Development of pH-Responsive Adsorptive Ultrafiltration Membrane for the treatment of Heavy Metals from Aqueous Solution

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Abstract *(Max 200 words).* This research presents a new amino-modified activated carbon (MAC) nanohybrid and its use in polylactic acid (PLA) ultrafiltration (UF) membranes for treating wastewater. The MAC composite was produced through three steps: activated carbon pretreatment, modification, and heat-induced cross-linking. The composite membranes were made using the phase inversion technique and optimized by varying the concentration of the MAC nanohybrid. The synthesis was confirmed through several methods, and the membranes were characterized using different techniques, such as SEM, surface zeta potential, water flux, and pore-size/porosity. Static adsorption and dynamic filtration experiments were conducted to investigate the membrane's flux-rejection performance and pH-responsiveness. The results showed that the MAC nanohybrid significantly improved the properties of the PLA membrane, such as increasing the pure water flux and enhancing heavy metal ions rejection, among others. The composite membranes also exhibited improved adsorption and desorption behavior. The study suggests that adding the MAC nanohybrid has promising potential for these composite membranes in the wastewater treatment industry.

Keywords: pH responsive, heavy metals, MXene, graphene oxide, two-dimensional materials

1. Introduction

The term SMART has been repeatedly used to describe the desired properties in adsorbents, which is "simple assembly, modifiable properties, adsorptive behavior, reusability and transferable nature". Smart adsorbents impose different responses under the variation of operation conditions such temperature, pH, intensity of light, solution ionic strength, magnetic field, electric field, and concentration of present contaminants. Thus, optimizing the chemical and physical conditions can result in a highly selective smart adsorbent towards a specific pollutant, compared to conventional adsorbents where almost all pollutants are adsorbed at the same efficiency. Smart adsorbents offer excellent reusability and high physiochemical stability, making them more effective, easily tunable, and highly selective [1]. In specific pH-stimuli polymers are synthesized from polyelectrolytes composing of acidic and basic chemical moiety that experiences structural and property alterations upon changes in the solution pH. Variations in pH subjects the polymer to distinct surface charge, conformation, configuration, and solubility exhibited by the protonation and deprotonation of the chemical functional groups [2]. pH-responsive adsorbents exhibit a single or multiple adsorption mechanism, namely, electrostatic attraction, ion exchange, chelation, size exclusion, σ-π interaction, π-π interaction, and host-guest interaction [3]. Understating the smart material adsorption mechanism(s) allows the selectivity, efficiency, and reusability of the material to be tuned.

In this study, a novel amino-functionalized activated carbon (MAC) incorporated into the matrix of polylactic acid (PLA) membrane has been fabricated through phase inversion (PI) technique. The membranes are to be tested for heavy metal adsorption and desorption at extreme acidic and basic conditions. The membranes selectivity, efficiency, and recyclability are evaluated against three common heavy metal ions; copper (Cu^{2+}), nickel (Ni^{2+}), and lead (Pb^{2+}). Static adsorption and dynamic filtration were performed as well to investigate the flux-rejection performance and the pH-responsiveness of the membranes.

2. Methodology

2.1. Phase inversion

All membranes were fabricated using the non-solvent induced phase inversion (NIPS) method. Pristine PLA and its composite counterparts were fabricated in a similar manner. First the filler was dispersed in dimethylacetamide (DMAc) solvent through sonication for 1h. Next, the pore-forming material – polyvinyl pyrrolidone (PVP) and the PLA polymer beads were added. The casting solution was kept at 70 °C for 3 h, then left to stir overnight at 60 °C. The homogeneous dope solution was sonicated in two interval, 45 min sonication, 15 min resting, then another 45 min

sonication to assure complete elimination of gas bubbles. The degassed dope solution was carefully poured on a nonwoven polyester support (170 μm thick), prefixed on a casting glass plate. Using 8" film casting knife the solution was evenly spread over the support with preset gap depth of 250 μm. The glass plate with cast film was left 30 s at 25 °C and then immersed into the coagulation bath until it changes color from transparent to opaque state indicating complete formation of the polymeric membrane. The formed membrane was rinsed then immersed in DI water for 48 h or until it was tested to ensure the removal of DMAc traces and water-soluble PVP.

3.1 Dynamic and static adsorptive performance

To assess the dynamic performance of the composite membranes, various parameters were calculated, including the pure water flux (PWF, J_w, L.m^{-2}.h^{-1}), and rejection of heavy metal ions (R_{cu}, R_{Ni}, R_{Pb}, %). A synthetic mixture composing of Cu, Pb, and Ni with a concentration of 25 ppm was used for testing. These parameters relied on the collected permeate obtained through a dead-end ultrafiltration experiment at 0.1 MPa. The PWF, R_i, and FRR were calculated using the following equations [4–6]:

$$PWF = \frac{V}{A \cdot \Delta t} \tag{1}$$

$$R_i = \frac{C_{f,i} - C_{p,i}}{C_{f,i}} \times 100, where\ i = Cu, Ni, Pb \tag{2}$$

where V, A, Δt, $C_{f,i}$, and $C_{p,i}$ is the permeate volume (L), membrane surface area (m^2), collection time interval (h), component i concentration in the feed (ppm), component i concentration in the permeate (ppm), respectively.

The static adsorption behavior was assessed through the equilibrium isotherms. Two common isotherms were fitted against the collected experimental data, namely, Langmuir and Freundlich isotherms. The effect of the initial adsorbate concentration on the equilibrium adsorbate concentration (C_e, mg.L^{-1}) and equilibrium adsorption capacity (q_e, mg.g^{-1}) was investigated. The linearized forms of the Langmuir and Freundlich isotherms were tested for fitting [7]:

$$Langmuir: \frac{C_e}{q_e} = \frac{1}{k_L \cdot q_m} + \frac{C_e}{q_m} \tag{3}$$

$$Freundlich: ln(q_e) = ln(k_F) + \frac{1}{n} \cdot ln(C_e) \tag{4}$$

where k_L, q_m, k_F, and n is the Langmuir rate constant (L. mg^{-1}), monolayer adsorption capacity (mg. g^{-1}), Freundlich rate constant ((mg.g^{-1})(L.mg^{-1})$^{1/n}$), and adsorption intensity, respectively.

3.2 Membrane characterization

Several membrane characterizations were performed on the pristine and composite PLA membranes. Equipment such as FEI Nova NanoSEM 650 high-resolution microscopy, goniometer, and Anton Paar SurPass 3 electrokinetic analyzer were used for SEM, water contact angle, and surface zeta potential analysis, respectively. The

effect of MAC loading on membrane porosity (ε, %), and mean pore radius (r_m, nm) was evaluated using the gravimetric method. This method relies on the difference in weight of the membrane when water is trapped within the pores after 24 h of immersion in deionized water (24 h) and when the membrane is completely dried. The porosity is calculated as follow [8]:

$$\varepsilon = \frac{m_w - m_d}{\rho_w \cdot A \cdot \delta} \times 100 \tag{5}$$

Where, m_w, m_d, ρ_w, and δ is the membrane's wet mass (g), membrane's dry mass (g), water density (g.cm^{-3}), and membrane thickness (cm), respectively.

The mean pore radius was estimated using the Guerout-Elford-Ferry equation [9]:

$$r_m = \sqrt{\frac{(2.9 - 1.75 \cdot \varepsilon) \cdot 8 \cdot \eta \cdot \delta \cdot Q}{\varepsilon \cdot A \cdot \Delta P}} \tag{6}$$

Where η, Q, and ΔP is the water viscosity (8.9×10^{-4} Pa.s), permeated pure water volumetric flowrate (m^3.s^{-1}), and operational pressure (0.1 MPa).

3. Membrane performance

The membranes were characterized using SEM, surface zeta potential, water flux, pore-size/porosity, and contact angle. The ε and r_m altered significantly upon MAC loading from 0 to 6 wt.% (**Figure 1**). An increase in porosity from 90.2±5.4 to 97.8±5.6% was observed upon incorporation of 3wt.% of MAC, as compared to PLA. The largest pore size was allocated to 1.5AC-PLA with a value of 37.6±3.1 nm reflecting a 12% increase. The r_m trend continued to decrease reaching a value of 34.8±3.5 nm after 3wt.% loading of MAC, yet it remained higher than that of the control membrane (33.6±1.5 nm). Surface hydroxyls and amine groups present in MAC can induced hydrophilic behavior in the polymer solution, impacting the exchange rate between DMAc solvent with water (non-solvent) during phase inversion. A selective dense top-layer can form from a lower exchange rate between DMAc and water caused by the increased viscosity of the dope solution after MAC loading [10].
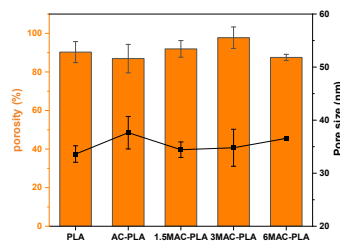

Figure 1: Porosity and mean pore radius trend of pristine and composite PLA membranes

Static adsorption and dynamic filtration were performed as well to investigate the flux-rejection performance and the pH-responsiveness (4, 7, and 10) of the membranes. The

results showed that the pure water flux increased from 1336 ± 96 L.m^{-2}.h^{-1} in the pristine PLA membrane to 2307 ± 10 L.m^{-2}.h^{-1} in the 3MAC-PLA (3wt.% MAC), illustrated in **Figure 2**. Furthermore, the heavy metal ions rejection improved from 18.15, 17.31, and 17.50% for Cu^{2+}, Pb^{2+}, Ni^{2+} ions at pH 4, to 99.95, 100, and 99.95% at pH 10 for 3MAC-PLA, respectively (**Figure 3 (a-c)**). Also, the composite membranes revealed improved adsorption (pH 10) and desorption (pH 4) behavior. For example, 3MAC-PLA membrane recovered $72.45\pm0.25\%$ of its initial flux compared to only $24.94\pm7.48\%$ in the pristine membrane after 4 cycles of heavy metal filtration and simple DI water cleaning (pH 4). The rejection of 3MAC-PLA against all metals was maintained above 99% by the end of the 5th cycle. For the adsorption isotherms, Freundlich better fitted the experimental data at a higher correlation coefficient than the Langmuir isotherm, suggesting a non-uniform affinity for adsorption on heterogenous surface through chemisorption. The parameter n laid between a value of 1 to 10 indicating a favorable adsorption. Overall, the addition of MAC nanohybrid enhanced the properties of the pristine PLA, creating new potential for such composite membranes in the wastewater treatment industry.
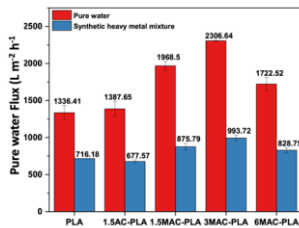

Figure 2: Pure water flux trend of MAC-PLA composites
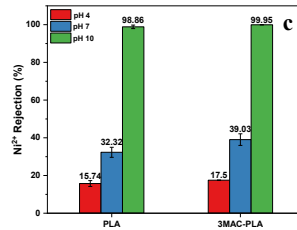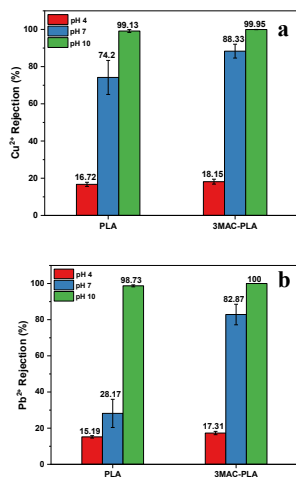

Figure 3: Effect of pH on PLA and 3MAC-PLA membranes rejection against (a) Cu, (b) Pb, and (c) Ni heavy metal ions

4. Conclusion

Modified activated carbon particles were synthesized, characterized, and used as fillers in mixed matrix membranes to perform adsorptive and desorptive behavior towards heavy metal ions present in wastewater upon solution pH alteration. Various filler loadings ranging from 0 to 6 wt.% were used to fabricate composite MAC/PLA membranes. Surface charge, topology, wettability, structural morphology, and the hybrid membranes' chemical characteristics were evaluated prior to the performance testing. Dead-end ultrafiltration experiments were conducted, and the results showed enhancement in flux up to values of 2307 ± 10 L.m^{-2}.h^{-1} at 3 wt.% loading of MAC. Optimal rejections of Cu, Pb, Ni were observed at pH 10, while the regeneration of the active-site (desorption) was observed at pH 4. The adsorption performance was influenced by the porosity, smoothness, hydrophilicity, and surface charge of the resulted hybrid membranes.

5. References

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