

# Performance enhancement of nanocomposite nanofiltration membranes modified by various amine groups: increase in flux and improvement of separation properties of pollutants from wastewater

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## Abstract

In the present study,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CS}$  biocompatible nanocomposites were synthesized using  $\text{Fe}_3\text{O}_4$  MNPs, amorphous silica extracted from rice husk and wheat straw agricultural wastes and APTMS and CS functional groups and applied as an efficient nanofiller to modify PES NF membranes structure. Structural analyses confirmed fine structure of synthesized nanocomposites and fabricated membranes. NFM-WS membrane modified by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CS}$  nanocomposite with  $70.6 \text{ L m}^{-2} \text{ h}^{-1}$  had higher pure water flux compared with NFM-RH membrane modified by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  nanocomposite with  $65.4 \text{ L m}^{-2} \text{ h}^{-1}$ . Both membranes showed the highest salt rejection with more than 80% for  $\text{Na}_2\text{SO}_4$  and the lowest salt rejection with about 10% for  $\text{MgCl}_2$ . Performance of NFM-RH and NFM-WS membranes for removal of  $\text{Cd}^{2+}$  heavy metal ions were almost same of 97 and 98%, respectively. NFM-RH and NFM-WS membranes indicated high performance with more than 98% for removal of MR dye. NFM-RH and NFM-WS membranes by FRR of more than 88 and 93%, respectively, demonstrated excellent flux recovery ratio. Also,  $R_t$  and  $R_{ir}$  of NFM-RH membrane were about 69 and 12%, respectively, and  $R_t$  and  $R_{ir}$  of NFM-WS membrane were about 50 and 7%, respectively, which displayed excellent antifouling properties of fabricated NF membranes. In conclusion, fabricated NF membranes are so efficient for water treatment and in term of environmental are low cost and due to their primary production source are biocompatible.

**Keywords:** Rice husk; wheat straw; biocompatible nanocomposites; NF membranes; wastewater treatment

## 1. Introduction

With population growth and industrialization, many environmental problems including water crisis created by industrial pollutants especially inorganic salts, heavy metals ions and organic dyes have been caused for human societies, which have necessitated the development of water and industrial wastewaters treatment technologies [1]. Industrial wastewaters, if treated and purified, can be considered as a valuable source of water for human consumption [2]. On the other hand, the discharge of industrial wastewaters containing salts, heavy metals ions and dyes in the environment leads to water and soil pollution and the accumulation of these pollutants in the environment [3]. The release of inorganic salts in water sources used by humans through industrial effluents can cause water salinity and reduce its quality for human consumption [4]. Heavy metals ions are also widely discharged in the environment through industrial wastewaters, which due to their stability and non-biodegradability in the environment, even at very low concentrations, cause bioaccumulation in the food chains and cause a wide range of complications and disorders

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including acute poisoning, cancer, mental and physical damage [5]. Also, many industrial wastewaters contain many organic dyes that by discharging in the environment contaminate surface water sources, cause various diseases and genetic mutations in human, reduce the transparency of water, prevent the penetration of light in the water and disrupt the photosynthetic activities of aquatic organisms [6]. Therefore, the concentration of these pollutants in industrial wastewaters before discharge to the environment should be reduced to standard levels to help solve the water crisis in addition to reducing environmental problems. Thus, the use of new, cost-effective and efficient methods for the treatment of industrial wastewaters from these pollutants in term of environmental and health is absolutely necessary. In this study,  $\text{Fe}_3\text{O}_4$  MNPs were coated with amorphous silica extracted from rice husk and wheat straw agricultural wastes and functionalized with APTMS and CS functional groups, and were used as new, biocompatible and inexpensive nanocomposites to modify the structure of PES NF membrane. The structure of synthesized nanocomposites and fabricated NF membranes was studied using XRD, FT-IR, VSM, SEM, zeta potential and water contact angle and porosity measurement analyses. The fabricated NF membranes were applied for measurement of pure water flux, rejection of inorganic salts, removal of heavy metal ions, retention of organic dyes and evaluation of antifouling properties experiments, and their performance was compared.

## **2. Materials and methods**

For the synthesis of biocompatible nanocomposites, agricultural wastes of rice husk and wheat straw were used as raw material. In this process,  $\text{Fe}_3\text{O}_4$  MNPs were first synthesized by chemical co-precipitation method [7]. In the next step, the extraction of amorphous silica ( $\text{SiO}_2$ ) from rice husk and wheat straw was done by acid leaching method and the extracted  $\text{SiO}_2$  was used as shell for coating of  $\text{Fe}_3\text{O}_4$  MNPs to produce  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  [8]. In the next step, the synthesized  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  was functionalized using APTMS and CS functional groups [9]. Finally, the modified nanofiltration membranes with 0.5 wt.% of synthesized nanocomposites of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$  and  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-CS}$  related to the total solution weight were fabricated by phase inversion method [3].

## **3. Results and discussion**

The crystal structure of  $\text{Fe}_3\text{O}_4$  MNPs, the amorphous nature of the extracted silica and the successful coating of  $\text{Fe}_3\text{O}_4$  MNPs using the extracted silica were confirmed by XRD analysis. FT-IR analysis confirmed successful functionalization of silica surfaces using APTMS and CS functional groups. SEM images of the membranes top-surface confirmed the smooth and without cracking top-surface of the fabricated NF membranes. The membranes cross-sectional SEM images confirmed the asymmetric and porous structure of the fabricated NF membranes. Also, other analyses showed that with the addition of the nanocomposites in the membranes structure by 0.5 wt.%, the water contact angle of the membranes decreased, the overall porosity and mean pore radius of the membranes increased and the negative charge of the membranes surface increased. In addition, the results of the membranes filtration experiments showed that with the addition of the nanocomposites in the membranes matrix, the pure water flux of the membranes increased significantly. The behavior of the fabricated NF membranes in rejection of salts was similar to the typical behavior of NF membranes. The membranes showed excellent performance in removal of heavy metal ions, retention of dye and antifouling properties.

## **4. Conclusions**

In general, the fabricated NF membranes in this study are efficient, biocompatible and inexpensive membranes for the treatment of water and industrial wastewaters contaminated with salts, heavy metal ions and dyes, and can be used for a variety of environmental applications.

## References

- [1] H. Jayasantha Kumari, P. Krishnamoorthy, T.K. Arumugam, S. Radhakrishnan, D. Vasudevan, An efficient removal of crystal violet dye from waste water by adsorption onto TLAC/Chitosan composite: A novel low cost adsorbent, *International Journal of Biological Macromolecules*, 96 (2017) 324-333.
- [2] T. Ahmad, T. Belwal, L. Li, S. Ramola, R.M. Aadil, Abdullah, Y. Xu, L. Zisheng, Utilization of wastewater from edible oil industry, turning waste into valuable products: A review, *Trends in Food Science & Technology*, 99 (2020) 21-33.
- [3] S. Kamari, A. Shahbazi, Biocompatible  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  nanocomposite as a green nanofiller embedded in PES–nanofiltration membrane matrix for salts, heavy metal ion and dye removal: Long–term operation and reusability tests, *Chemosphere*, 243 (2020) 125282.
- [4] J. Wang, Y. Zhang, J. Zhu, J. Hou, J. Liu, B. Van der Bruggen, Zwitterionic functionalized layered double hydroxides nanosheets for a novel charged mosaic membrane with high salt permeability, *Journal of Membrane Science*, 51 (2016) 27-37.
- [5] G. Moradi, S. Zinadini, L. Rajabi, A. Ashraf Derakhshan, Removal of heavy metal ions using a new high performance nanofiltration membrane modified with curcumin boehmite nanoparticles, *Chemical Engineering Journal*, 390 (2020) 124546.
- [6] J. Wang, J. Zhu, M.T. Tsehaye, J. Li, G. Dong, S. Yuan, X. Li, Y. Zhang, J. Liu, B. Van der Bruggen, High flux electroneutral loose nanofiltration membranes based on rapid deposition of polydopamine/polyethyleneimine, *Journal of Materials Chemistry A*, 5(28) (2017) 14847-14857.
- [7] A.M. Sanati, S. Kamari, F. Ghorbani, Application of response surface methodology for optimization of cadmium adsorption from aqueous solutions by  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{APTMS}$  core–shell magnetic nanohybrid, *Surfaces and Interfaces*, 17 (2019) 100374.
- [8] S. Kamari, F. Ghorbani, Extraction of highly pure silica from rice husk as an agricultural by-product and its application in the production of magnetic mesoporous silica MCM–41, *Biomass Conversion and Biorefinery*, (2020).
- [9] L. Fan, C. Luo, X. Li, F. Lu, H. Qiu, M. Sun, Fabrication of novel magnetic chitosan grafted with graphene oxide to enhance adsorption properties for methyl blue, *Journal of Hazardous Materials*, 215-216 (2012) 272-279.