



## Mixed-matrix membranes for efficient ammonium removal from wastewaters



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### ABSTRACT

Novel mixed matrix membranes and fibers were fabricated to investigate ammonium removal for the first time from wastewaters especially aquaculture wastewaters. Several approaches were adopted to fabricate these mixed-matrix membranes including a wet phase inversion process as well as pore filling of commercially available membranes. Natural zeolite particles were effectively incorporated into polysulfone polymer matrices. These composite materials are found to be efficient for ammonium removal with high capacity and high stability. No leaching of zeolite materials was detected. These mixed-matrix membranes demonstrate high water flux and are easy to regenerate. Over 90% of total ammonia nitrogen (TAN) can be removed from relatively low TAN concentration aquaculture wastewaters. These novel adsorptive membranes are reusable and exhibit high viability for large scale industrial applications.

### 1. Introduction

Ammonia nitrogen, both the molecular and ionic species ( $\text{NH}_3$  and  $\text{NH}_4^+$ ) is the major protein metabolite from fish. It is excreted through the gills of the fish and fish waste. Total ammonia nitrogen (TAN) excreted depends on the fish species and the amount of proteins in their diet. Ammonia nitrogen also enters into the aquaculture water via bacterial decomposition of organic matter including uneaten feed, dead algae and aquatic plants. Uptake (assimilation) of ammonia by plankton algae and nitrification by bacteria decrease ammonia nitrogen in aquaculture system [1,2]. The unionized  $\text{NH}_3$  is very toxic to aquatic life and needs to be removed from aquaculture waters. Often ammonia concentration is kept below toxic levels ( $\sim 0.05$  ppm) by partial replacement of the water with fresh water as well as by biological conversion of ammonia to nitrate. Bacterial digestion of ammonia is expensive and slow due to the long start-up time. It will also be ineffective when there is sudden spike of ammonia nitrogen. Another major disadvantage of the current practice is the increased water usage as well as high level of TAN discharge into the rivers and streams that cause unchecked algae growth with harmful environmental effects. Further, TAN production will be greatly enhanced when the fish stocking density is high. Finally, frequent replacement of water during transportation of fish with high stocking density will be difficult. On the other hand, both ammonia nitrogen and nitrate are nutrients for plants

and costly to produce. It will be more economical if recycle and reuse of these nutrients are possible. An alternative solution to capture these nutrients and remove them from the aquaculture water will promote water recycle and reuse.

The  $\text{pK}_a$  of ammonium ( $\text{NH}_4^+$ , the protonated conjugate acid of  $\text{NH}_3$ ) is around 9.2. Only a small fraction (around 5% at  $\text{pH}=8$  and temperature= $25^\circ\text{C}$ ) of the total ammonia nitrogen exists as toxic (unionized)  $\text{NH}_3$ . For each pH unit increase, the amount of un-ionized toxic ammonia increases by about 10 times [1,3].

A variety of biological and physicochemical methods have been employed for the removal of ammonia nitrogen from the water systems [4,5]. Biological methods are commonly used to remove ammonium via nitrification–denitrification process by the microorganisms [6,7]. However, the effectiveness of this approach is limited by slow bioconversion process and when significant TAN fluctuations exist [8]. Hydrophobic membrane contactors have been widely used for stripping ammonia from water streams using dilute sulfuric acid as a stripping solution [9–12]. This method is more efficient at higher pH ( $> 10$ ) where significant un-ionized ammonia is present. Thus, the pH of the water is often adjusted using alkaline solutions to enhance the ammonia removal efficiency, and ultimately readjusted to neutral after ammonia removal [13]. However, this requires additional equipment and chemicals with increased operation cost. Ion-exchange process has also occasionally been employed for ammonium removal from waste-

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waters [14–16]. However, most of these processes using organic exchangers suffer from high cost and high maintenance. Therefore, employing cheaper and abundantly available ion exchanger materials such as natural zeolites is cost effective for ammonium removal from wastewaters [17]. Natural zeolites formed from volcanic ashes are porous aluminosilicate minerals containing tetrahedral  $\text{AlO}_4$  and  $\text{SiO}_4$  sites. Replacing a  $\text{SiO}_4$  tetrahedron with a  $\text{AlO}_4$  tetrahedron results in a negative charge which is balanced by a positively cation [18]. Natural zeolites have been investigated to remove  $\text{NH}_4^+$  from municipal, industrial, and aquaculture wastewaters [14,17–27]. However, these zeolites are unstable and can be easily dissolved in water therefore impractical to use directly for ammonium removal in wastewaters. Here mixed matrix membranes incorporating these zeolite particles were fabricated and used for ammonium removal from wastewaters for the first time.

Zeolite 13X is a byproduct from the synthesis of potassium carbonate via hydrothermal treatment of insoluble pot ash ores [21]. The inexpensive and abundantly available zeolite 13X were found to be efficient and effective to remove ammonium ion from synthetic TAN concentration feed solutions [21]. Previous studies [21] show that zeolite 13X adsorption of ammonium ion follows Langmuir isotherm. However, the fit at low ammonium concentration appears to be relatively poor. Here the potential of zeolite 13X for ammonia nitrogen removal in aquaculture wastewaters at low TAN concentration is investigated. Zeolite 13X particles are incorporated into various polymer matrices and their ammonium removal efficacies were determined using synthetic TAN feed solutions. In particular, mixed matrix membranes incorporating zeolite particles were fabricated. Additional steps including zeolite recrystallization and ion exchange were investigated in order to enhance the stability, ammonium removal efficacy and to prevent undesirable zeolite leaching. No leaching of zeolite materials was found and the membranes can be easily regenerated and used repeatedly.

## 2. Experimental

### 2.1. Materials

1-methyl-2-pyrrolidinone (NMP) (Alfa Aesar,  $\geq 99\%$ ), N, N-dimethylformamide (DMF) (VWR,  $\geq 99.8\%$ ), polyethylene glycol (PEG) (Sigma-Aldrich, MW avg. 400 Da), polysulfone (PSU) (BASF, Ultrason® S 6010 P, 75 kDa), polyethersulfone (PES) (BASF, Ultrason® E 6020 P, 60 kDa), ammonium chloride (Alfa Aesar,  $\geq 99\%$ ), liquid phenol (Sigma-Aldrich,  $> 89\%$ ), sodium nitroprusside dihydrate (Fluka,  $\geq 98\%$ ), sodium hydroxide (Amresco), sodium citrate dihydrate (J.T. Baker), sodium hypochlorite (VWR, 4–6%), poly(diallyldimethylammonium chloride) (PDADMAC) (Sigma-Aldrich, Mw~100–200 kDa, 20 wt% in  $\text{H}_2\text{O}$ ), poly(sodium 4-styrenesulfonate) (PSS) (Sigma-Aldrich, Mw~70 kDa), piperazine (PIP) (EMD Millipore), 1,3,5-benzenetricarbonyl chloride (TMC) (Alfa Aesar,  $\geq 98\%$ ), n-hexane (Fisher-Scientific,  $\geq 95\%$ ) were all used as received. Zeolite 13X molecular sieve (Stream Chemicals, 1/16" pellets (Linde 13X)) was grinded (average particle size =1.5  $\mu\text{m}$ ) before usage. PES membranes (PES, MWCO=30 kDa, EMD Millipore) were used for preparation of pore-filled membranes. De-ionized (DI) water (Milli-Q, 18.2 M $\Omega$  cm) was employed for all the synthesis and filtration experiments.

### 2.2. Zeolite 13X preparation and ammonium adsorption studies

The ammonium adsorption kinetics and capacity with mechanically grinded zeolite 13X particles were studied using ammonium chloride ( $\text{NH}_4\text{Cl}$ ) feed solutions varying the time, amount of zeolite and zeolite particle sizes (as shown in the ). In addition, zeolite 13X powders were modified via partial dissolution in NaOH solutions followed by recrystallization using templates [28] to prepare zeolite powders termed RZEO1, RZEO2 and RZEO3. Three sets of 5 g of zeolite powders were

treated for 30 min in 50 mL of 0.4, 0.8 and 1.6 M NaOH solutions. A total of 14.6 g of cetyltrimethylammonium bromide (CTAB) was added to the mixture (CTAB/zeolite ratio of 0.008 mol/g). After 30 min of mixing, solutions were treated hydrothermally at 100 °C for 24 h in a stainless steel reactor. The zeolite powders were then filtered and rinsed several times and dried in the oven.

In a separate experiment, zeolite powders were treated with NaCl solution (10,000 ppm) to exchange all the  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and other cations with  $\text{Na}^+$ . Pristine zeolite as well as re-crystallized and ion exchanged particles were used for ammonium adsorption studies.

### 2.3. Fabrication of mixed matrix membranes

Mixed matrix membranes were prepared using a wet phase inversion process. In denoting the various membranes synthesized in this work, the following naming nomenclature was used: x%PSU–y% zeolite–z. Here, x is weight percentage (wt%) of PSU in the casting solution mixture, y is a the wt% of zeolite 13X with respect to PSU in the casting solution mixture, and z indicates the presence or absence of 'PEG', to denote PEG porogen-containing or PEG-free casting solutions respectively.

To prepare zeolite-PSU mixed matrix membranes using phase inversion, the desired amount of grinded zeolite 13X, with particle size distribution represented in Fig. 1, was suspended in NMP. The mixture was then subject to ultrasonication using a bath sonicator. For certain membrane compositions, PEG was added as a porogen into the casting mixture. Desired amount of PSU was then added. The casting mixture was then stirred until the complete dissolution of polymer was achieved. The solution was then casted onto a glass plate as 300  $\mu\text{m}$  film using a micrometric film applicator. The casted film was immersed into a non-solvent (water) coagulation bath. To prevent shrinkage, casted film was subject to a 45 s evaporation prior to the immersion.

### 2.4. Synthesis zeolite-containing fibers

Polymeric solutions containing zeolite 13X were prepared according to the procedure described earlier for fabricating mixed matrix membranes. Prepared solutions were dispensed into a water bath using 50 mL syringes. The water bath was kept under vigorous stirring to spin the dispensed polymeric solution into continuous thin fibers. Prepared fibers were used in ammonium adsorption experiments using 2 g of fibers and a total of 500 mL of ammonium chloride solutions (7 mg/L of TAN) kept under stirring for 1 h.

### 2.5. Zeolite pore-filled membranes

A total of 0.5 g zeolite 13X powder was suspended in 50 mL DI water and sonicated for 10 min. The suspension was then filtered through a 30 kD PES membrane with the support structure facing up in order to impart the zeolite particles into the membrane macrovoids. Subsequently, the zeolite filled membrane was rinsed thoroughly to remove excess zeolite particles from the surface. The as-prepared zeolite pore-filled membrane was used for ammonium removal studies.

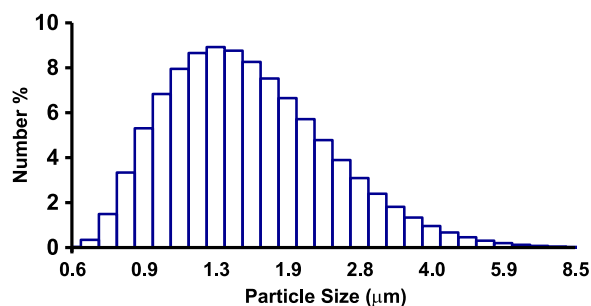


Fig. 1. Typical zeolite 13X particle size distribution after mechanical grinding.

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