



Zeolite-Functionalized Polyacrylonitrile Nanofiber Composite Membranes for Ammonium Removal: A Comparative Study of Dispersion and Electrospinning-Integration Methods

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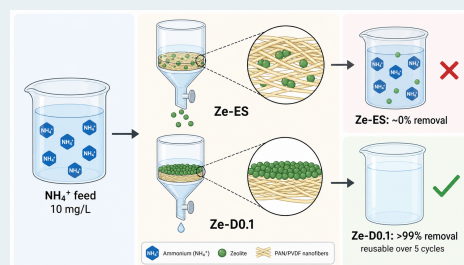
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ABSTRACT

Eutrophication driven by ammonium (NH_4^+) accumulation in surface waters calls for decentralised, passive removal technologies that combine high capacity with simple operation. We compare two routes for incorporating natural clinoptilolite zeolite into polyacrylonitrile (PAN) nanofiber composite membranes for NH_4^+ removal by dead-end vacuum filtration: *dispersion* of zeolite onto a preformed PAN/PVDF substrate (Ze-Dx, $x = 0.01, 0.05, 0.1$ g) and *electrospinning-integration* of zeolite into the PAN dope prior to spinning (Ze-ESx, $x = 0.3, 0.5$ g). FTIR, SEM, and water contact angle data show that the dispersion route places zeolite at the upstream surface, producing a uniform and strongly hydrophilic interface (WCA as low as $(32.8 \pm 4.1)^\circ$ for Ze-D0.1 vs. $(83.0 \pm 0.9)^\circ$ for the unmodified PAN/PVDF control), whereas the electrospinning-integration route encapsulates a substantial fraction of the zeolite inside the fibre matrix and aggregates at higher loadings. At a feed concentration of $C_0 = 10$ mg/L, Ze-D0.1 is the only formulation that combines near-quantitative first-cycle removal with sustained performance ($\geq 47\%$ by cycle 5 over five consecutive cycles), while both electrospinning-integration samples collapse to zero removal within a few cycles through zeolite leaching, a mechanism corroborated by SEM. A concentration study on Ze-D0.1 across $C_0 = 2$ mg/L–15 mg/L reveals essentially quantitative and reusable removal at 2 mg/L and progressive saturation above 10 mg L⁻¹. For NH_4^+ capture, surface dispersion is therefore the preferred integration route, extending a previously established dye-removal nanofiber platform to nutrient species.

Keywords: nanofiber membrane; natural zeolite; ammonium removal; vacuum filtration; electrospinning; polyacrylonitrile



1. Introduction

Eutrophication is a persistent and globally distributed water-quality problem driven by the accumulation of nitrogen species in surface waters [1]. In aquatic systems at near-neutral pH, ammonium (NH_4^+) is the dominant inorganic-nitrogen species and the entry point for the nitrogen cycle through nitrification [2]. Anthropogenic inputs—industrial discharge, agricultural runoff, livestock effluent, and municipal wastewater—routinely enrich natural waters with NH_4^+ above the assimilation capacity of receiving ecosystems [3,4]. The ensuing algal blooms and their decomposition draw dissolved oxygen below the thresholds required by aquatic biota, producing hypoxic and anoxic zones that degrade biodiversity and compromise downstream water uses [5,6,7]. Controlling the NH_4^+ load that reaches receiving waters is therefore a precondition for sustainable water-quality management, and is increasingly a regulatory target for decentralised and on-site wastewater handling.

Existing NH_4^+ removal technologies fall into three broad classes. Physical approaches include air stripping, ion exchange, membrane separations, capacitive deionisation, and membrane bioreactors [8]. Chemical approaches include stru-

vite precipitation, electrochemical oxidation, and electrocoagulation [9]. Biological approaches encompass microalgal uptake, the anammox pathway, bioelectrochemical systems, and treatment with photosynthetic bacteria [3]. Each class carries well-documented limitations: sensitivity to pH and temperature fluctuations, slow kinetics relative to industrially acceptable residence times, secondary waste or brine streams, and specialised microbial consortia that are not robust to real-world feed variability [3]. Among these, adsorption remains attractive for decentralised and point-of-use treatment because the unit operation is simple to implement, tolerant to feed composition variability, and readily engineered into passive filtration geometries.

Natural zeolites, particularly those of the clinoptilolite type, have a long-established capacity for NH_4^+ uptake through cation exchange on the aluminosilicate framework [10,11,12], and their high cation-exchange capacity makes them competitive with synthetic adsorbents for a wide range of water-treatment and environmental applications [13,14,15]. Prior work from our group demonstrated that a desiccated natural zeolite from Lampung (Indonesia) reaches NH_4^+ adsorption capacities of 22 mg g⁻¹ from

aqueous solution [16], and independent column studies report 60 %–80 % removal at optimal operating conditions for zeolite beds packed with treated municipal effluent [17,18]. Loose-powder deployment, however, has three practical limitations in flow-through applications: particles require downstream separation, the adsorbent bed introduces pressure drop proportional to its depth, and fine fractions migrate into the treated effluent. Integrating the adsorbent into an engineered membrane format can address all three limitations simultaneously. Electrospun polyacrylonitrile (PAN) nanofiber mats are a versatile platform for this purpose: their high surface-area-to-volume ratio, tensile robustness, and compatibility with common adsorbent slurries make them a natural host for cation-exchange particles [19,20,21,22], and hybrid nanofiber architectures have been developed across a wide range of water-treatment targets [23,24]. Prior exemplars combining zeolite with PAN- or PVDF-based matrices span from recyclable catalysis [25] to proton-conducting composite membranes [26], silica-modified aerogel fibres for coloured wastewater [27], and more recent antibacterial and air-filter designs [28]. Our group has recently demonstrated a PAN/PVDF–zeolite composite platform for efficient dye removal from aqueous streams [29,30], but its application to nutrient-species capture—specifically NH_4^+ —has not been explored.

Two conceptually different methods can be used to integrate particulate adsorbent into an electrospun polymer matrix. In the *dispersion* method, particles are deposited on the upstream surface of a preformed nanofiber substrate by vacuum-assisted coating. In the *electrospinning-integration* method, particles are suspended in the polymer dope prior to spinning and are encapsulated inside the fibres during jet elongation. The two routes are not interchangeable: dispersion preserves unrestricted access to the particle surface but relies on relatively weak mechanical attachment, while electrospinning-integration stabilises the particle within the fibre but may bury a large fraction of the adsorption-active surface inside the polymer. Which route is preferable depends sensitively on the adsorbate, the filtration geometry, and the mass-transport regime. For dye removal from aqueous streams both routes have been reported to work in our lab's earlier studies [29] [30]. For NH_4^+ capture, where the active step is ion exchange at exposed aluminosilicate sites rather than diffusion of a bulky organic dye through the matrix, the methodology question has not been systematically resolved, and the outcome is not obvious from the existing dye-removal literature.

Here, we address that gap. We fabricate two parallel series of zeolite-PAN composite nanofiber membranes—Ze-Dx by surface dispersion of natural zeolite onto a preformed PAN/PVDF substrate, and Ze-ESx by electrospinning-integration of zeolite into a PAN dope, where x denotes the zeolite mass used in the batch. All membranes are characterised by Fourier-transform infrared spectroscopy to verify component incorporation, by scanning electron microscopy to image particle distribution across the fibre network, and by water contact angle to quantify the functional hydrophilicity of each surface. NH_4^+ removal performance is then evaluated in a dead-end vacuum filtration geometry, first as a screening across all formulations at fixed feed concentration and then as a concentration- and reusability-dependence study on the best-performing sample. We show that the two fabrication routes produce qualitatively different surface-availability regimes, that the dispersion route at the high-

est zeolite loading (Ze-D0.1) alone delivers sustained near-quantitative NH_4^+ removal at low feed concentrations with good reusability, and that the electrospinning-integration route fails outright due to progressive zeolite leaching during flow. These findings extend our group's prior Ze-PAN/PVDF dye-removal platform to nutrient capture and resolve the method-selection question, for the specific case of NH_4^+ removal, in favour of surface dispersion.

2. Materials and Methods

2.1 Materials

Polyacrylonitrile (PAN, $M_w = 150000$ g/mol, Sigma-Aldrich) and N,N-dimethylformamide (DMF, $\geq 99\%$, Merck) were used for the preparation of the PAN dope solution. Natural zeolite of the clinoptilolite type, sourced from PT Paragon Perdana Mining (Lampung, Indonesia) and ground to a particle size of 200 mesh, was used as the active adsorbent. Ammonium chloride (NH_4Cl , $M_w = 53.49$ g/mol, Merck) was used to prepare ammonium-bearing feed solutions, and Nessler's reagent (Merck, for ammonium salts) was used for colorimetric NH_4^+ quantification. A commercial poly(acrylonitrile)/poly(vinylidene fluoride) (PAN/PVDF) composite nanofiber membrane served both as the support substrate for the dispersion method and as an unmodified control in filtration tests. Deionized water was used throughout.

2.2 Membrane fabrication

Two complementary routes for integrating zeolite into the PAN nanofiber matrix were compared (Fig. 1): (i) direct *electrospinning-integration* (ES), in which zeolite particles were blended into the PAN dope prior to spinning, and (ii) surface *dispersion* of zeolite particles onto a preformed PAN/PVDF substrate. The resulting membranes are denoted Ze-ESx and Ze-Dx, respectively, where x is the zeolite mass (in grams) used per batch.

2.2.1 PAN dope solution

A PAN dope was prepared by dissolving 0.6 g of PAN in 10 mL of DMF in a beaker inside a fume hood. The beaker was sealed with parafilm to prevent solvent evaporation and stirred on a magnetic stirrer at 500 rpm and 60 °C for 2 h until a homogeneous, viscous solution was obtained. For the electrospinning-integration method, zeolite (0.3 g or 0.5 g, yielding samples Ze-ES0.3 and Ze-ES0.5, respectively) was then added stepwise under continued stirring until the particulate phase was visually uniformly suspended.

2.2.2 Electrospinning

Nanofiber membranes were fabricated using a single-needle electrospinning setup. A grounded iron collector plate was covered with aluminium foil to facilitate peel-off of the deposited fibres. The dope solution was loaded into a syringe mounted on a syringe pump, and the needle tip-to-collector distance, applied voltage, and feed rate were set to fixed values across all experiments. An applied voltage of 9 kV and a feed rate of $0.5 \mu\text{m s}^{-1}$ were used throughout. Electrospinning continued until the syringe was fully discharged, after which the voltage was ramped down stepwise to 0 kV to avoid corona damage to the freshly deposited fibres. The collected nanofiber mat was peeled from the aluminium foil and stored in a sealed bag prior to further use.

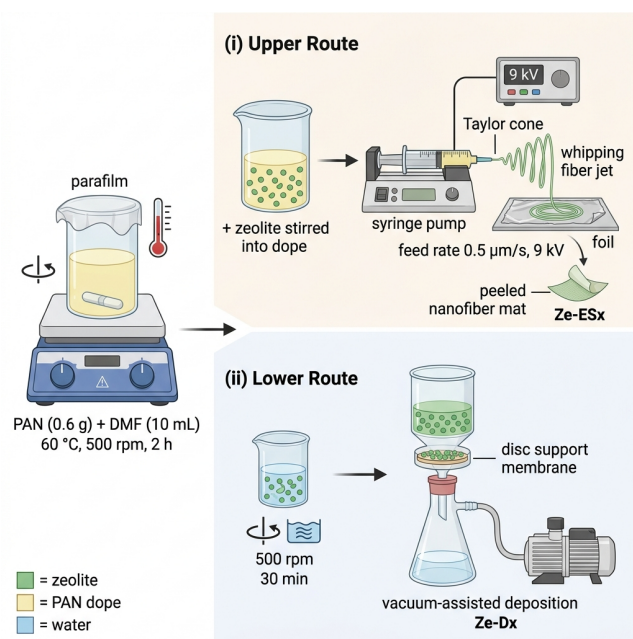


Figure 1. Schematic of the two fabrication routes compared in this study, both departing from a shared PAN-in-DMF dope (0.6 g PAN in 10 mL DMF, 60 °C, 500 rpm, 2 h). Upper route (i) *electrospinning-integration*: zeolite particles are stirred directly into the dope and co-spun through a syringe pump at 9 kV and $0.5 \mu\text{m s}^{-1}$ feed rate onto a grounded aluminium-foil collector, yielding the Ze-ESx series after peel-off. Lower route (ii) *surface dispersion*: zeolite is suspended in 20 mL deionized water, stirred (500 rpm, 10 min) and ultrasonicated (30 min), then vacuum-deposited onto a commercial PAN/PVDF support disc, yielding the Ze-Dx series.

2.2.3 Surface dispersion of zeolite on PAN/PVDF

For the Ze-Dx series, zeolite (0.01 g, 0.05 g, & 0.1 g, yielding Ze-D0.01, Ze-D0.05, and Ze-D0.1, respectively) was suspended in 20 mL of deionized water and stirred at 500 rpm for 10 min, then ultrasonicated for 30 min to break up agglomerates and improve dispersion stability. The resulting suspension was poured onto a commercial PAN/PVDF support membrane mounted in a vacuum filter holder; the liquid phase was drawn through the membrane under vacuum and discarded, leaving the zeolite particles deposited on the upstream membrane surface. The zeolite-loaded membrane was used directly in subsequent NH_4^+ removal tests without any drying or post-treatment.

2.3 Membrane characterization

The fabricated membranes and the bare natural zeolite reference were characterised by three complementary techniques spanning chemical composition, morphology, and surface wettability. Fourier-transform infrared spectroscopy (FTIR) was used to probe the chemical signature of each component over the range 400 cm^{-1} – 4000 cm^{-1} , using the $\text{C}\equiv\text{N}$ (nitrile) and CH stretches of PAN, the CF stretch of PVDF, and the SiOSi / AlOSi framework vibrations together with OH stretches of the aluminosilicate zeolite as diagnostic bands. Surface morphology was examined by scanning electron microscopy (SEM) at four magnifications ($1000\times$, $3000\times$, $5000\times$, and $10\,000\times$) to resolve features from the nanofiber-mat scale down to in-

dividual zeolite particles, allowing assessment of nanofiber uniformity, zeolite particle distribution on or within the matrix, and any aggregation or dead-zone formation that could limit mass transport. Surface wettability was quantified by static sessile-drop water contact angle (WCA) measurements: a microlitre-scale droplet of deionized water was dispensed onto the membrane surface and imaged from the side with the camera axis horizontal to the substrate; the contact angle was extracted in ImageJ using the Drop Snake plug-in, which fits a polynomial to the drop profile and reports left and right contact angles independently [31]. Five droplets were measured per sample at distinct positions on a homogeneous region, and the per-sample WCA is reported as the mean of the five droplet-averaged values with the spread expressed as one standard deviation.

2.4 Ammonium quantification and calibration

NH_4^+ concentration was measured by UV-Vis spectrophotometry using the Nessler method. To 5 mL of sample, 0.1 mL of Nessler's reagent was added; the mixture was shaken briefly and incubated for 10 min at room temperature to allow the yellow-orange NH_4^+ –Nessler chromophore to develop. Absorbance was then measured at $\lambda_{\text{max}} = 425\text{ nm}$ [32] against a matched blank consisting of 5 mL deionized water and 0.1 mL Nessler's reagent. The choice of 425 nm as λ_{max} was confirmed beforehand from a full-spectrum scan (200 nm–800 nm) of a representative complex solution. A five-point external calibration curve covering $C_0 = 1, 2, 4, 6, 8\text{ mg/L}$ was constructed from freshly diluted NH_4Cl stock. Linear regression of absorbance (A) on concentration gave $A = 0.0825 C_0 + 0.0356$ with $R^2 = 0.9943$, confirming Beer–Lambert linearity across the calibration range [33]; this regression was used throughout the filtration tests to convert post-filtration absorbance back to NH_4^+ concentration. Feed concentrations of 10 and 15 mg L^{-1} used in the performance tests lie above the calibration maximum of 8 mg L^{-1} ; the resulting cycle-1 readings at those concentrations are modest extrapolations (up to $2\times$) under an assumption of continued Beer–Lambert linearity and are flagged again where they occur in the performance discussion.

2.5 Dead-end vacuum filtration tests

Ammonium removal performance was evaluated in a batch dead-end vacuum filtration configuration. A disk of the test membrane with effective filtration area $A = 1.194 \times 10^{-3}\text{ m}^2$ was mounted on a glass filter holder, and 50 mL of NH_4Cl feed solution was added to the funnel. A vacuum of 500 mbar was applied to drive the feed through the membrane, and the filtration time t was recorded for each run. The collected filtrate was then analysed for residual NH_4^+ concentration following the Nessler protocol described above. Each membrane was subjected to five consecutive filtration cycles, with fresh feed in every cycle, to probe both short-term removal efficiency and reusability.

Two series of experiments were conducted. In the *screening series*, all five membrane formulations (Ze-D0.01, Ze-D0.05, Ze-D0.1, Ze-ES0.3, Ze-ES0.5) plus the unmodified PAN/PVDF control were tested at a single feed concentration of $C_0 = 10\text{ mg/L}$ (single run, $n = 1$). In the *concentration series*, the best-performing formulation from screening (Ze-D0.1) was tested at four feed concentrations $C_0 = 2, 5, 10, 15\text{ mg/L}$ in independent duplicate runs ($n = 2$), from which per-cycle means and standard deviations were computed.

Removal efficiency (Eq. (1)) and permeate flux (Eq. (2)) were calculated for each cycle:

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$J = \frac{V}{A \cdot t} \quad (2)$$

where C_0 and C_t (mg L^{-1}) are the feed and post-filtration NH_4^+ concentrations, respectively; V (L) is the filtrate volume collected in a cycle; A (m^2) is the effective membrane area; and t (h) is the filtration time for the cycle.

3. Results and Discussion

3.1 Membrane characterization

The membranes were characterized by FTIR to verify successful incorporation of zeolite into the PAN matrix, by SEM to visualize how each fabrication route distributes the zeolite across the membrane, and by water contact angle to translate those morphological differences into a functional surface property. Together the three techniques build a consistent picture: the dispersion route delivers zeolite at the membrane surface, while the electrospinning-integration route leaves a substantial fraction of the zeolite buried within, or aggregated between, the PAN fibres.

3.1.1 Fourier-transform infrared spectroscopy

Figure 2 shows the FTIR spectra of the PAN/PVDF control, the dispersion-method sample Ze-D0.1, and the two electrospinning-integration samples Ze-ES0.3 and Ze-ES0.5, together with the natural zeolite reference. Each component has diagnostic bands used to probe its presence at the membrane surface: the nitrile $\text{C}\equiv\text{N}$ stretch of PAN near 2240 cm^{-1} , the aliphatic CH stretch near 2930 cm^{-1} , the CF stretch of PVDF between 1200 cm^{-1} and 1400 cm^{-1} , and the framework SiOSi and AlOSi vibrations of the aluminosilicate zeolite between 950 cm^{-1} and 1050 cm^{-1} . A broad OH stretch near 3450 cm^{-1} and its bending partner near 1650 cm^{-1} indicate water adsorbed on the zeolite framework [29,30].

For the dispersion-method sample Ze-D0.1 (Fig. 2a, c), the zeolite framework band at 1050 cm^{-1} is the dominant spectral feature, consistent with zeolite particles exposed directly at the upstream surface of the membrane and strongly attenuating probe-beam transmission at aluminosilicate frequencies. The characteristic PAN/PVDF polymer bands are correspondingly weaker: zeolite dominates the surface-sensitive FTIR signal even though the underlying polymer support is unchanged. The broad OH feature is also stronger than in the other samples, because water is easily adsorbed onto the hydrophilic zeolite surface during sample handling. These observations are a direct optical confirmation that the dispersion route deposits zeolite on—rather than within—the support membrane.

For the electrospinning-integration samples Ze-ES0.3 and Ze-ES0.5 (Fig. 2b), both the PAN $\text{C}\equiv\text{N}$ band (intact) and the zeolite SiOSi band are observed. Higher zeolite loading (Ze-ES0.5) intensifies the zeolite feature only modestly, far less than the doubled loading would suggest. This is consistent with a substantial fraction of the zeolite being encapsulated within the PAN fibre matrix after spinning, where it is less accessible to the infrared beam than the surface-deposited zeolite of Ze-D0.1. The preservation of the PAN nitrile feature in both ES samples confirms that the electrospinning step does not chemically modify the polymer.

3.1.2 Scanning electron microscopy

SEM imaging (Fig. 3) provides complementary morphological evidence for how each fabrication route distributes zeolite within the membrane. Four magnifications were used ($\times 1000$, $\times 3000$, $\times 5000$, $\times 10\,000$), covering the mat, the fibre network, and individual zeolite particles.

In the dispersion series (Fig. 3a), the coverage density of zeolite on the PAN/PVDF support increases monotonically with the added zeolite mass. At the lowest loading, Ze-D0.01, the surface is only partially covered and gaps expose bare nanofiber substrate, so the adsorption-active area is inherently limited. At the intermediate loading Ze-D0.05, coverage is more uniform but residual agglomeration clusters remain visible. At the highest tested loading, Ze-D0.1, zeolite is uniformly distributed across the support surface with minimal agglomeration, producing the densest and most morphologically homogeneous interface of the three.

In the electrospinning-integration series (Fig. 3b), the PAN nanofiber network itself is well-formed at both loadings, but the zeolite is clearly displaced from the fibre interior: particles decorate fibre surfaces and interstitial spaces rather than being uniformly encapsulated within the fibres. For Ze-ES0.3, aggregation is evident at intermediate magnifications ($\times 3000$ and $\times 5000$), where multi-particle clusters sit across fibre bundles [29]. For Ze-ES0.5, the higher zeolite fraction produces still-larger aggregates that lodge between fibres, locally disrupting fibre continuity and forming dead zones that bulk solution will bypass during filtration. The chosen electrospinning formulation (0.6 g PAN in 10 mL DMF) is therefore insufficient on its own to keep the zeolite uniformly dispersed throughout the jet elongation phase of spinning; a sacrificial co-polymer or surfactant would be required to stabilize the suspension [34].

3.1.3 Water contact angle

Water contact angle (WCA) translates the surface chemistry and morphology inferred from FTIR and SEM into a single macroscopic wettability number per sample. Figure 4 collects the measurements across the five formulations.

The unmodified PAN/PVDF control is moderately hydrophobic, with $\text{WCA} = (82.99 \pm 0.87)^\circ$, consistent with the low-polarity CF groups of PVDF dominating the accessible surface. Pure electrospun PAN is less hydrophobic, $(71.41 \pm 0.55)^\circ$, reflecting the polar nitrile group in the PAN backbone. Both zeolite-functionalized formulations are substantially more hydrophilic: Ze-D0.1 shows $\text{WCA} = (32.77 \pm 4.09)^\circ$; the electrospinning-integration samples Ze-ES0.3 and Ze-ES0.5 show $(35.52 \pm 6.64)^\circ$ and $(24.11 \pm 2.91)^\circ$, respectively. The shift of more than 50° between the PAN/PVDF control and the zeolite-bearing samples is consistent with the high cation-exchange capacity of clinoptilolite, whose exposed aluminosilicate surface readily hydrogen-bonds with water [35,36]. The monotonic decrease of WCA as zeolite loading increases confirms that the surface trends inferred spectroscopically (Fig. 2) and morphologically (Fig. 3) translate to a functional wetting property.

Two secondary features of the WCA data are worth noting. First, the standard deviation on Ze-ES0.3 ($\pm 6.64^\circ$) is the largest of the five samples and visibly exceeds that of Ze-D0.1 and Ze-ES0.5. This elevated spread reflects the morphological heterogeneity already visible at intermediate SEM magnifications in Fig. 3b: individual droplets land on surface patches with different local zeolite density, so the measurement is reproducible within a patch but varies across patches. Second,

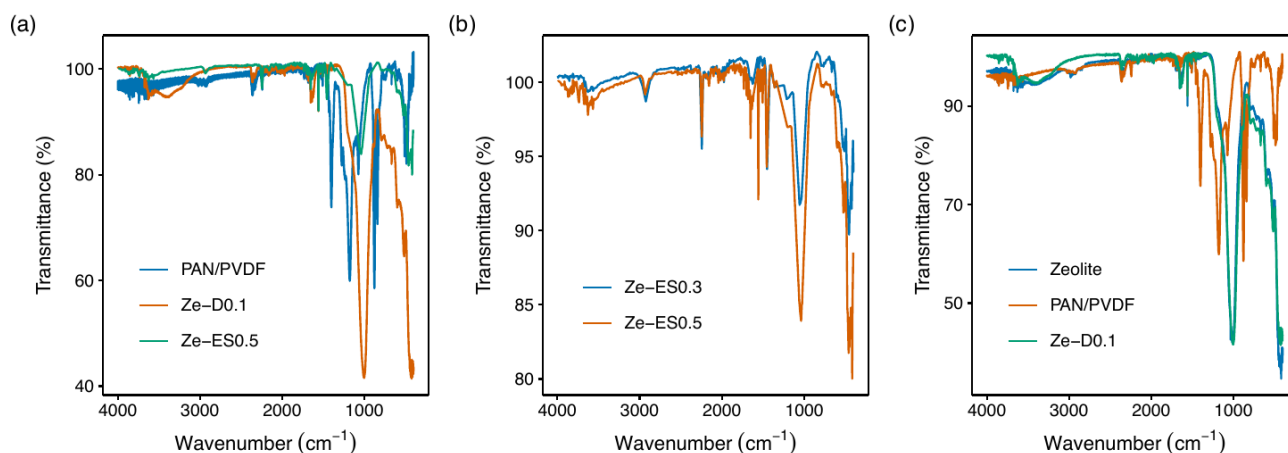


Figure 2. FTIR spectra of the PAN-based composite nanofiber membranes and reference materials. (a) Overlay of the PAN/PVDF control, the dispersion-route Ze-D0.1, and the electrospinning-integration Ze-ES0.5. (b) Comparison of the two electrospinning-integration formulations Ze-ES0.3 and Ze-ES0.5. (c) The dispersion composite Ze-D0.1 alongside its natural-zeolite and PAN/PVDF endpoints, highlighting that the dispersion route places zeolite at the surface.

Ze-ES0.5 has the lowest contact angle of all samples, slightly lower than Ze-D0.1, even though its bulk zeolite loading is higher than Ze-D0.1's. This does not contradict the FTIR picture: WCA is sensitive to the *outermost* exposed chemistry, including the protruding zeolite aggregates that the SEM reveals at the Ze-ES0.5 surface, so the wetting response can be high even when much of the bulk zeolite is buried within the fibre matrix.

3.2 Ammonium removal performance

3.2.1 Screening across membrane formulations

The six tested formulations (Ze-D0.01, Ze-D0.05, Ze-D0.1, Ze-ES0.3, Ze-ES0.5, and the unmodified PAN/PVDF control) were compared at a feed concentration of $C_0 = 10$ mg/L over five consecutive filtration cycles. Figure 6 collects the per-cycle removal efficiency across all six samples.

The dispersion-method samples form a clear performance rank that tracks the zeolite loading. At the highest loading, Ze-D0.1 approaches quantitative removal in the first two cycles and retains 47 % removal by cycle 5, consistent with the densest zeolite coverage seen by SEM (Fig. 3a). At intermediate loading, Ze-D0.05 begins at 91 % and degrades steeply to 22 % by cycle 5: coverage is sufficient for first-cycle capture but saturates rapidly. The lowest-loading sample Ze-D0.01 shows a more gradual decline, from 66 % to 35 % across cycles 1–5, but never matches the first-cycle efficiency of the higher-loaded samples, confirming that sparse zeolite coverage limits even the initial removal. The monotonic Ze-Dx ordering by loading is in full agreement with the morphological picture from SEM.

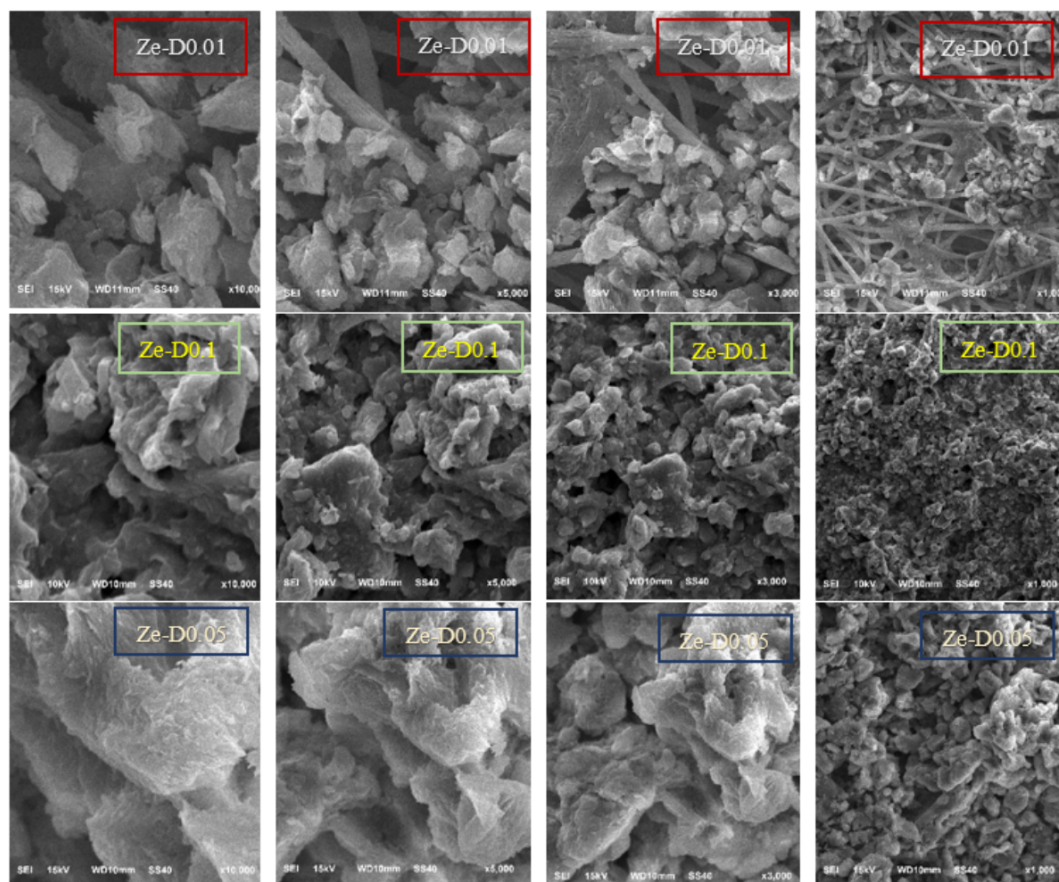
The two electrospinning-integration samples behave qualitatively differently. Ze-ES0.3 starts at 12 % removal in cycle 1, falls to 10 % in cycle 2, 3 % in cycle 3, and reaches effectively zero removal at cycles 4–5. Ze-ES0.5 is even worse: 1.7 % in cycle 1 and zero thereafter. At the cycles reported as zero, the raw Nessler-reported NH_4^+ concentration in the filtrate in fact matches or exceeds the feed concentration; since a membrane cannot produce more NH_4^+ than it receives, the apparent super-feed reading is clipped to zero in Fig. 6 and interpreted as no net removal plus an additive background.

That background is consistent with zeolite leaching from the PAN matrix during filtration: loosely-held particles detach under vacuum-driven flow, co-elute with NH_4^+ , and release adsorbed cations, inflating the apparent residual concentration. The SEM images of the Ze-ES samples (Fig. 3b) support this mechanism directly: the ES formulation fails to stably embed zeolite in the PAN fibre matrix, so the weakly-held particles shed mechanically during filtration.

The PAN/PVDF control maintains removal efficiency within noise of zero (never exceeding 12 % in any cycle, with several cycles reading at or near zero), with no monotonic trend. This confirms the intended baseline: the polymer matrix itself does not adsorb NH_4^+ meaningfully, so any removal observed in the Ze-D or Ze-ES series is attributable to the zeolite component rather than to the polymer.

Permeate flux data (Fig. 5) provide an independent, mechanistically informative view of the same screening runs and reinforce the removal-efficiency picture described above. Three features are most diagnostic. First, across the dispersion series, cycle-1 flux decreases monotonically as zeolite loading increases: ~ 7400 L m² h⁻¹ for Ze-D0.01, ~ 110 L m² h⁻¹ for Ze-D0.05, and ~ 60 L m² h⁻¹ for Ze-D0.1, spanning more than two orders of magnitude. The inverse scaling of flux with loading directly confirms that the dispersed zeolite forms a resistive surface layer on the support rather than simply resting on it [9]. Second, the Ze-D0.1 flux is essentially constant across all five cycles (60.8 L m² h⁻¹ in cycle 1 to 54.2 L m² h⁻¹ in cycle 5, a decline of only ~ 11 %), indicating that the zeolite coating is mechanically stable under repeated vacuum-driven flow. Third, and most diagnostically, the Ze-ES0.5 flux *increases* from 3870 L m² h⁻¹ in cycle 1 to 11265 L m² h⁻¹ in cycle 5—an almost threefold rise over the same five cycles in which its removal efficiency falls to zero. A rising flux with a falling removal can be explained only by a progressive loss of active adsorbent from the flow path: as loosely-held zeolite detaches cycle by cycle, the hydraulic resistance of the membrane drops while the NH_4^+ capture surface is simultaneously lost. Flux and removal thus corroborate each other on the leaching mechanism already inferred from SEM (Fig. 3b), and the contrast

(a)



(b)

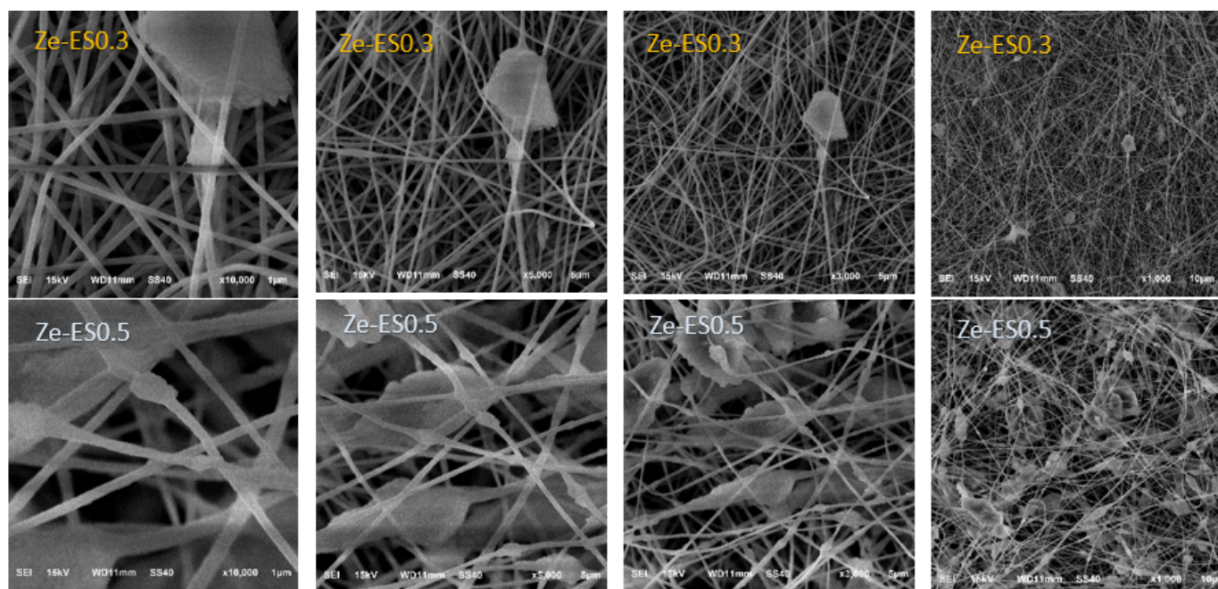


Figure 3. SEM images of the two fabrication routes. (a) Dispersion series: Ze-D0.01, Ze-D0.05 and Ze-D0.1 imaged at magnifications of $\times 1000$, $\times 3000$, $\times 5000$ and $\times 10\,000$. (b) Electrospinning-integration series: Ze-ES0.3 and Ze-ES0.5 at the same magnifications. Zeolite coverage scales monotonically with loading in the dispersion route, while the integration route produces progressive agglomeration rather than uniform encapsulation.

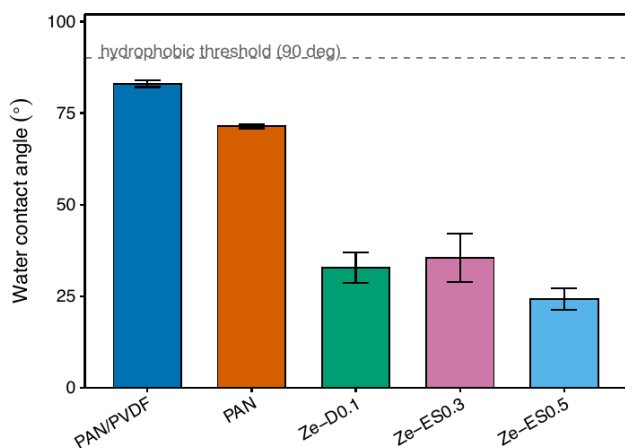


Figure 4. Static sessile-drop water contact angles of the five tested membrane formulations (PAN/PVDF, pure PAN, Ze-D0.1, Ze-ES0.3, Ze-ES0.5), with bars showing the mean across five droplets per sample and error bars showing one standard deviation. Inset droplet photographs illustrate the hydrophobic-to-hydrophilic transition driven by zeolite exposure.

with the mechanically stable Ze-D0.1 flux profile establishes dispersion as the route of choice for durable NH_4^+ capture. The PAN/PVDF control follows an orthogonal trajectory—a two-orders-of-magnitude flux collapse ($251000 \text{ L m}^{-2} \text{ h}^{-1}$ down to $2200 \text{ L m}^{-2} \text{ h}^{-1}$)—driven by cumulative compaction and fouling of the bare polymer matrix rather than by any adsorbent dynamics.

Taken together, the screening identifies Ze-D0.1 as the only formulation that combines high first-cycle efficiency with sustained performance across the five-cycle test [29]. It was therefore selected for the concentration-dependence study described next.

3.2.2 Concentration-dependence and reusability of the selected formulation

Ze-D0.1 was further evaluated at four feed concentrations ($C_0 = 2, 5, 10, 15 \text{ mg/L}$), each in independent duplicate ($n = 2$), across five consecutive filtration cycles. Figure 7 collects the per-cycle removal efficiency averaged across the two replicates, with error bars showing one standard deviation.

In the low-concentration regime ($C_0 = 2 \text{ mg/L}$), Ze-D0.1 maintains essentially quantitative removal across all five cycles, with standard deviation of 7%–11%. At this concentration the zeolite sorption capacity clearly exceeds the NH_4^+ supply per cycle, and cycle-to-cycle decay is not resolvable above measurement noise. The raw duplicate-mean cycle values reach 104–108% at two of the cycles because the Nessler blank carries a small positive absorbance intercept ($b = 0.0356$ in the calibration of §2.4) that is not perfectly reproducible from run to run; since a membrane cannot physically remove more NH_4^+ than it receives, these nominally super-quantitative readings are clipped to 100% in Fig. 7 and interpreted as “complete removal within experimental noise”.

At intermediate and high concentrations the expected saturation-plus-fouling pattern emerges. At $C_0 = 5 \text{ mg/L}$ mean efficiency declines from 90% in cycle 1 to 15% in cycle 5. At $C_0 = 10 \text{ mg/L}$ the raw cycle-1 mean is nominally above 100% (replicate-level values of 118% and 90%, plotted at

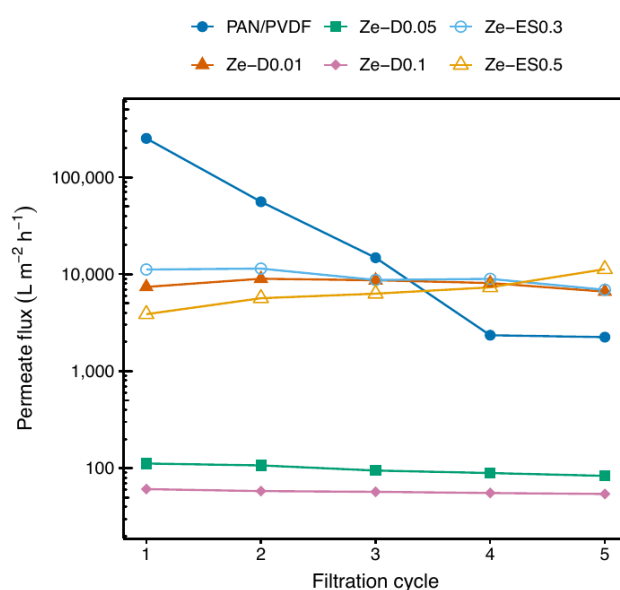


Figure 5. Permeate flux of the six tested membrane formulations over five consecutive vacuum-filtration cycles at $C_0 = 10 \text{ mg/L}$. The y -axis is logarithmic to accommodate the four orders of magnitude spanned by the data. The dispersion series shows flux decreasing monotonically with zeolite loading ($\text{Ze-D0.01} > \text{Ze-D0.05} > \text{Ze-D0.1}$), confirming that dispersed zeolite forms a surface-resistive layer. Ze-D0.1 flux is essentially constant across all cycles, indicating mechanical stability. Ze-ES0.5 flux rises more than threefold from cycle 1 to 5 while removal drops to zero (see Fig. 6), the characteristic signature of zeolite leaching under vacuum-driven flow. The PAN/PVDF control exhibits a steep flux collapse attributable to compaction and fouling of the bare polymer matrix.

100% in Fig. 7 per the clipping convention above), declining to 29% by cycle 5 with substantially larger replicate spread (SD up to 50%) that indicates slightly different saturation trajectories in the two membrane pieces. At $C_0 = 15 \text{ mg/L}$ cycle 1 starts at 76% and declines to 13% by cycle 5, with the replicate divergence becoming more pronounced from cycle 2 onward.

Three quantitative caveats are consolidated here. First, nominal removal values above 100% at low and moderate C_0 are blank-correction artefacts; raw numbers are preserved in the running text for integrity, while Fig. 7 clips them to 100% since a membrane cannot physically exceed complete removal, and the physically meaningful interpretation is $\geq 99\%$ removal. Second, cycle-1 absorbance readings at $C_0 = 10$ and 15 mg L^{-1} lie above the maximum of the calibration curve ($C_{\text{max}} = 8 \text{ mg/L}$; see §2.4): their conversion to concentration involves extrapolation of up to $2\times$ under an assumption of continued Beer–Lambert linearity. No non-linearity is expected in this regime, but the resulting concentrations carry a systematic uncertainty not captured by the replicate-level standard deviation. Third, the progressive increase of standard deviation with cycle number at every concentration reflects fouling of the membrane surface that compacts slightly differently in replicate runs of an ostensibly identical preparation [37,38,39]. Regeneration strategies reported for related sorbents [40] are a natural direction for recovering the used membrane and are discussed briefly below.

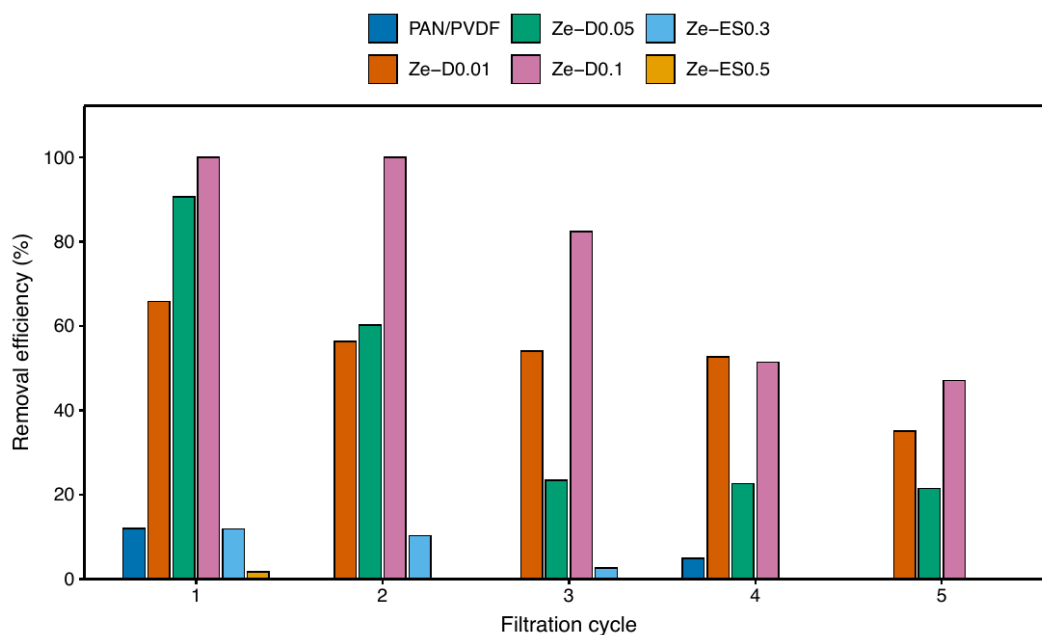


Figure 6. Ammonium removal efficiency over five consecutive vacuum-filtration cycles at a fixed feed concentration of $C_0 = 10 \text{ mg/L}$ for the six tested formulations. The dispersion-method series (Ze-D0.01, Ze-D0.05, Ze-D0.1) shows a clear loading-dependent ranking; the electrospinning-integration series (Ze-ES0.3, Ze-ES0.5) and the PAN/PVDF control drop to zero by the later cycles, with several raw readings going slightly negative (diagnostic of zeolite leaching; see text). For clarity, values below zero are plotted at zero since removal efficiency is physically non-negative.

From an operational standpoint, these results define an envelope for the Ze-D0.1 formulation: single-pass removal of NH_4^+ at feed concentrations at or below 2 mg L^{-1} is essentially quantitative and reusable over at least five cycles, while at concentrations approaching or exceeding 10 mg L^{-1} a single membrane saturates within 2–3 cycles and must be regenerated or replaced. Although the per-membrane NH_4^+ capacity of the Ze-D0.1 formulation is intrinsically lower than that of loose-powder natural zeolite on a per-gram basis ($\sim 22 \text{ mg/g}$ for desilicated Lampung zeolite) [16], the integrated-membrane format eliminates the downstream separation step and enables direct incorporation into flow-through treatment units. This positions Ze-D0.1 most naturally as a polishing step on already-low-concentration streams (secondary wastewater effluent, aquaculture recirculation, environmental monitoring sampling lines) rather than as a bulk-removal unit on concentrated feeds.

4. Conclusions

Two zeolite-PAN composite nanofiber membranes were fabricated via contrasting routes—surface dispersion (Ze-D series) and electrospinning-integration (Ze-ES series)—and compared for NH_4^+ removal by dead-end vacuum filtration across five consecutive cycles. FTIR, SEM, and water contact angle measurements established that the dispersion route places zeolite at the upstream membrane surface, producing a dense and strongly hydrophilic interface (WCA (32.8 ± 4.1) for Ze-D0.1 vs. (83.0 ± 0.9) for the unmodified PAN/PVDF control), whereas the electrospinning-integration route encapsulates a substantial fraction of the adsorbent inside the fibre matrix with progressive aggregation at higher loading. The best-performing formulation, Ze-D0.1, delivered near-quantitative NH_4^+ removal in the first two cycles at $C_0 = 10 \text{ mg/L}$ and retained 47 % by cycle 5, with permeate

flux held essentially constant at $54 \text{ L m}^{-2} \text{ h}^{-1}$ – $61 \text{ L m}^{-2} \text{ h}^{-1}$ across all five cycles. Both electrospinning-integration samples, by contrast, collapsed to zero removal within a few cycles as flux rose as much as threefold—the characteristic signature of progressive zeolite leaching directly corroborated by SEM. Surface availability of the adsorbent, not its bulk loading, therefore dominates NH_4^+ capture performance in this membrane format. Ze-D0.1 is well suited as a polishing step on already-low-concentration streams such as secondary wastewater effluent and aquaculture recirculation, extending the Ze-PAN/PVDF platform from dye removal to nutrient-species capture. Future work should extend the UV-Vis calibration beyond 8 mg L^{-1} , directly confirm zeolite leaching in the Ze-ES series via ICP analysis of filtrate Si and Al, and characterise pH and ionic-strength effects on the Ze-D0.1 performance envelope.

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AUTHOR CONTRIBUTIONS

Rizka Affah Sirait: Investigation, Methodology, Formal analysis, Data curation, Visualization, Writing – original draft. **Sephia Amanda Muhtar:** Investigation, Validation, Writing – review & editing. **Andika Munandar:** Supervision, Methodology, Validation, Writing – review & editing. **Tarmizi Taher:** Conceptualization, Supervision, Project administration, Resources, Formal analysis, Visualization, Software, Writing – original draft, Writing – review & editing.

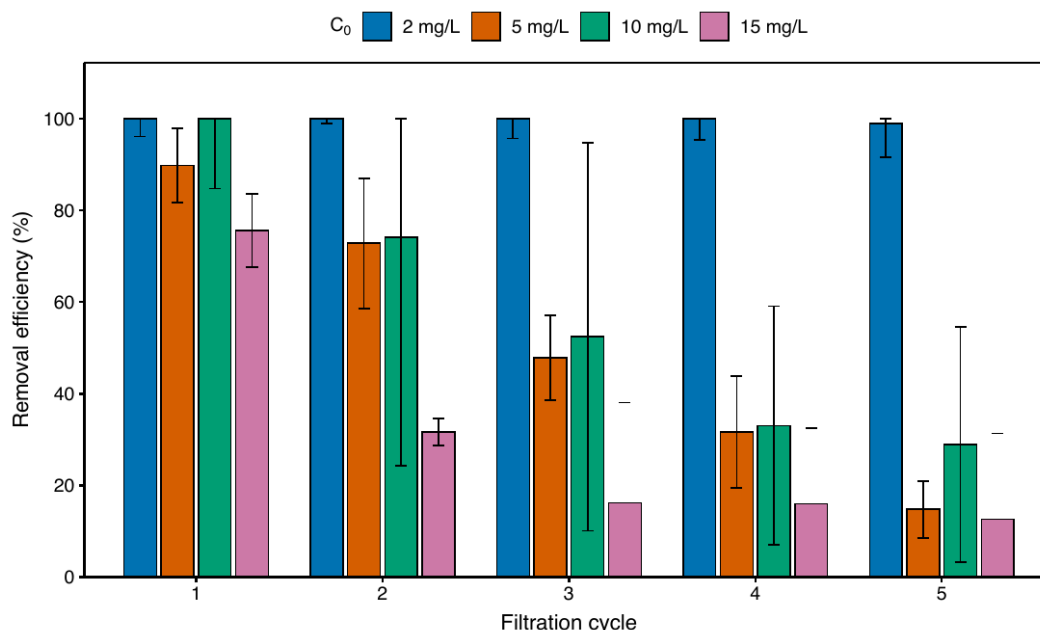


Figure 7. Ammonium removal efficiency of Ze-D0.1 over five consecutive vacuum-filtration cycles at four feed concentrations ($C_0 = 2, 5, 10, 15$ mg/L). Bars show the mean of two independent replicates; error bars show one standard deviation. At $C_0 = 2$ mg/L removal is quantitative and stable across all cycles; at higher C_0 , saturation and progressive fouling drive per-cycle decay. Values nominally above 100 % (blank-intercept artefacts discussed in the text) are clipped to 100 % since removal cannot physically exceed complete capture.

DECLARATION OF COMPETING INTEREST

The authors declare no competing financial or personal interests that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- [1] Liao K, You J, Han C, Cheng H, Ren H, Hu H. Dissolved organic nitrogen depresses the expected outcome of wastewater treatment upgrading on effluent eutrophication potential mitigation: Molecular mechanistic insight. *Water Research*. 2024;267:122535. doi:10.1016/j.watres.2024.122535.
- [2] Zhu Y, Hou J, Meng F, Xu M, Lin L, Yang L, Chen X. Comparative enrichment of complete ammonium oxidation bacteria in floccular sludge reactors: Sequencing batch reactor vs. Continuous stirred tank reactor. *Water Research X*. 2025;27:100305. doi:10.1016/j.wroa.2025.100305.
- [3] Thi My Hanh N, Hong Van N, Thi Minh Trang P. Ammonium recovering from domestic wastewater toward circular economy: A short review. *Desalination and Water Treatment*. 2025;321:100906. doi:10.1016/j.dwt.2024.100906.
- [4] Lima PDM, Edström M, Aronsson H, Nordberg Å, Sindhöj E. Comparative analysis of manure treatment scenarios on climate change and eutrophication in the baltic sea. *Resources, Conservation and Recycling*. 2025;212:108017. doi:10.1016/j.resconrec.2024.108017.
- [5] Skovsholt LJ, Matheson F, Riis T, Hawes I. Trait-specific groups of aquatic macrophytes respond differently to eutrophication of unshaded lowland streams. *Science of The Total Environment*. 2024;954:176724. doi:10.1016/j.scitotenv.2024.176724.
- [6] Parn O, Duteil O, Garcia-Gorritz E, Ferreira-Cordeiro N, Lessin G, Macias D, Miladinova S, Piroddi C, Polimene L, Serpetti N, Stips A. Effects of sea ice on baltic sea eutrophication. *Marine Pollution Bulletin*. 2024;209:117067. doi:10.1016/j.marpolbul.2024.117067.
- [7] Liu X, Huang W, Qi Z, Li C, Cheng G, Cai Y. Seasonal water storage of large reservoirs exacerbates eutrophication risk in the fluctuating backwater zone: A case study of three gorges reservoir, china. *Ecological Indicators*. 2025;171:113100. doi:10.1016/j.ecolind.2025.113100.
- [8] Yin S, Chen K, Srinivasakannan C, Guo S, Li S, Peng J, Zhang L. Enhancing recovery of ammonia from rare earth wastewater by air stripping combination of microwave heating and high gravity technology. *Chemical Engineering Journal*. 2018;337:515-521. doi:10.1016/j.cej.2017.12.147.
- [9] Xie M, Shon HK, Gray SR, Elimelech M. Membrane-based processes for wastewater nutrient recovery: Technology, challenges, and future direction. *Water Research*. 2016;89:210-221. doi:10.1016/j.watres.2015.11.045.
- [10] Bahmanzadegan F, Ghaemi A. A comprehensive review on novel zeolite-based adsorbents for environmental pollutant. *Journal of Hazardous Materials Advances*. 2025;17:100617. doi:10.1016/j.hazadv.2025.100617.
- [11] Li J, Ullah R, Jiao J, Sun J, Bai S. Ion exchange of cations from different groups with ammonium-modified clinoptilolite and selectivity for methane and nitrogen. *Materials Chemistry and Physics*. 2020;256:123760. doi:10.1016/j.matchemphys.2020.123760.
- [12] Zijun Z, Effene G, Millar GJ, Stephen M. Synthesis and cation exchange capacity of zeolite w from ultra-fine natural zeolite waste. *Environmental Technology & Innovation*. 2021;23:101595. doi:10.1016/j.eti.2021.101595.
- [13] Ferri BB, Wernke G, Resende JF, Ribeiro AC, Cusioli LF, Bergamasco R, Vieira MF. Natural zeolite as adsorbent for metformin removal from aqueous solutions: Adsorption and regeneration properties. *Desalination and Water Treatment*. 2024;320:100602. doi:10.1016/j.dwt.2024.100602.
- [14] Nikolov A, Nugteren H, Rostovsky I. Optimization of geopolymer based on natural zeolite clinoptilolite by calcination and use of aluminate activators. *Construction and Building Materials*. 2020;243:118257. doi:10.1016/j.conbuildmat.2020.118257.

- [15] Ugrina M, Gaberšek M, Daković A, Nuić I. Preparation and characterization of the sulfur-impregnated natural zeolite clinoptilolite for hg(II) removal from aqueous solutions. *Processes*. 2021;9(2):217. doi:10.3390/pr9020217.
- [16] Taher T, Melati EKA, Febrina M, Maulana S, Asagabaldan MA, Rianjanu A, Lesbani A, Mukti RR. Effect of desilication on indonesian natural zeolite for the enhancement of ammonium ion removal from aqueous solutions. *Silicon*. 2023;16(3):1309–1319. doi:10.1007/s12633-023-02758-z.
- [17] Bulacio Fischer PT, Di Trapani D, Laudicina VA, Mineo A, Muscarella SM, Mannina G. Adsorption and desorption of ammonium from treated wastewater by zeolite filled columns: An experimental study at the water resource recovery facility of palermo university – italy. *Journal of Environmental Management*. 2025;375:124241. doi:10.1016/j.jenvman.2025.124241.
- [18] Paliaga S, Muscarella SM, Alduina R, Badalucco L, Bulacio Fischer PT, Di Leto Y, Gallo G, Mannina G, Laudicina VA. The effects of enriched biochar and zeolite and treated wastewater irrigation on soil fertility and tomato growth. *Journal of Environmental Management*. 2025;380:124990. doi:10.1016/j.jenvman.2025.124990.
- [19] Zhao Y, Chen L, Zuo Y, Zhu B, Liu X, Jia Y. Boron nitride modified PAN ultrafiltration membranes with improved water permeance and dye rejection performance. *Desalination and Water Treatment*. 2025;321:100962. doi:10.1016/j.dwt.2024.100962.
- [20] Uslu E, Gavali M, Erdal MO, Yazman Ş, Gemi L. Determination of mechanical properties of polymer matrix composites reinforced with electrospinning N66, PAN, PVA and PVC nanofibers: A comparative study. *Materials Today Communications*. 2021;26:101939. doi:10.1016/j.mtcomm.2020.101939.
- [21] Shao S, Pandita SD, Liu Y, An B, Morris T, Ma T, Fernando GF. The effect of end-tapping methods on the tensile properties of electro-spun highly aligned PAN nano-fibres. *Polymer Testing*. 2024;141:108645. doi:10.1016/j.polymertesting.2024.108645.
- [22] HMTShirazi R, Mohammadi T, Asadi AA, Tofighy MA. Electrospun nanofiber affinity membranes for water treatment applications: A review. *Journal of Water Process Engineering*. 2022;47:102795. doi:10.1016/j.jwpe.2022.102795.
- [23] Cao W, Zhang M, Ma W, Huang C. Multifunctional electrospun nanofibrous membrane: An effective method for water purification. *Separation and Purification Technology*. 2023;327:124952. doi:10.1016/j.seppur.2023.124952.
- [24] Rasekh A, Raisi A. Electrospun nanofibrous polyether-block-amide membrane containing silica nanoparticles for water desalination by vacuum membrane distillation. *Separation and Purification Technology*. 2021;275:119149. doi:10.1016/j.seppur.2021.119149.
- [25] Choi J, Chan S, Yip G, Joo H, Yang H, Ko FK. Palladium-zeolite nanofiber as an effective recyclable catalyst membrane for water treatment. *Water Research*. 2016;101:46–54. doi:10.1016/j.watres.2016.05.051.
- [26] Martinelli A, Navarra MA, Matic A, Panero S, Jacobsson P, Börjesson L, Scrosati B. Structure and functionality of PVdF/PAN based, composite proton conducting membranes. *Electrochimica Acta*. 2005;50(19):3992–3997. doi:10.1016/j.electacta.2005.02.055.
- [27] Mahmoodi NM, Mokhtari-Shourijeh Z, Langari S, Naeimi A, Hayati B, Jalili M, Seifpanahi-Shabani K. Silica aerogel/polyacrylonitrile/polyvinylidene fluoride nanofiber and its ability for treatment of colored wastewater. *Journal of Molecular Structure*. 2021;1227:129418. doi:10.1016/j.molstruc.2020.129418.
- [28] Sriyanti I, Almafie MR, Nuha Ap Idjan MK, Dani R, Solihah I, Syafri E, Yulianti, Marlina L. Electrospun nanofiber membrane of piper beetle loaded PVDF/PAN for medical mask applications: Psychochemical characteristics, antibacterial and air filter test. *Advanced Membranes*. 2025;5:100149. doi:10.1016/j.advmem.2025.100149.
- [29] Arif ME, Muhtar SA, Siburian C, Marpaung KDP, Yulianto N, Abdi FE, Taher T, Wasisto HS, Rianjanu A. Zeolite-PAN/PVDF composite nanofiber membranes for highly efficient and selective removal of cationic dyes from wastewater. *Case Studies in Chemical and Environmental Engineering*. 2024;10:100806. doi:10.1016/j.cscee.2024.100806.
- [30] Muhtar SA, Amanda T, Kurnia NR, Putra SEM, Khairurrijal K, Arif ME, Taher T, Rianjanu A. Complex mixture dye removal using natural zeolite modified polyacrylonitrile/polyvinylidene fluoride (Ze-PAN/PVDF) composite nanofiber membrane via vacuum filtration technique. *Materials Today Communications*. 2025;42:111357. doi:10.1016/j.mtcomm.2024.111357.
- [31] Martinez-Urrutia A, Fernandez de Arroiabe P, Ramirez M, Martinez-Agirre M, Mounir Bou-Ali M. Contact angle measurement for LiBr aqueous solutions on different surface materials used in absorption systems. *International Journal of Refrigeration*. 2018;95:182–188. doi:10.1016/j.ijrefrig.2018.05.041.
- [32] Niedzielski P, Kurzyca I, Siepak J. A new tool for inorganic nitrogen speciation study: Simultaneous determination of ammonium ion, nitrite and nitrate by ion chromatography with post-column ammonium derivatization by nessler reagent and diode-array detection in rain water samples. *Analytica Chimica Acta*. 2006;577(2):220–224. doi:10.1016/j.aca.2006.06.057.
- [33] Salido EM, Servalli LN, Gomez JC, Verrastro C. Phototransduction early steps model based on beer-lambert optical law. *Vision Research*. 2017;131:75–81. doi:10.1016/j.visres.2016.12.012.
- [34] He W, Lu R, Fang K, San E, Gong H, Wang K. Fabrication of zeolite NaX-doped electrospun porous fiber membrane for simultaneous ammonium recovery and organic carbon enrichment. *Journal of Membrane Science*. 2020;603:118030. doi:10.1016/j.memsci.2020.118030.
- [35] Zhong Y, Zhou A, Du J, Zhan S. Dependence of clay–water contact angle on surface charge and ambient temperature: A study from molecular dynamics perspective. *Journal of Molecular Liquids*. 2024;415:126258. doi:10.1016/j.molliq.2024.126258.
- [36] Kim E, Kim D, Kwak K, Nagata Y, Bonn M, Cho M. Wettability of graphene, water contact angle, and interfacial water structure. *Chem*. 2022;8(5):1187–1200. doi:10.1016/j.chempr.2022.04.002.
- [37] Winans JD, Smith KJP, Gaborski TR, Roussie JA, McGrath JL. Membrane capacity and fouling mechanisms for ultrathin nanomembranes in dead-end filtration. *Journal of Membrane Science*. 2016;499:282–289. doi:10.1016/j.memsci.2015.10.053.
- [38] Jhaveri JH, Murthy ZVP. A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes. *Desalination*. 2016;379:137–154. doi:10.1016/j.desal.2015.11.009.
- [39] Gao F, Wang L, Zhang H, Wang J. Realtime and in-situ monitoring of membrane fouling with fiber-optic reflectance UV-vis spectrophotometry (FORUS). *Chemical Engineering Journal Advances*. 2020;4:100058. doi:10.1016/j.cej.2020.100058.
- [40] Usuda H, Mishima Y, Kawamoto T, Minami K. Desorption of ammonia adsorbed on prussian blue analogs by washing with saturated ammonium hydrogen carbonate solution. *Molecules*. 2022;27(24):8840. doi:10.3390/molecules27248840.