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Research Paper

Investigating the effect of titanium dioxide nanoparticles on the performance of polyvinyl chloride membranes in the separation of humic acid

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1. ABSTRACT

Considering the water quality problems and the strict laws established for drinking water treatment, the need to use more effective and economical methods to remove water pollutants is felt. Meanwhile, the use of membrane processes is considered one of the most important methods to remove pollutants as well as possible. Based on this, in the current research, microporous polyvinyl chloride (PVC) membranes containing titanium dioxide (TiO_2) nanoparticles (NPs) were made using the nonsolvent induction phase separation method for use in humic acid separation as a model of polluted water. A set of characterization tests including contact angle, average pore radius, tensile strength, and humic acid rejection test was carried out. The obtained results showed the presence of NPs in the structure of nanocomposite membranes significantly improved the tensile strength of these membranes compared to pure PVC membrane. A point that should be noted is that with the increase in the weight percentage of NPs from 1 to 2, the tensile strength of the membranes increased, but with its increase from 2 to 3, a slight decrease in the amount of tensile strength is observed. Moreover, the obtained results indicated an increase in the hydrophilic properties of the membranes due to the presence of TiO_2 NPs. Also, the analysis of the results of humic acid rejection test showed that the membrane with 2 wt% of NPs with the smallest average radius of the surface pores had the highest separation efficiency with a value of 80%.

Keywords: Polyvinyl Chloride, Nonsolvent Induction Phase Separation, Titanium Dioxide, Water Pollutants, Humic Acid Rejection.

2. INTRODUCTION

In general, among natural organic substances, humic substances make up half of the total organic carbon content in water [1]. Considering the water quality problems and the strict rules established for drinking water treatment, the need to use more effective and economical methods to remove NOM is felt. In the meantime, using the coagulation process along with the membrane process is one of the most important steps to remove NOM as best as possible [2, 3].

Meanwhile, polymer membranes are especially important in the field of water purification. High porosity is one of the main and important characteristics of polymer membranes. The conducted studies show that despite the great importance of PVC membranes in the field of water purification, limited research is available on the surface modification of this type of membranes for the intended process. In the meantime, the many advantages of PVC membranes, including very low price and mass production in the country, as well as favorable chemical and thermal resistance, were the attractions that led the upcoming research to use this type of polymer in making membranes. Thus, the main innovation of this work is the fabrication of PVC nanocomposite membranes containing TiO_2 NPs and the addition of polyethylene glycol with a molecular weight of 6000 (PEG 6000) for use in the separation of humic acid as a model of polluted water. It should be noted that, based on the investigations carried out so far, no comprehensive study has been conducted on the construction of PVC/PEG/TiO_2 flat membrane for the separation of humic acid as a model of polluted water.

3. MATERIALS AND METHODS

3.1 materials

PVC as the material used in making the membrane was obtained from Ghadir Petrochemical Company. Dimethylformamide (DMF) as solvent and TiO_2 as NPs were purchased from Shiraz Chemical Company. Also, PEG

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6000 as an additive, ethanol to be used in the coagulation bath, and isobutanol to perform the porosity test were purchased from Merck.

3.2. Membrane Characterizations

3.2.1. Contact angle and tensile strength

To determine the hydrophilicity of pure and nanocomposite membranes, the contact angle measurement test was used. For this purpose, a CAG-20 Jikan device was used. The amount of tensile strength of pure and nanocomposite membranes was obtained by STM-1 tensile device.

3.2.2. Pure water flux, average pores radius and humic acid rejection

Pure water flux of membranes was determined using a dead-end filtration system consisting of a nitrogen gas cylinder, a pressure controller and feed reservoir with a magnetic stirrer. Water flux was calculated using the following equation:

$$J_0 = \frac{V}{At} \qquad (1)$$

Where J_0 is pure water flux, V is volume of collected water (l), A is membrane area (m^2), and t is the time (h).
The presented method based on pure water permeability was used to determine the average radius of surface pores of membranes. Equation (2) was used to calculate the average pores radius [4, 5]:

$$r_m = \sqrt{\frac{8l\eta Q(2.9-1.75\epsilon)}{\epsilon A \Delta P}} \qquad (2)$$

Where, r_m is the average pores radius, l is the thickness of the membrane, η is the viscosity of pure water, Q is the volume of water passed through the membrane, ϵ is the total porosity, A is the surface area of the membrane and ΔP is the pressure applied on the membrane.
The humic acid rejection (R (%)) of membranes was calculated according to equation (3), based on the absorption method with Bio Quest spectrometer model CE2501:

$$R(\%) = \left(1 - \frac{C_{permeate}}{C_{feed}}\right) \times 100 \qquad (3)$$

Where, $C_{permeate}$ and C_{feed} are the concentration of humic acid in the phase passing through the membranes and feed, respectively.

4. RESULTS AND DISCUSSION

4.1. Contact angle analysis

Figure 1 shows the average results obtained from measuring the contact angle of membranes. As can be seen from the figure, the contact angle of the nanocomposite membranes with different percentages of TiO_2 NPs is lower compared to the pure PVC membrane. One of the main reasons for reducing the size of the contact angle of nanocomposite membranes is the presence of TiO_2 NPs and the addition of PEG 6000 on the surface of these membranes.

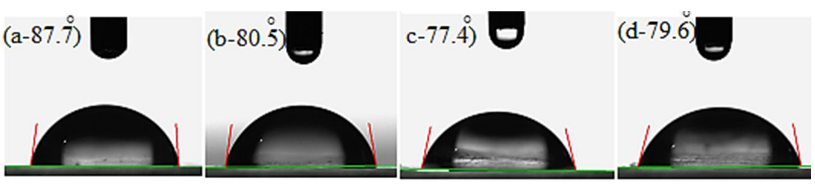

Figure 1. Water contact angles of the PVC membrane samples; (a) pure membrane, (b) composite membrane (1 wt% NPs), (c) composite membrane (2 wt% NPs), and (d) composite membrane (3 wt% NPs).

4.2. Investigating the tensile strength of membranes

Stress at the break point were used to test the membranes' mechanical strength, as illustrated in Figure 2. According to the results, it can be seen that the presence of NPs in the structure of nanocomposite membranes has significantly improved the tensile strength of these membranes compared to the pure PVC membrane. In general, the increase in the tensile strength of the membranes can be attributed to the reinforcing effect of TiO_2 inorganic NPs in the PVC polymer network.

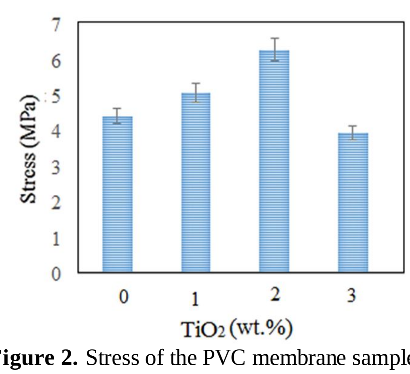

Figure 2. Stress of the PVC membrane samples.

4.3. Separation of humic acid solution

Figure 3 shows the humic acid rejection of membrane samples. It can be seen carefully in the figure that by increasing the amount of TiO_2 from 0 to 2 wt. %, the humic acid rejection increases, but by increasing the amount of TiO_2 up to 3 wt. %, the humic acid rejection decreases. This phenomenon can be justified based on the results obtained from the average radius of surface pores. Figure 4 shows the average radius of surface pores of membrane samples. Studies have shown that by reducing the size of the surface pores, the ability of humic acid macromolecules to pass through the membranes decreases, and as a result, the amount of removal or in other words, the separation efficiency of the membranes increases. In this way, it can be said that the membrane with 2 wt. % of TiO_2 NPs with the smallest average radius of the surface pores has the highest separation efficiency with a value of 80%.

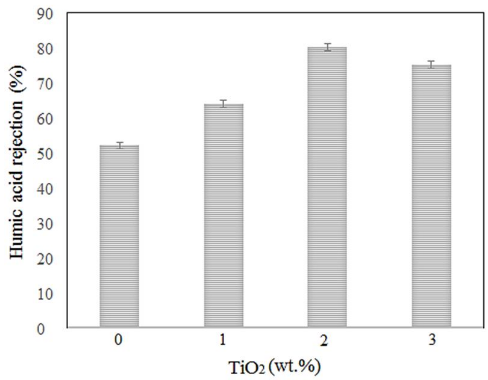

Figure 3. Humic acid rejection of the PVC membrane samples.

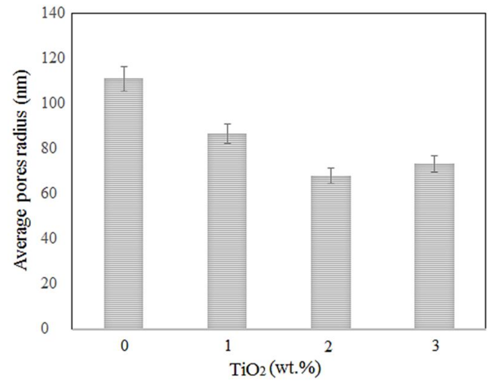

Figure 4. Average pores radius of the PVC membrane samples.

5. CONCLUSION

PVC microporous membranes containing TiO_2 NPs were made by nonsolvent induction phase separation method. The obtained results showed that the presence of NPs in the structure of nanocomposite membranes significantly improved the tensile strength of these membranes compared to pure PVC membrane. Also, the obtained results indicated an increase in the hydrophilic properties of the membranes due to the presence of TiO_2 NPs. In addition, the analysis of the results obtained from the humic acid rejection showed that the membrane with 2 wt. % of TiO_2 NPs having the smallest average radius of the surface pores has the highest separation efficiency with a value of 80%.

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