Electrospun microbial protein and cellulose acetate nanocomposite fibers for heavy metals-contaminated water remediation

MARRA S.[1,*], VENEZIA V.[2], MARAVIGLIA C.[1], LUCIANI G. [2], MATASSA S. [1], CESARO A. [1], SILVESTRI B. [1]

[1]DICEA, Department of Civil, Architectural and Environmental Engineering, University of Naples Federico II, Via Claudio 21, 80125 Naples, Italy

[2]DICMaPI, Department of Chemical, Materials and Industrial Production Engineering, University of Naples Federico II, Naples, Italy

*corresponding author
e-mail: sebastiano.marra@unina.it

Abstract Heavy metal pollution is a major environmental issue, with industrial and agricultural activities increasing metal concentrations in water. Effective treatment methods are crucial, and adsorption is one of the most efficient techniques. This study combines microbial proteins (MPs) from waste cheese whey permeate with biodegradable cellulose acetate to create nanocomposite mats via electrospinning. The resulting mats exhibit high adsorption capacity for lead (66.23 mg/g) and stability, demonstrating their potential as sustainable bio-adsorbents for wastewater treatment. The material's reproducibility, high efficiency, and eco-friendly nature make it a promising solution for heavy metal removal.

Keywords: electrospinning, cellulose acetate-based membrane, microbial protein, sustainable process, heavy metals water treatment.

1. Introduction

The rapid growth of global industrial activities has caused severe heavy metal pollution, posing serious risks to human health and the environment. Among existing removal methods, chemical precipitation generates secondary waste, while electrochemical reduction is costly and inefficient. Membrane separation and adsorption are more promising due to their affordability, selectivity, and reusability, with adsorption being particularly attractive for its low cost and ease of use. Various sorbents, such as activated carbon, carbon nanotubes, metal oxides, and functionalized polymers, have been used for heavy metal removal. Activated carbon and carbon nanotubes are unsustainable due to high energy consumption for activation and regeneration, while metal oxides require costly synthesis. In contrast, functionalized polymeric materials offer a practical, biodegradable, and easily modifiable alternative for metal adsorption.Cellulose, an abundant natural polymer, has hydroxyl groups that bind metal ions, yet its poor solubility restricts direct use. Its derivative, cellulose acetate (CA), is widely employed in filtration membranes, including electrospun nanofibers, which offer high surface area and excellent adsorption capacity. To enhance CA's performance, hybrid composites have been developed. Hamad et al. impregnated hydroxyapatite onto CA electrospun membranes for Pb(II) and Fe(III) removal. Du et al. blended CA with chitosan for metal complexation, while Xia et al. used lignin/CA nanofibers for Cu(II) and Co(II) removal. Based on a waste to wealth approach, microbial proteins (MPs) from cheese permeate biowaste fermentation offer a sustainable alternative. Rich in hydroxyl, carboxyl, and amide groups, MPs have strong potential for metal ion adsorption. This study investigates MPs as functional additives and active materials in CA-based electrospun membranes (CAMP) tested to lead and zinc ions removal for potential water treatment.

2. Experimental

CAMP fiber were prepared by dissolving 8.33% wt./vol. CA in acetone under stirring overnight, while MPs were dispersed separately (15.00% wt./vol. in water). The MP suspension was then gradually added to the CA solution and stirred for 2 hours to produce a homogeneous mixture. The final solution was electrospun using a 0.34 mm needle at 10.0 mL/h and 21.4 ± 0.3 kV, with a 19 cm tip-to-collector distance. Neat CA fiber was prepared at the same way without MPs, but adding the same amount of water. Finally, CAMP and CA fibers were thermally stabilized at 150°C for 2.5 hours. The morphology and diameter distribution of electrospun fibers were observed using a scanning electron microscopy (SEM). Adsorption tests were carried out prepared stock solution at fixed concentration (15-25-35-50-100 mg/mL) of lead and zinc ions using lead (II) dinitrate and zinc nitrate hexahydrate, respectively. Isotherms adsorption capacity at room temperature have been conducted in a single and binary metals systems. 10 mL of these solution were kept in contant for 24 hours with 5 mg CA or CAMP fibers. After reaching adsorption equilibrium, the fibers were removed. The concentration of metal ions into the supernatants were measured using Atomic Absorption Spectroscopy (AAS) to evaluate adsorption equilibrium capacity (Q_e) using equation 1. The experimental point has been fitted thought Langmuir and Freundlich models.

$$Q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

where Ci and Ce are the initial and final (equilibrium) concentrations of the metal ion in solution (mg/L), V is the solution volume (L), Q_e is the adsorbent phase concentration after equilibrium, mg metal ion/g adsorbent, and m is the mass of the sorbent (g).

3. Results and discussion

The morphology of the fibers was analyzed using SEM. **Figure 2** shows as both cellulose acetate-based membrane was characterized by bead formation, which was due to inherent electrospinning challenges and poor molecular entanglement of CA, especially using green solvent like acetone. This instability occurs because acetone, a safe solvent, doesn't provide sufficient molecular entanglement. The heterogeneity of the CA fibers is further shown in **Figure 1a**, where the diameter distribution varies significantly in a broad range of 600-2400 nm. In contrast, CAMP fiber (**Figure 1b**) was more homogeneous than neat CA, showing a more consistent structure. This improvement is attributed to the presence of MPs, which acted as additives, enhancing the spinnability and reducing bead formation. The diameter distribution of CAMP fibers was narrower than neat CA, with an average diameter of 300±100 nm. The addition of MPs not only stabilized the electrospinning process but also led to smaller fibers, which increased the specific surface area of the material, enhancing its potential for adsorption. About isotherm adsorption tests carried out on single metal system neat CA showed some affinity for Pb^{2+} ions, while functionalizing with MPs significantly increased the adsorption capacity of CAMP. However, for Zn^{2+} ions, the presence of MPs did not improve the membrane's performance, indicating a lower affinity for Zn^{2+} compared to Pb^{2+}. The experimental data for CAMP followed the Langmuir model more closely, with R^2 values close to one, indicating that adsorption is mainly driven by active sites. The maximum adsorption capacity for Pb^{2+} was 66.23 mg/g at 25°C, outperforming many other literature cellulose-based adsorbents. Due to the high lead affinity of CAMP, binary metal system isotherm study was carried out varying Pb2+ concentration, while Zn^2+ concentration was fixed at a specific value. **Figure 1c** shows that for CAMP, lead adsorption capacity remained close to single system, while zinc adsorption decreased drastically when lead concentrations were increased in solutions. These results suggested that CAMP exhibited good targeted adsorption of lead ion in polyionic solutions. This behavior can be explained by the covalency index function of electronegativity Xm and ionic radius r ($X_m{}^2r$), which describes the acidic nature of the ion. Lead ion has higher covalent index than zinc, indicating that Pb^{2+} exhibits stronger soft acidity, which is preferentially bind to the O and N functional groups present on microbial protein.

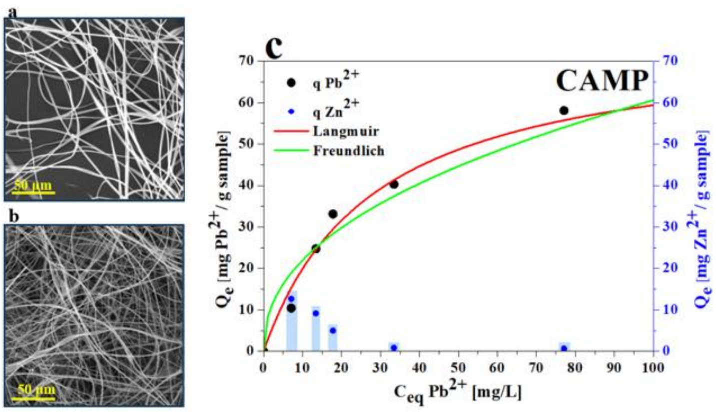

Figure 1. (a) SEM image of CA; SEM image of CAMP (b); isotherm adsorption tests on binary heavy metals system.

4. Conclusion

In this study, CAMP membrane was produced though a sustainable electropinning process, using cellulose acetate, green solvents and microbial proteins as active material. The resulting fibers showed more stable and consistent respect to neat CA membrane. Moreover, the inherent spinnability difficult of CA was overcame by the presence of MPs as additives. CAMP membrane was evaluated for heavy metals water remediation, testing the fiber into lead and zinc aqueous solution. Lead affinity of fiber was drastically increased thanks to MPs, in particular adsorption capacity for Pb^{2+} was around 66 mg/g and this value remained also stable into binary metals system. These results have shown the microbial proteins potential for sustainable membrane production and heavy metals removal.

References

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