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.

Keywords: ammonium removal; mixed matrix membranes; zeolite 13X; pore-filled membranes.

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1. Introduction

Ammonia nitrogen, both the molecular and ionic species (NH_3 and 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 NH_3 is very toxic to aquatic life and needs to be removed from aquaculture waters. Often ammonia concentration is kept below toxic levels (~ 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 pK_a of ammonium (NH_4^+ , the protonated conjugate acid of NH_3) is around 9.2. Only a small fraction (around 5% at $\text{pH} = 8$ and temperature = 25°C) of the total ammonia nitrogen exists as toxic (un-ionized) 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 wastewaters [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 AlO_4 and SiO_4 sites. Replacing a SiO_4 tetrahedron with a AlO_4 tetrahedron results in a negative charge which is balanced by a positively cation [18]. Natural zeolites have been investigated to remove 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 H₂O), 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, $18.2\ \text{M}\Omega\ \text{cm}$) 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 (NH_4Cl) feed solutions varying the time, amount of zeolite and zeolite particle sizes (as shown in the supplementary document). In addition, zeolite 13X powders were modified via partial dissolution in NaOH solutions followed by re-crystallization 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 (10000 ppm) to exchange all the Ca^{2+} , Mg^{2+} and other cations with 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: $x\%\text{PSU}-y\%\text{zeolite}-z$. 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 Figure 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 μm 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 second evaporation prior to the immersion.

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

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.

2.6. Capping of Pore-filled Membranes

The pore-filled membranes can be further capped in order to prevent the particles from leaching using the following two approaches:

A) Interfacial Polymerization (IP) method. The pore-filled membranes were immersed in 1 wt% PIP aqueous solution for 15 min. After removing the membrane from the solution, the excess liquid on the membrane was removed by positioning it vertically. Subsequently, the membrane was placed in the membrane holder horizontally. Organic solvent n-hexane (kept in a freezer at -18 °C) containing a 0.15 wt% TMC solution was charged onto the membrane surface for 5 min during which the interfacial polymerization took place. After the excess TMC was

removed from the membrane surface, the membrane was placed in an oven at 50 °C for 30 min. Finally, the resulting membrane was washed and rinsed thoroughly with DI water before use.

B) Layer-by-layer (LBL) deposition of polyelectrolyte multilayer (PEM). Pore-filled membranes were placed in a stirred dead-end filtration cell (Amicon 8050, membrane area of 13.4 cm²), and 15 mL of polyelectrolyte (PE) poly (diallyldimethylammonium chloride) (PDADMAC) solution (1 g/L) was then poured into the cell and stirred for 5 min. The solution was discarded and the membrane was rinsed thoroughly with DI water. The PE-adsorption and rinsing steps were repeated to form a total of 5 and 10 PE bilayers on the zeolite pore-filled membranes. PE solutions contained no added salt and the pH of the solutions was not adjusted.

2.6. Characterization

2.6.1. Particle size analysis

The size distribution of mechanically grinded zeolite 13X particles suspended in water by bath sonication was recorded using a laser diffraction particle size analyzer (LS 13 320, Beckman Coulter, Inc., USA). The zeolite 13X suspension in DI water was continuously circulated through the optical unit of the instrument.

2.6.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) of mixed matrix membranes and fibers were recorded using an FIB (Focused Ion Beam) Nova Nanolab 200 Dual-Beam Workstation. Cross-sectional images of the membranes were obtained by fracturing the membranes in liquid nitrogen.

2.6.3. Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS was used for elemental analysis of the water samples using a Nu Plasma II mass spectrometer (Nu Plasma™, UK).

2.7. Performances of Mixed Matrix Membranes and Fibers

Filtration experiments were performed using a stirred Amicon 8050 dead-end UF cell (EMD Millipore) connected to a pressurized feed vessel. The system was pressurized with N₂ gas to 40 psi (275.8 kPa). During filtration the feed solution was stirred to minimize concentration polarization. Prior to each test, the membrane coupons were compacted by filtering DI water until a steady permeate flux was attained. ~~The permeate flux was calculated based on the time-derivative of the permeate mass, which was measured by collecting the filtered water on a digital balance (Mettler Toledo, PL602-s) interfaced with a computer. The data from the balance was logged to a computer using BalanceLink software.~~

To evaluate membrane performance, 7 ppm (mg/L, TAN) aqueous solutions of ammonium chloride (NH₄Cl) were filtered through the compacted membranes using the same dead-end filtration cell. Filtration pressure was adjusted for testing different membranes in order to attain equal permeate flux ($\sim 11.2 \text{ L m}^{-2} \text{ h}^{-1}$ (LMH)) and eliminate the effects of residence time on ammonium exchange. Permeate samples were collected at 10 mL interval for each membrane to evaluate its ammonium removal capacity. TAN concentration in the solution was determined via phenol hypochlorite method [29] using a UV–VIS spectrophotometer (Thermo Scientific™ GENESYS 10S UV-Vis).

3. Results and Discussion

3.1. Static TAN Removal with Zeolite 13X Particles

The ammonium adsorption kinetics and capacity using zeolite 13X particles were investigated as shown in the supplementary document. In short, the kinetics for zeolite particles uptake of ammonium ion is rather fast in the time scale of minutes for reaching 90% of TAN adsorption capacity. The adsorption isotherm follows Freundlich model, in contrast to the earlier investigation [21] where the fit at low TAN concentration is poor. As the structure and

composition of zeolites can vary significantly, it is no surprising that the kinetics and thermodynamics of the ammonium ion-exchange process could be quite different. Earlier studies [21] used home-made zeolite 13X whereas commercial product was used directly in the current studies.

Sequential batch TAN removal was then investigated using 150 mg of zeolite once, twice and up to four times with 10 mL 600 ppm (TAN) NH_4Cl solutions. The amount of TAN removed and retained in the solutions was plotted in Figure 2. It can be seen that more TAN was removed when more zeolite was used. Results also show that 150 mg zeolite twice is more effective in removing ammonium than once with 300 mg zeolite. Single extraction using 300 mg zeolite decreased the concentration of TAN to 146 ppm (1.47 mg) from whereas two extractions using the half of this amount decreased the TAN level to 107 ppm (1.07 mg). Single extraction above 300 mg did not show any improvement in ammonium removal. Sequential extraction using 300 mg two times decreased the concentration to 62 ppm (0.62 mg). Furthermore, four sequential extraction steps using 150 mg zeolite each decreased the TAN concentration to 42 ppm (0.42 mg). A system containing multiple cascade steps will efficiently remove ammonium to a lower level compared to a single step removal process. The pH values of the solutions after the equilibration are also shown in Figure 2. It can be seen that the solutions become more basic as more TAN is removed. The initial NH_4Cl solution is slightly acidic due to the following equilibration: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$. However, as the NH_4^+ ions are removed, the equilibration shifts toward the left. As the pH turns more basic, the following equilibration occurs instead: $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$. As a result, the solution turns toward basic to pH as high as above 10.

Figure 2. Sequential TAN removal using various multiples of 150 mg zeolite 13X after 30 min of equilibration with 10 mL 600 ppm (TAN) NH_4Cl solution.

As discussed earlier, the natural zeolite 13X contains many different elements and minerals. The particles are also water solvable. One of the main disadvantages of using natural zeolite is the stability of the particles after treating the wastewater. Table 1 shows the elemental analysis using ICP-MS for 25 ml of the 600 ppm (TAN) NH_4Cl solution before and after equilibration with 300 mg of zeolite 13X. It can be seen that the initial solution contains large amount of Cl^- ion, and less than 1 ppm of Na^+ , K^+ , Ca^{2+} ions as well as some trace amount of S and Si compounds. The presence and amount of these elements are expected for the $(\text{NH}_4)\text{Cl}$ salt dissolved in DI water. However, after 1 h of equilibration with 300 mg zeolite 13X, the Cl^- concentration further increases due to the dissolution of some of the zeolite particles. The Na^+ ion concentration increases from 0.8 ppm to almost 300 ppm due probably both the ammonium exchange and zeolite dissolution. Moreover, there are large amount of S, Si and P compounds in

solution probably resulting from the particle dissolution. There are also many metal ions being exchanged/dissolved in the solution as shown in Table 1. Clearly, the natural zeolite particles are not stable and dissolution is occurring strongly within one hour of equilibration in water. In order to use zeolite particles practically for ammonium removal for wastewater treatment, additional steps are needed in order to stabilize these particles and prevent them from leaching into the solution.

Table 1 Elemental ICP-MS analysis of water sample containing 600 ppm (TAN) NH_4Cl before and after its equilibration with 300 mg zeolite 13X

Element/Ion Type	Initial Concentration (C_i, ppm)	Final Concentration (C_f, ppm)
Cl^-	1293.0	1457.0
Na^+	0.8	297.0
S	0.1	65.6
Si	0.2	39.2
P	0.0	19.6
Al^{3+}	0.0	10.7
Mg^{2+}	0.0	6.9
$\text{Fe}^{2+}/\text{Fe}^{3+}$	0.0	3.0
K^+	0.5	2.8
B	0.0	2.4
Ca^{2+}	0.3	1.6
Cr	0.0	0.2

3.2. Treated Zeolite 13X Particles for Ammonium Removal

Unmodified zeolite 13X particles, recrystallized zeolites at different NaOH concentrations, RZEO1, RZEO2, RZEO3, and 1 M NaCl solution treated zeolite particle were investigated for their capacities of ammonium removal from aqueous solutions. For each sample, a total of 0.5 g zeolite powder was added into 150 mL of ammonium chloride solution (600 ppm TAN) and stirred vigorously for 1 h. Water samples were then filtered through 0.2 micron filters to remove

dispersed zeolite particles in the solutions. Ammonium removal capacity of pristine zeolite as well as re-crystallized and ion exchanged particles are shown in Figure 3. Among all the modifications, zeolite particles treated with 1 M NaCl solution showed highest enhancement in TAN removal capacity.

Figure 3. TAN removal capacity of pristine and modified zeolite particles.

3.2. Mixed Matrix Membranes Incorporating Zeolite 13X Particles

Several mixed matrix membranes were prepared according to the composition shown in Table 2. SEM images of cross-sections and planar view of the skin of mixed matrix membranes with 30 wt% loading of zeolite 13X are shown in Figure 4. It can be seen that zeolite 13X particles are uniformly dispersed within the walls of membrane's finger-like macropores. Addition of PEG leads to the formation of a more porous skin layer. PEG is very hydrophilic and can easily diffuse into the water in the coagulation bath leading to the formation of more porous

membranes [30]. Incorporating more than 50% zeolite into the casting solution results in membranes with weak mechanical strength and low stability.

Table 2. Composition of the casting solutions for fabricating the mixed matrix membranes

Identification code	PSU (g)	Zeolite 13X (g)	PEG (g)	NMP (g)
15%PSU-30%Zeolite	2.25	0.675	0	12.75
15%PSU-40%Zeolite	2.25	0.900	0	12.75
15%PSU-50%Zeolite	2.25	1.125	0	12.75
15%PSU-50%Zeolite (NaCl) [*]	2.25	1.125	0	12.75
15%PSU-30%Zeolite-PEG	2.25	0.675	2.25	10.50

^{*} NaCl-treated zeolite particles were used for fabricating this membrane

Figure 4. Surface (a-b) and cross view (c-f) SEM images of composite membranes: 15%PSU-30%Zeolite (a, c, e); 15%PSU-30%Zeolite-PEG (b, d, f).

In order to determine the capacities for ammonium removal during filtration, the membranes were cut into disks with 2 inch in diameter. The mixed matrix membranes were initially compacted by filtering DI water until a steady permeate flux was attained. These membranes were then used in the subsequent ammonium removal filtration experiments. DI water flux and ammonium removal performances of the prepared membranes are shown in Figure 5 following the protocol discussed earlier. To exclude the effect of residence time on TAN adsorption, trans-membrane pressure (TMP) was adjusted to obtain the same flux (11.2 LMH) for different membrane samples during the ammonium removal filtration experiments. As can be seen Figure 5a, the DI water flux is around 15 LMH/bar for the membrane with 30% zeolite loading. The DI water flux decreases to around 5 LMH/bar when zeolite loading increases to 40% and finally to 50%. The difference in fluxes for membranes with 40% and 50% zeolite loadings is negligible. The decrease in water flux at higher zeolite loadings is due to the denser membranes formed at higher concentrations of zeolite particles. The cations from the zeolite particles interact strongly with the negatively charged O atoms in PSU leading to the formation of a higher viscous casting solution and subsequent a slower phase inversion process forming membranes with less porosity [31]. It can also be seen that flux is much higher for the membrane formed in the presence of PEG as the membrane porosity is much higher. Figure 5b shows the percentage TAN removal using mixed matrix membranes with 30-50% zeolite loadings. The capacities for 50% zeolite loading membranes after post-treated with 1 M NaCl solution as well as after adding porogen PEG in the casting solution were also shown. The percentage TAN removal is plotted as a function of the feed NH_4Cl volume processed ranging from 10 to 100 mL. It can be seen that the higher the zeolite loading, the higher the ammonium removal capacity. The mixed matrix membrane post-treated with 1 M NaCl has the highest

capacity. The membrane with PEG has the lowest capacity. As mentioned earlier, ammonium exchange capacity increases after the cations in zeolite particles have exchanged with the Na^+ ions. Na^+ ion has a similar size to NH_4^+ and is generally much more mobile than the divalent cations leading to a higher NH_4^+ exchange capability. The mixed-matrix membrane formed with PEG tends to have a lower amount of zeolite incorporated due to the stronger zeolite-PEG interaction mediated by the cations. As a result, the highly hydrophilic PEG polymers together with zeolite particles are retained in the aqueous phase leading to the lower zeolite incorporation into the membrane. However, for all the membranes fabricated, the percentage TAN removal decreases as the feed volume increases. The higher capacity membrane has a higher initial removal and has slower decline over time. The initial percentage removal is lower for the lower capacity membrane with a much higher rate of decline. Figure 5c shows the normalized TAN removal capacity per membrane surface area in mg/m^2 for the first 100 mL of feed solutions.

Figure 5. DI water flux (a), ammonium removal (b) and ammonium removal capacity (c) for composite membranes.

ICP-MS analysis was also performed for the permeate samples collected for the two mixed matrix membranes prepared with 50% loadings of pristine (membrane A) and NaCl-treated zeolite 13X particles (membrane B) respectively as shown in Table 3. It can be seen that there is no leaching of the cations into the filtrate in both cases. The permeate solutions collected only contain Na^+ , Cl^- ions and 0.1 ppm or less Ca^{2+} ion. This is a clear advantage compared to use zeolite particles directly for ammonium removal. These mixed matrix membranes can also be regenerated by filtering 1 M NaCl solution through the membranes followed by rinsing with DI water. The regenerated membranes exhibit reproducible TAN removal capacities and no cation was observed to leach out from the zeolite particles.

Table 3. ICP-MS results of the initial feed solution and various permeates. Membranes A and B denote mixed matrix membranes prepared using 50% loading of pristine and NaCl-treated zeolite 13X respectively

Mineral	Concentration (ppm)				
	Feed	Permeate			
		Membrane A	Membrane B	Membrane B 1 st regeneration	Membrane B 2 nd regeneration
Cl⁻	7.0	17.3	6.9	9.6	9.1
Na⁺	0.0	11.4	5.8	5.5	5.1
S	0.0	0.0	0.0	0.0	0.0
Si	0.0	0.2	0.0	0.0	0.0
P	0.0	0.0	0.1	0.0	0.0
Al³⁺	0.0	0.0	0.0	0.0	0.0
Mg²⁺	0.0	0.0	0.0	0.0	0.0
Fe²⁺/Fe³⁺	0.0	0.0	0.0	0.0	0.0
K⁺	0.0	0.0	0.0	0.0	0.0
B	0.0	0.0	0.0	0.0	0.0
Ca²⁺	0.0	0.1	0.07	0.0	0.0
Cr	0.0	0.0	0.0	0.0	0.0

Since the mechanism for TAN removal by zeolite particles is cation-exchange, the presence of other cations in solution will likely affect the removal efficiency and capacity. The performance of the mixed matrix membranes in the presence of other cations was investigated. Competitive binding experiments in the presence of Na^+ , Ca^{2+} , and Mg^{2+} ions were conducted since these ions exist commonly in wastewaters [16]. Figure 6(a) shows the percentage TAN removal via filtration in the presence of Na^+ ion for the mixed matrix membranes with 30-50% zeolite loadings. The feed solution contains 0.43 meq of NH_4Cl and NaCl . TMP was adjusted so that the same permeate flux was obtained for all the membranes in order to exclude the effect of residence time (kinetics) on TAN removal performance. All membranes showed a lower percentage TAN removal in the presence of Na^+ ion. The membrane prepared with NaCl -treated particles (15%PSU-50%zeolite (NaCl)) showed the highest percentage TAN removal even though there is an obvious degradation in the performance when Na^+ ion is present. The performances for other mixed-matrix membranes demonstrate much lower percentage of TAN removal. This is probably due to the fact that Na^+ ion competes with NH_4^+ ion for adsorption on zeolite. If the zeolite has been treated with Na^+ , the presence of Na^+ in solution can no longer compete with NH_4^+ ion for adsorption on the zeolite particles. The thermodynamic equilibrium process dictates the amount of ions adsorbed and the amount of ions in the solution. The membranes with NaCl -treated zeolite particles were also investigated for competitive adsorption of the divalent Mg^{2+} and Ca^{2+} ions. The feed solutions containing 0.1 meq of NaCl , MgCl_2 and CaCl_2 respectively were added to 6 ppm TAN solutions and filtration experiments were performed to determine the amount of TAN removed. Figure 6(b) shows percentage TAN removal of 15%PSU-50%zeolite (NaCl) membrane in the presence of competitive cations. It seems that Ca^{2+} ion has the strongest reduction on TAN removal followed by Mg^{2+} and Na^+ ions.

Figure 6. Competitive TAN removal performance of mixed matrix membranes: (a) different mixed-matrix membranes using a feed containing 0.43 meq of NH_4Cl and NaCl ; (b) 15%PSU-50% zeolite (NaCl) membrane using a feed containing 0.43 meq of different salts.

The effects of ion specificity on TAN removal demonstrate that different ions due to their different sizes and charges have different interactions with the zeolite particles. The divalent ions have a stronger electrostatic interaction with the negatively charged tetrahedral O atoms in zeolite than the monovalent ions. As a result, Mg^{2+} and Ca^{2+} ions bind more strongly to the zeolite than the monovalent NH_4^+ and Na^+ ions leading to a decrease in the number of NH_4^+ ions that can be adsorbed. In addition, the adsorption of the doubly charged Mg^{2+} and Ca^{2+} ions will lead to a stronger electrostatic repulsion of the positively charged NH_4^+ ion. Finally, the adsorption to zeolite is slightly more favorable in the presence of Mg^{2+} ion than the corresponding Ca^{2+} ion. This is due to the fact that Mg^{2+} ion has a higher hydration free energy than the Ca^{2+} ion leading to a more favorable adsorption of the Ca^{2+} ion by the zeolite [32].

3.3. Zeolite 13X-PSU Fibers

Besides mixed matrix membranes fabricated using phase inversion method, other approaches to incorporate zeolite particles such as forming mixed fibers were also attempted and compared with the performance of mixed matrix membranes. Several zeolite 13X-fibers with zeolite loading ranging from 30% to 50% with and without PEG were spun from polymeric solutions with the compositions reported in Table 4. SEM images of prepared fibers with 30% zeolite 13X loading are shown in Figures 7(a) and 7(b). It can be seen that fibers have a diameter of about 450 μm . It appears that zeolite 13X particles are uniformly distributed throughout the fiber. These fibers were used directly for static TAN removal investigation using 500 mL 6 ppm (TAN) NH_4Cl stock solutions. Fiber TAN removal capacity was calculated by the amount of TAN removed divided by the weight of dry fiber. The capacities from these fibers are shown in Figure 7(c). The results show that incorporating PEG in the polymer solutions lead to a reduction

in TAN removal capacity from 1.84 mg/g to 1.58 mg/g for the 15%PSU-30%Zeolite fibers. As described earlier, this can be attributed to the higher zeolite 13X loss during the phase inversion process when PEG was used. Increasing zeolite content in the fibers resulted in an increased TAN removal capacity due to the availability of more adsorption sites. Increasing polymer content resulted in the reduction in TAN removal capacity due probably to the formation of denser fibers leading to higher particle occlusion and lower particle accessibility.

Table 4. Composition of zeolite 13X-PSU fibers

Identification code	PSU, g	Zeolite 13X, g	PEG, g	NMP, g
15%PSU-30%Zeolite	2.25	0.675	0	12.75
15%PSU-30%Zeolite-PEG	2.25	0.675	2.25	10.50
18%PSU-30%Zeolite-PEG	2.70	0.810	2.25	10.05
18%PSU-40%Zeolite-PEG	2.70	1.080	2.25	10.05
18%PSU-50%Zeolite-PEG	2.70	1.350	2.25	10.05
20%PSU-30%Zeolite-PEG	3.00	0.900	2.25	9.75

Figure 7. SEM images of prepared 18%PSU-30%zeolite-PEG composite fibers (*a* and *b*); (c) TAN removal capacity of PSU-zeolite 13X composite fibers at different zeolite loadings, PSU content, with and without PEG.

3.4. Zeolite Pore-filled Membranes

Since the pores on the backside of asymmetric 30 kDa PES membranes are larger than the zeolite 13X particles investigated here, these pores were then used to fill zeolite particles for TAN removal studies. Since the pore size in the membrane barrier layer is generally smaller than these zeolite particles, zeolite particles are therefore retained inside the membrane if the filtration is performed with the membranes backside up. Figures 8(a) and 8(b) show the SEM images of a pore-filled membrane. These pore-filled membranes were compacted by filtering DI water until a

steady permeate flux was attained. The membranes were then used for ammonium removal filtration experiments. Membranes showed average DI water flux of 490 LMH/bar. In order to determine the stability of these pore-filled membranes, membranes were regenerated via filtration of NaCl solution (10 g/L) once they have been used for TAN removal. Repeated adsorption/regeneration cycles were carried out. Results of TAN removal performance for a pore-filled membrane with repeated removal/regeneration cycles are shown in Figure 8 (c). A total of 100 mL NH_4Cl feed solution (7 ppm TAN) was filtered through the membranes. Membranes showed reproducible TAN removal performances over repeated cycles implying minimal particle loss during the filtration experiments. Percentage TAN removal all reached above 90% during the sequent regenerations. ICP-MS analysis (not shown) also confirmed that particles did not leach out from the pore-filled membranes.

Figure 8. Scanning electron microscopy (SEM) images of the cross-section (*a*) and surface (*b*) of pore-filled membrane. The performance of TAN removal with these pore-filled membranes over repeated removal/regeneration cycles (*c*).

3.5. Capping of the Pore-filled Membranes

In order to permanently keep the zeolite particles inside the membrane pores, membranes pores at the backside were capped by depositing polyelectrolyte multilayers (PEM) and by interfacial polymerization (IP). Capped membranes were compacted by filtering DI water until a steady permeate flux was attained. The membranes were then used to conduct ammonium removal filtration experiments. A total of 100 mL NH_4Cl solution with 7 ppm TAN was filtered through the membranes. DI water flux and TAN removal performance of the prepared membranes are shown in Figure 9(a) and 9(b) respectively. Membranes capped via IP method showed a lower DI water flux and a lower TAN removal capacity compared to the corresponding uncapped

membranes. The lower flux is probably due to the fact that IP forms a dense film on membrane back surface leading to the low permeability. A decrease in TAN removal capacity for IP capped membranes is probably due to the partial occlusion of the particles and thus reduced accessibility of the zeolite particles. Membranes capped via the layer-by-layer deposition of polyelectrolyte showed reduced DI water flux than the uncapped membranes, but higher flux than the IP capped membranes. The TAN ammonium removal capacity for the PEM capped membrane is similar to those of uncapped membranes. This is due to the high porosity of the PEM films deposited without reducing the accessibility of the zeolite particles. As a result, comparable TAN removal capacities were obtained. Increasing the number of bilayers from 5 to 10 resulted in a decrease in DI water flux which is attributed to increased thickness and therefor a higher permeation resistance. Increasing the number of bilayers did not have any effect on TAN removal capacity of PEM capped membranes.

Figure 9. DI-water flux (*a*) and TAN removal performance (*b*) of uncapped and capped pore-filled membranes.

3.6. Performance Comparison

Three different methods have been used to incorporate zeolite 13X particles into polymeric matrices for TAN removal from aquaculture wastewaters. In order to compare the performances of mixed-matrix and pore-filled membranes as well as composite fibers, their TAN removal capacities defined by mg TAN removed per gram of zeolite material used are shown in Table 5. As can be seen, the capacity for TAN removal is lowest for the composite fibers. Mixed-matrix membranes formed by phase inversion show highest TAN removal capacity with pore-filled membranes in between. However, the pore-filled membranes have higher TAN removal capacities per membrane surface area and demonstrate higher fluxes.

Table 5. Comparison of TAN removal capacities of composite adsorbents defined as mg TAN removed per g of zeolite for NH_4Cl solutions containing 7 ppm TAN

Adsorbent	TAN removal capacity (mg/g _{zeolite})
Composite fiber (15%PSU-50%Zeolite)	5.4
Pore-filled membrane	10.4
Mixed matrix membrane (15%PSU-50%Zeolite)	19.8

4. Conclusions

Zeolite 13X has been shown to be effective in removing ammonium from wastewaters, particularly fishery water with low concentration of TAN. The stand-alone zeolite 13X particles show leaching of ions and other elements to water thus unsuitable for ammonium removal in water and in particular for recirculating aquaculture wastewaters. Here three different approaches have been used to incorporate these zeolite particles into polymer matrices forming stable mixed-matrix membranes and composite fibers. PSU based mixed matrix membranes were fabricated via phase inversion. Adding PEG resulted in membranes with higher permeability but lower TAN removal capacity. Increasing zeolite particle loading resulted in a decreased permeability but enhanced TAN removal capacity. These membranes are stable and can be regenerated using NaCl solution. No degradation of performance was observed after regeneration compared to the initial run. Composite fibers were synthesized and effective for TAN removal. However, the capacity is somewhat lower compared to mixed matrix membranes. Pore-filled membranes were also fabricated and capped via IP and PEM deposition. IP capping resulted in significant flux decline and reduction in TAN removal capacity whereas PEM capped membranes demonstrated no reduction in TAN removal capacity. The TAN removal capacity for these membranes and fibers follows: composite fibers < pore-filled membranes < mixed matrix membranes.

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- Mixed matrix membranes for efficient capture of ammonium ion from wastewaters
- No leaching of incorporated natural zeolite particles
- Membranes are stable and can be easily regenerated