Investigation of the effect of time on polypyrrole adsorbent membrane for nickel metal removal

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ABSTRACT

One of the common methods for removing heavy metals from aqueous solutions is the use of membranes. In this study, a sorbent (polypyrrole) was used to enhance the efficiency of a polyether sulfone membrane in removing nickel metal ions from water. It is worth mentioning that the synthesis method of the polyether sulfone membrane was carried out through surface polymerization. This study was conducted under neutral pH conditions and ambient temperature, with various contact times from zero to 180 minutes to investigate the percentage of nickel adsorption in a batch system. The chemical structure of the membrane was characterized using the water contact angle (WCA) test, and the surface morphology was examined using a field emission scanning electron microscope (FESEM). The results indicate that polypyrrole formed on the pure membrane and has the ability to remove nickel ions from the aqueous solution. In this study, it was observed that the adsorption percentage initially increased with the contact time and then reached equilibrium.

Keywords: *Interfacial Polymerization, Polypyrrole, Adsorbent Membrane, Nickel.*

1. *INTRODUCTION*

Every year, millions of people lose their lives due to severe water-related diseases. This issue is particularly acute in certain regions, and water scarcity is rapidly spreading to other parts of the world [1]. Water pollutants include contaminants from household waste, food processing waste, pesticides, chemical waste, and heavy metals. Heavy metals, as elements with high atomic weights, pose potential risks to human health and the environment, which is concerning [2]. To reduce water pollution, the development of advanced, low-cost water treatment technologies with high efficiency is essential. One effective method for removing heavy metals from water is the membrane filtration process, which plays a crucial role in purifying contaminated water. This method is considered a promising technology for pollutant removal due to its ease of operation and low space requirements [3,4].

2. *METHOD AND MATERIALS*

2.1 materials

Polypyrrole is purified by distillation to polymerization, polyethersulfone (PES), Ferric chloride ($FeCl3$), The purity of n-hexane was about 99%, For nickle ion removal test, hexa nickel nitrate($Ni(No3)2.6H2O$), dymethylacetamide (DMF), polyvinylpyrrolidone (PVP) all of them are used in Merck (Germany), Distillate water, for preparation of PES support polyester was used.

2.2 Preparation of the polyethersulfone (PES) porous substrate

The substrate was prepared using the phase inversion technique (PIT) with a casting solution consisting of 14 wt% polyethersulfone (PES), along with dimethylformamide (DMF) and polyvinyl pyrrolidone (PVP) as additives. Initially, PVP was added to DMF, followed by the gradual addition of PES to the solution while stirring gently for 6 hours. Afterward, the mixture was allowed to rest for 2 hours to degas and remove air bubbles. The polyester fabric was adhered to a glass surface, and the homogeneous solution was then poured *onto the polyester using a casting knife. This mixture was then smoothly immersed in a water bath for phase inversion for 24 hours at room temperature. Finally, two sheets of paper were used to dry the PES substrate membrane at room temperature for an additional 24 hours. [5]*

2.3 Preparation of PPy membranes

Initially, 1.21 gr of polypyrrole were mixed with 60 mL of hexane and then placed in an ultrasonic mixer. Next, 3.41 gr of iron (III) chloride ($FeCl_3$) were added to 60 mL of distilled water and mixed. The pure polyether sulfone membrane was immersed in the $FeCl_3$ solution for 10 minutes and then immediately placed in the solution containing polypyrrole and hexane. After these steps, the membrane was washed three times with water and ethanol. Finally, to dry, the membrane was placed in an oven at 60 °C. [6]

3. *ADSORPTION EXPERIMENTS FOR THE REMOVAL OF NICKEL (II)*

3.1 Batch adsorption experiments

The sorption test was conducted using a batch system in aqueous medium. A stock solution of nickel(II) ions was prepared, containing 500 mg L^{-1} of nickel ions, by dissolving nickel nitrate in distilled water. In the initial phase, 1 gr of the modified membrane, which contained 0.03 grams of polypyrrole sorbent, was crushed and mixed with 15 mL of a nickel solution with an initial concentration of 50 ppm and neutral pH. This mixture was allowed to stand for approximately 2 hours to facilitate separation. Sorption processes were carried out at room temperature, with time intervals of 5, 15, 20, 30, 60, 90, 120, and 180 minutes, maintaining a pH of 7. The experiments were executed in a batch shaker system operating at 200 rpm, after which the extent of adsorption was measured using an Atomic Absorption Spectrometer. The percentage of nickel removal can be calculated using the following formula: (1)

$$R\%=\frac{c_0-c_e}{c_0}\times 100 \qquad (1)$$

Where C_0 the initial concentration (mg/l) and C_e is equilibrium concentration (mg/l) of Ni, V refers to the solution volume (L) and m stands for the adsorbent mass (ppy)(gr) (35,36). The adsorbed amount of Ni (II) per unit is q_t (mg/l) [7].

4. *RESULTS AND DISCUSSION*

4.1 Contact angle measurement

The effect of polarization on the permeability of polypyrrole (PPy) coated and neat membranes has been investigated. The PPy coating reduced the wettability of the membranes, as illustrated in Fig. 1. The results indicate that the modified membranes exhibit higher water contact angles (WCA). In the uncoated membrane, the WCA was approximately 54°. Following the application of the coating, the WCA increased to about 61° for the PPy membrane.

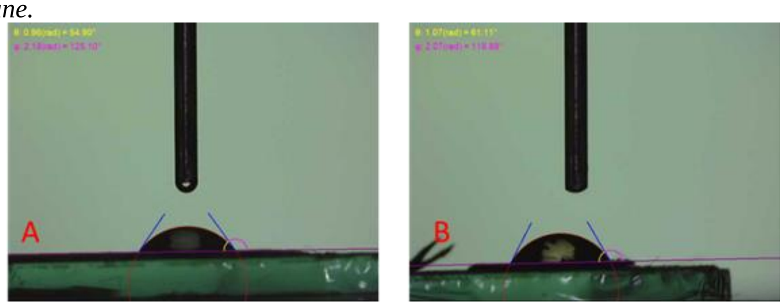

Fig. 1. Contact angle measurement: (A) neat membrane, (B) modified membrane

2.4 FE-SEM

The images presented in Fig. 2 illustrate the surface and cross-sectional characteristics of both pristine and modified membranes. Microscopic analysis reveals a dense formation of polypyrrole (PPy) particles on the polyethersulfone layer, creating a noticeable surface layer. Both membrane types exhibit an asymmetric structure due to phase inversion, characterized by a thin dense selective layer and a porous sub-layer with finger-like pores. In Fig. 2(b), uniform and Cavity-like pores are evident on the surface of the modified membrane, while Fig. 2(a) shows a smooth and homogeneous surface for the unmodified membrane. A comparative analysis between the neat membrane (A) and the modified membrane (B) indicates the presence of an additional dense layer at the cross-section of the latter. This observation suggests differences in structural composition, likely resulting from the modification process.

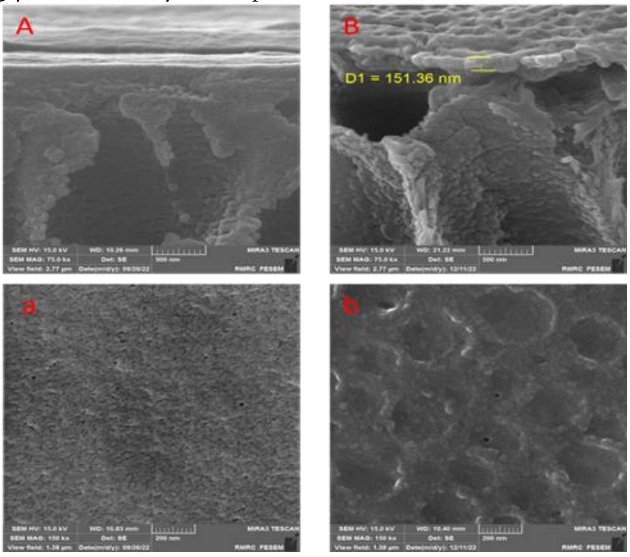

Fig. 2. FE-SEM surface and cross-sectional: (A,a) neat membrane, (B,b) modified membrane

4.2 Effect of contact time

The contact time was depicted in Fig. 3, where the performance of nickel adsorption ions was evaluated as a function of contact time varying from 5 min to 180 min by keeping the parameters constant in a batch experiment. It was observed that the removal percentage and uptake efficiency increases significantly with increasing contact time. As indicated in Fig. 3 the maximum level of efficiency was reached at 120 min and approximately 75.6% of Ni2+ ions were removed. Moreover, after that there was no significant change and it reached to equilibrium adsorption. The similar adsorption efficiency action was also reported [8]. This can be clarified the fact that the availability of more number of adsorption sites at first it was high because of vacant adsorbent sites. Consequently, the achievement of equilibrium adsorption may be due to the reduction of active adsorption sites on the adsorbent [9].

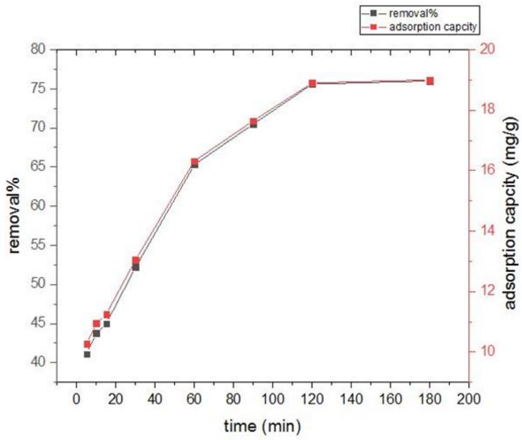

Fig. 3. the effect of time on removal percentage

5. CONCLUSION

In this study, it was observed that the adsorption percentage increased with prolonged contact time up to a certain point and then stabilized. The results of the Water Contact Angle (WCA) analysis indicate the formation of polypyrrole on the polyethersulfone. Additionally, the scanning electron microscope (FESEM) images demonstrate the formation of a polypyrrole layer on the pure polyethersulfone membrane, confirming the accuracy of the synthesis. The maximum adsorption efficiency was achieved at 120 minutes, during which almost all Ni^{2+} ions were removed. After this time, no significant changes were observed, and the system reached an equilibrium state. This phenomenon may indicate that in the initial stages, the availability of a greater number of adsorption sites due to the presence of vacant sites contributed to the increased adsorption efficiency. Furthermore, achieving equilibrium adsorption may be related to a decrease in the number of active adsorption sites on the adsorbent.

REFERENCES

[1] *S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco, and W. Gernjak, "Decontamination and disinfection of water by solar photocatalysis: recent overview and trends," Catalysis today, vol. 147, no. 1, pp. 1-59, 2009.*

[2] *M. N. Chong, B. Jin, C. W. Chow, and C. Saint, "Recent developments in photocatalytic water treatment technology: a review," Water research, vol. 44, no. 10, pp. 2997-3027, 2010.*

[3] *Li, Xianfeng, Pieter Vandezande, and Ivo FJ Vankelecom. "Polypyrrole modified solvent resistant nanofiltration membranes." Journal of Membrane Science 320.1-2 (2008): 143-150.*

[4] *Carolin, C.F., Kumar, P.S., Saravanan, A., Joshiba, G.J. and Naushad, M.; "Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review", Journal of Environmental Chemical Engineering, pp.2782-2799, 2017.*

[5] *Darabi, Rezvaneh Ramezani, Majid Peyravi, and Mohsen Jahanshahi. "Forward osmosis process membranes incorporated with functionalized P. ZnO nanoparticles for organic fouling control." Korean Journal of Chemical Engineering 38 (2021): 843-851.*

[6] *Teng, Xiangguo, et al. "Polypyrrole thin film composite membrane prepared via interfacial polymerization with high selectivity for vanadium redox flow battery." Reactive and Functional Polymers 157 (2020): 104777.*

[7] *Amiri, Afsaneh, Mohsen Ghorbani, and Mansoor Jahangiri. "A novel chitosan/polyrhodanine nanocomposite: preparation, characterisation and application for Ni (II) ions removal from aqueous solution." Journal of Experimental Nanoscience 10.18 (2015): 1374-1386.*

[8] *Sun, Ping, et al. "Efficient adsorption of Cu (II), Pb (II) and Ni (II) from waste water by PANI@ APTS-magnetic attapulgite composites." Applied Clay Science 209 (2021): 106151.*

[9] *Tirtom, Vedia Nüket, et al. "Comparative adsorption of Ni (II) and Cd (II) ions on epichlorohydrin crosslinked chitosan–clay composite beads in aqueous solution." Chemical Engineering Journal 197 (2012): 379-386.*