17th International Conference on Environmental Science and Technology

Athens, Greece, 1 to 4 September 2021

Synthesis of Fe_3O_4-Ag Nanocomposite and Their Performance as Surface Modifiers for TiO_2 Membranes in Treating Oily Wastewater

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Abstract. Membrane technology has shown extraordinary performance in treating oily wastewater. Yet, more research is focused towards enhancing the performance of the separation process. In this work, Fe_3O_4-Ag composite nanoparticles (NPs) were synthesized using the co-precipitation technique and applied on the surface of TiO_2 ceramic membranes to enhance their performance in terms of oil emulsions separation. The NPs were characterized using the FTIR, XRD, among others. The Fe_3O_4-Ag NPs were coated on the surface of the ceramic membranes using vacuum coating method by which a uniform layer of the NPs was formed on the surface. Results showed that the contact angle of the pristine ceramic membrane was found to be $75° \pm 2.2°$.On the other hand, the modified membrane contact angle was found to be $10.1° \pm 2.2°$ indicating a super hydrophilic surface. Furthermore, the modified membranes showed water flux of 1065 $L \cdot m \cdot h^{-1}$ (LMH) which is 2.8 higher than the pristine membrane (380 LMH). Lastly, the surface-coated membranes showed a total oil rejection of 61.8% compared to 56.5% in the pristine membranes. These results showed the potential of using these modified membranes in treating oily wastewater from refineries.

Keywords: Membrane technology, Oily wastewater, Nanoparticles, Surface Modification.

1. Introduction

Water scarcity, is a global conundrum that attracted the attention of the science community in the last decades. It poses a significant threat to the stability of economics, societies, and the growth of businesses [1]. Furthermore, the pollution of the freshwater resources in many places increased the severity of this conundrum. One way to reduce this severity is through the recycling wastewater. Treatment of PW has been implemented through numerous conventional methods, such as adsorption, hydrocyclones, and media filtration and many other methods [2]. From those, membrane technology showed superior performance when compared to the other technologies. This include the high separation efficiency, low energy requirements, low capital cost, design simplicity, compactness [3]. Various efforts were made to enhance the properties of the membranes through the addition of different metal oxides NPs. From those, the incorporation of Fe_3O_4 NPs has proven to increase the antifouling resistivity, catalytic activity, and surface hydrophilicity of the membranes after coating the surface of the membrane with these NPs [4]. In addition, Ag NPs were found to improve the antimicrobial abilities due to their unique physical and chemical properties [5]. Therefore, in this study, Fe_3O_4-Ag nanomaterial was synthesized and used to surface coat TiO_2 ceramic membranes. The performance of these membranes in terms of water flux, oil rejection, anti-fouling was evaluated. The membranes and nanocomposites were also characterized using SEM, FTIR, XRD, among others.

2. Materials and Methods

2.1. Materials

The oily wastewater used in this study (COD concentration=21800 mg/L) was obtained from an oil refinery near Abu Dhabi, UAE. Iron (III) chloride ($FeCl_3$), iron chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), ammonia solution NH_4OH, silver nitrate ($AgNO_3$), L-Arginine ($C_6H_{14}N_4O_2$), tetraethyl orthosilicate (TEOS), and nitric acid (HNO_3) were obtained from Sigma-Aldrich. The ultrafiltration (UF) TiO_2 ceramic membranes (D = 47 mm, thickness=2.5 mm, mean pore size =1 kDa) were supplied by Sterlitech, USA.

2.2. Synthesis of Fe_3O_4-Ag nanoparticles, and Membrane

The membranes were surface coated using a vacuum coating setup as illustrated in the literature [6]. The Fe_3O_4 NPs were prepared following coprecipitation method. Initially, 14.6 g of $FeCl_3$ and 11.9 $FeCl_2 \cdot 4H_2O$ were dissolved in 200 mL deionized (DI) water and heated to 90 °C. Afterwards, 60 mL of NH_4OH was added to the above solution under vigorous stirring at 80 °C for 1 hr. The mixture was then allowed to cool down to the room temperature and the precipitate was collected via

centrifugation at 4000 rpm. Lastly, the precipitate was washed several times with DI water and dried at room temperature.

As for the Ag NPs, L-Arginine ($C_6H_{14}N_4O_2$) used as a reducing agent to reduce $AgNO_3$ into Ag and NO_3. The L-Arginine solution was prepared by adding 1 g of L-arginine to 50 mL DI water. Following that, the L-arginine was added to the $AgNO_3$ mixtures under vigorous stirring for 1 hour. Afterwards, the Fe_3O_4 NPs were added to the L-arginine-$AgNO_3$ solution and left for vigorous stirring for 8 hours at $70\ °C$. Permanent magnet was used to collect the Fe_3O_4-Ag nanocomposites.

The composite membranes were fabricated with different concentrations of the NPs. Prior to the surface coating, all membranes were dipped in a TEOS solution prepared by mixing 90% ethanol, 5% DI water, 5% HNO_3, and 2 ml of TEOS for 4 hours, to formulate a layer that can act as a binder between the surface of the membrane and the Fe_3O_4-Ag nanocomposite.

3. Results and Discussion

3.1. Characterization of the synthesized Fe_3O_4-Ag

The FTIR analysis of the Fe_3O_4-Ag nanocomposite displayed in Figure 1 revealed a peak at 550 cm-1 that is related to the stretching modes of the Fe-O band. The peak at 1645 cm-1 indicates the presence of N-Ag, which occurred due to the replacement of the H atoms from the N-H bond with Ag+ ions from the $AgNO_3$ [7]. The peak at around 1550 - 1750 is correlated to the adsorbed water molecules on the surface of Fe_3O_4-Ag nanocomposite.

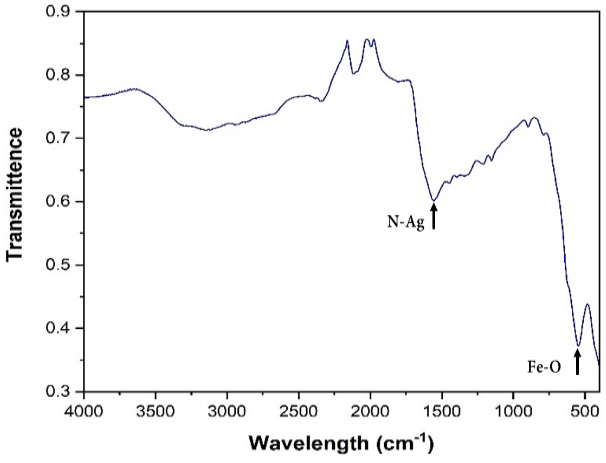

Figure 1. The FTIR spectrum for the synthesized Fe_3O_4-Ag nanocomposite.

The XRD results (Figure 2) showed four peaks that are frequently found in the XRD spectrum of Ag [8]. These peaks are located at (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of the face centered cubic and correspond to $2\theta = 38.6, 44.7, 63.5, and\ 77.5$, respectively. These peaks confirm the successful incorporation of the Ag NPs onto the Fe_3O_4 NPs.

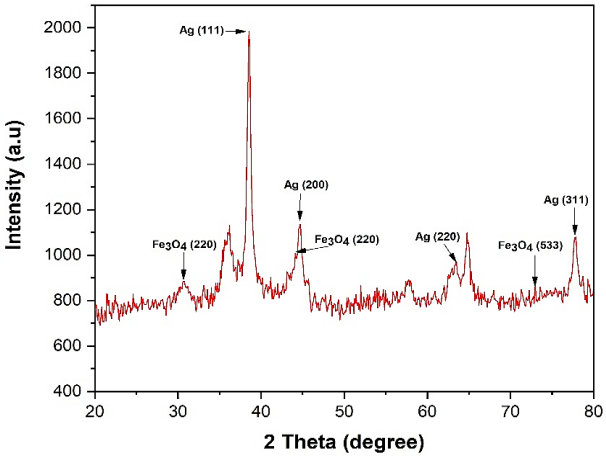

Figure 2. The XRD spectrum for the synthesized Fe_3O_4-Ag nanocomposite.

3.2. Characterization and performance evaluation of the membrane

The SEM images of the membranes show the surface of the pristine membrane, as well as the modified membrane. It can be clearly seen that the nanocomposites were uniformly deposited on the membrane. The pristine membrane showed water flux of $\mathbf{380}$ LMH of the permeate, at the same time showed $\mathbf{56.5}$% separation of oil emulsions. On the other hand, the coated membrane showed a flux of $\mathbf{1065}$ LMH which is $\mathbf{2.8}$ times higher than the pristine membrane, while showing $\mathbf{61.8}$% rejection of oil emulsions.

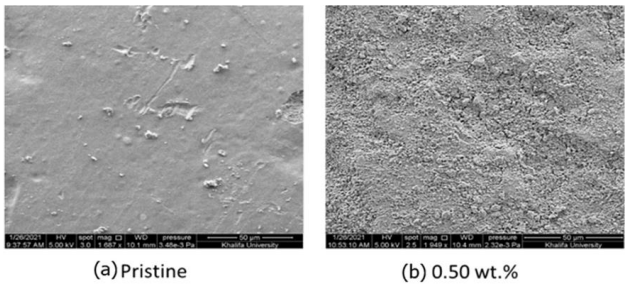

Figure 3. SEM images of the pristine and 0.50 wt.% membrane.

4. Conclusion

The synthesis of Fe_3O_4-Ag nanoparticles was successfully implemented via the coprecipitation technique. The attachment of the Ag nanoparticles to the Fe_3O_4 nanoparticles was inspected using the FTIR and the XRD analyses. The nanocomposites showed superhydrophilic behavior with a contact angle of $\mathbf{10.1° \pm 2.2°}$ after coating it on the membrane**.** The coating of the membranes was implemented using the vacuum coating technique, in which a uniform layer was formed on the surface of the membrane, the water flux of the modified membrane was 2.8 higher than the flux of the pristine membrane, while showing a slight increase in the rejection of the membrane. Overall, modifying the surface of TiO_2 membranes with Fe_3O_4-Ag composite nanoparticles enhanced the performance of the membranes.

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