable for nitrate removal using PEI as a polymer agent.

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