Review Article

Efficiency of Polymeric Membrane Graphene Oxide-TiO₂ for Removal of Azo Dye

Elahe Dadvar,¹ Roshanak Rezaei Kalantary,² Homayon Ahmad Panahi,³ and Majid Peyravi⁴

¹Department of Environmental Engineering, Faculty of Environment and Energy, Islamic Azad University, Science and Research Branch, Tehran, Iran
²Department of Environmental Engineering, School of Public Health, Iran University of Medical Sciences, P.O. Box 15875-4199, Tehran, Iran
³Chemistry Department, Islamic Azad University, Central Tehran Branch, Tehran, Iran
⁴Nanotechnology Research Institute, Chemical Engineering Department, Babol University of Technology, Babol, Iran

Correspondence should be addressed to Roshanak Rezaei Kalantary; rezaei.r@iums.ac.ir

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Achieving the desired standard of drinking water quality has been one of the concerns across water treatment plants in the developing countries. Processes such as grid chamber, coagulation, sedimentation, clarification, filtration, and disinfection are typically used in water purification plants. Among these methods, unit filtration which employs polymers is one of the new technologies. There have been many studies about the use of semiconductive TiO₂ with graphene oxide (GO) on the base of different polymeric membranes for the removal of azo dyes, especially methylene blue (MB). Polymeric GO-TiO₂ membranes have high photocatalytic, antifouling property and permeate the flux removal of organic pollutants. The aim of this study was to investigate the characteristics of different polymeric membranes such as anionic perfluorinated polymer (Nafion), cellulose acetate, polycarbonate (PC), polysulfone fluoride (PSF), and polyvinylidene fluoride (PVDF). The result of this study showed that the GO-TiO₂ membrane can be used in the field of water treatment and will be used for the removal of polycyclic aromatic hydrocarbons (PAHs) from wastewater.

1. Introduction

With the development of heavy industries in recent decades, obtaining healthy drinking water has become a global concern [1]. Organic substances, industrial dyes, microorganisms, and heavy metals (heavy metals include cobalt, cadmium, mercury, chromium, and lead) are among the water pollutants [2–7]. In recent decades, there has been increasing interest in the use of clean water [8–10]. With high efficiency and low energy consumption, filtration is one of the most appropriate technologies for decreasing pollution [11–15]. The formation of a good membrane is an important and practical step toward increasing the efficiency of water treatment; this film could be made from materials such as polymer, fiber, ceramic, and carbon nanotubes [16–19].

In recent decades, ceramic and polymeric membranes have been increasingly used due to their strong mechanical properties, chemical stability, high efficiency in minimizing pollutants, high photocatalytic power, and odor reduction ability [20, 21]. The photocatalytic process of separating organic pollutants from the membrane, under visible light and UV radiation, can occur without any energy or chemical consumption. This process is especially important for the removal of different types of environmental pollutants [22]. The photocatalytic process of isolating organic pollutants from membrane, under visible light and UV radiation, can demonstrate higher efficiency [23]. Titanium dioxide is one of the important semiconductors, having properties such as low toxicity, low cost, and highly efficient removal of pollutants [21, 24, 25].

TiO₂ has the ability to degrade organic materials (organic dye, oil, and toxic pollutants) into H₂O and CO₂ [24, 25]. As a semiconductor, nanoparticles of anatase titanium dioxide have higher photocatalytic power than rutile and brookite.
crystals and exhibit absorption at 390 nm when exposed to UV radiation [26]. The present study includes a review of the semiconductive properties of TiO\(_2\) semiconductor and its photocatalytic power. Different methods, such as doping and surface chemical modification, were used to increase the photocatalytic power of TiO\(_2\) [27]. It is worth mentioning that, in different industries, such as the textile industry, TiO\(_2\) graphene membranes are increasingly used to improve the efficiency of water treatment.

In recent decades, there have been many reports on the mechanical and chemical properties of graphene (G) and graphene oxide (GO) [28]. In studies concerning water treatment and purification, nanostructured carbon has been used in the form of carbon nanotube and graphene. These structures have high absorption capacity and the ability to absorb organic materials in aqueous solutions [29]. After studies on the absorption of organic aromatic pollutants by graphene, carbon nanotube, and granular activated carbon, Onu et al. discovered that graphene possessed higher efficiency in the absorption of natural organic materials.

The presence of natural organic matter (NOM) reduced the absorption of synthetic organic compound (SOC) in carbon nanotube, granular activated carbon, and, finally, graphene [30]. After comparing the absorption of methylene blue and atrazine pollutants by super fine powdered activated carbon (SPAC), carbon nanotubes (CNTs), and graphene, Ellerie et al. found that SPAC had the highest efficiency, while multiwalled carbon nanotube (MWCNT) was the least efficient in absorbing pollutants [31].

Compared to membranes without absorbents, the direct use of absorbents in membrane structure improves the efficiency of absorbed pollutants. GO consists of graphene sheets having functional groups (R-O-H, epoxy, COOH, and C=O). Therefore, the GO-TiO\(_2\) nanocomposite, under UV radiation and visible light, has the capability of photocatalytic degradation, high absorption capacity, and the capability of being more exposed to water pollutants as a result of its huge surface area of 2360 m\(^2\)/gr [32]. Liu et al. studied the nanorod of TiO\(_2\) on the surface of graphene oxide sheets interface water and toulene. They produced a high efficiency nanorod (GO-TiO\(_2\) NRCs) composite. The TiO\(_2\) nanorod was stabilized with oleic acid, low temperature, and hydrolysis approach. The photocatalytic activity (GO-TiO\(_2\) NRCs) desired in the degradation of methylene blue (MB) under UV radiation was higher than GO-25 and the other original TiO\(_2\) nanorod states [33].

Rao et al. reported efficient removal of 4-chlorophene, 2,4-dichlorophene, and 2,4,6-trichlorophene by ZrO\(_2\) graphene composite and, herein, removal efficiency of 4-chlorophene was by far better than the others, and the absorbability decreased with the increase in pH [34].

According to the report of Zhang et al., TiO\(_2\) nanowire membrane was able to remove TOC and HA pollution with a removal efficiency of 93.6 and 100%, respectively. This membrane was able to degrade organic materials and produce CO\(_2\) [35].

Mele et al. carried out a characterization of polycrystalline bare TiO\(_2\) for the degradation of 4-nitrophenol (4-NP) in aqueous suspension using TRMC, EPR, and XPS. The results of this study showed that propyline impregnated on the surface of TiO\(_2\) improved the photocatalytic properties compared to bare TiO\(_2\) [35].

Afzal et al. synthesized anatase TiO\(_2\)/TCPP (meso-tetra(4-carboxyphenyl)porphyrin) coated with cotton. TiO\(_2\)/TCPP coated with cotton for the purpose of making comparison with bare TiO\(_2\) was found to be better. There was complete degradation of methylene blue in 110 min and removal of coffee and red wine in 16 h by visible light [36].

There are many studies regarding the TiO\(_2\) semiconductor and its photocatalytic features in removing pollutants, especially industrial dyes and heavy metals; however, to date, there has been no comprehensive study regarding the photocatalytic features, flow permeability, and antifouling property. Fouling resistance in GO-TiO\(_2\) membrane, with regard to various polymer bases, has been used in this article.

### Table 1: The structural properties of TiO\(_2\) crystals [43–45].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>(a = 4.5936)</td>
<td>(a = 3.784)</td>
<td>(a = 9.184)</td>
</tr>
<tr>
<td></td>
<td>(c = 2.9587)</td>
<td>(c = 9.515)</td>
<td>(b = 5.447)</td>
</tr>
<tr>
<td>Space group</td>
<td>(p4_1/mnm)</td>
<td>(I4_1/amd)</td>
<td>(pbc)</td>
</tr>
<tr>
<td>Molecule (cell)</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Volume/molecule (Å(^3))</td>
<td>31/2160</td>
<td>34.061</td>
<td>32/172</td>
</tr>
<tr>
<td>Density (g cm(^{-3}))</td>
<td>4.13</td>
<td>3.79</td>
<td>3.99</td>
</tr>
<tr>
<td>Ti-O band length (Å)</td>
<td>1.949 (4)</td>
<td>1.937 (4)</td>
<td>1.87–2.04</td>
</tr>
<tr>
<td>O-Ti-O band</td>
<td>81.2(^\circ)</td>
<td>77.7(^\circ)</td>
<td>77.0–105(^\circ)</td>
</tr>
</tbody>
</table>

### 1.1. Titanium Dioxide

Titanium(IV) oxide is the oxide of titanium, with a molecular weight of 79.87 g/mol and chemical formula of TiO\(_2\). When used as a pigment, it is called white titanium or pigment white. Titanium dioxide is used in industries as a mineral pigment. It occurs in nature in three forms: brookite, rutile, and anatase. White titanium dioxide is 200 to 300 nm in diameter and has a particular geometric form and structure. Table 1 shows the properties of different kinds of titanium. The first production of TiO\(_2\) was manufactured in Norway, USA, and Germany in 1918 [39–42].

### 1.2. Photocatalysts

For several years in industrialized countries, photocatalysts have been used for the removal of pollutants which are not removed by bioprocesses. Most photocatalysts are semiconductor solid oxides which, under radiation, are activated with sufficient energy [47]. Chlorophyll in plants acts in a similar manner to photocatalysts. When compared with photosynthesis in which chlorophyll absorbs sunlight and produces oxygen and glucose by water and carbon dioxide, in the process of photocatalysis, organic materials are converted into water and carbon dioxide in the presence of light, water, and catalyst (Figure 1) [48].
TABLE 2: Band gap energy for some common semiconductor materials [46].

<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>5.4</td>
</tr>
<tr>
<td>CdS</td>
<td>2.42</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.6</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.436</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.03</td>
</tr>
<tr>
<td>CdS</td>
<td>2.582</td>
</tr>
<tr>
<td>SnO₂</td>
<td>3.54</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.7</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.76</td>
</tr>
<tr>
<td>Si</td>
<td>1.17</td>
</tr>
<tr>
<td>Ge</td>
<td>0.744</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.3</td>
</tr>
<tr>
<td>PbS</td>
<td>0.286</td>
</tr>
<tr>
<td>PbSe</td>
<td>0.165</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>3.87</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>2.172</td>
</tr>
</tbody>
</table>

1.3. TiO₂ Photocatalytic Degradation Mechanism. One of the important properties of TiO₂ solid and inorganic nanomaterials is the photocatalytic activity. In many cases, this feature is used for antibacterial surfaces. Also, the photocatalytic activity of TiO₂ has been applied in a wide range of metal oxides and their sulfides [49, 50] including ZnO [51], WO₃ [52], WS₂ [53], Fe₂O₃ [54], V₂O₃ [55], CeO₂ [56], Cds [57], and ZnS [58]. The band gap energy values for some common semiconductor materials are presented in Table 2 [46].

TiO₂ was found to be the best semiconductor because of its chemical stability and nontoxicity. Also, it is cost-effective and has an excellent photocatalytic activity in the presence of UV irradiation [59–62].

One of the commercial uses of TiO₂ is P₂5, which is often used as a photocatalytic material. It consists of 70 to 80% anatase and 20 to 30% rutile, with specific surface area of 50 m²/g. There exists an energy gap between the valence band and the conduction band in semiconductors (Figure 2). Contrary to nonconductors, it is small; therefore, after radiation of light to the photocatalysts of semiconductors, photons with energy equal to or higher than the gap energy are absorbed, and electrons can be excited from the valence band to the conduction band.

After receiving solar energy (photons), semiconductors gain more energy than usual, and, as a result, electrons travel from the valence band to the conduction band and create holes in the valence band (h⁺) (Figure 3).

TiO₂ produces this energy by receiving sunlight or UV radiation and acts as an important photocatalyst [63]. Moreover, the use of TiO₂ nanomaterials as a photocatalyst for the removal of pollutants has attracted much attention due to its physical and chemical properties, high efficiency, low cost, and low toxicity.

(1) TiO₂ + hν → e−(cb) + h⁺(vb) hν < 390 nm

h⁺ is suitable for producing OH⁺ hydroxyl radicals on the surface of TiO₂ and also allows excitation of electrons from the valence band to the conduction band [51] and excitation of conduction band electrons to reduce the oxygen molecule.

(2) e− + O₂ → O₂ads
(3) e− + Hads → Hads
(4) h⁺ + OHads → OHads (in alkaline solution)
(5) h⁺(vb) + H₂Oads → H⁺ + OHads (in neutral solution)

Anatase and rutile are the two main types of TiO₂ with energies of 3.2 and 3.1 eV, respectively, showing that the photocatalytic activity of anatase is much greater than that of rutile [64, 65].

The photocatalytic power of TiO₂ is dependent not only on the energy band but also on the surface characteristics. The presence of a high surface area in each mass increases the photocatalytic power. The degradation of azo dye, especially methylene blue, by TiO₂ film, depends on the surface of the photocatalyst. This film could be either in anatase crystal form, having different thicknesses and surfaces, or in low pressure and chemical deposition, from which vapor is produced [66].

TiO₂ nanomaterials can be used for the photocatalytic cleaning of different types of organic compounds, such as...
chlorinated hydrocarbons (like organic dye, insecticides, surfactants, CCl₄, CHCl₃, C₂HCl₃, and phenol), decreasing heavy metals such as Pt⁴⁺, Pb⁴⁺, Au⁺³, Rh⁺³, and Cr³⁺, and are also capable of the high efficiency removal of bacteria and viruses [65–69].

The pH of the solution has a great influence on the degradation of dye and TiO₂ surface charge. The surface of TiO₂ is positively charged in acidic pH and negatively charged in alkaline condition. The anionic dyes have strong adsorption in acidic pH while the cationic dyes have weak adsorption in alkaline pH [70, 71].

2. Background of Azo Dye

Dyes of textile industries and other kinds of dyes are dangerous to humans and the environment. During coloring, 1 to 20% of dyes are expelled from the wastewater of textile industries [72–75].

The discharge of wastewater from textile industries into the environment is regarded as a major source of pollution and main cause of eutrophication in rivers and lakes. Also, the oxidation, hydrolysis, and chemical activities in the discharged wastewater cause potential dangers [76–78].

The application of old processes (such as absorption, activated carbon, ultrafiltration, reverse osmosis, coagulation, and ion exchange) for the removal of dyes shows high efficiency. The transmission of organic materials from water to other phases, regeneration of absorbents and wastewater pretreatment, is quite expensive [79–82].

Due to high levels of aromatic compounds in dyes and their stability, the biological treatment takes a longer time and the crystals produced are not suitable for degradation [83–86]. Chlorination and ozonation are practical for the removal of some kinds of dyes. Both methods are expensive since they consume chemical materials, consume power, have low efficiency and limitations in the removal of carbon, and are not suitable for degradation [87–90].

In recent decades, advanced oxidation processes (AOPs) have become widespread. This process is based on the production of super active species like hydroxyl (‘OH), which is capable of oxidizing a wide range of materials, but its action is nonselective. Fenton and photo-Fenton, photocatalytic activities [91–95], UV/H₂O₂ [96, 97], and modified photocatalytic activity of TiO₂ [98–101] are some of the advanced oxidation processes (AOPs). In AOPs, the use of TiO₂ as a photocatalyst has been recognized as a suitable technology [102–107].

Finally, the use of TiO₂ as a photocatalyst under visible light has attracted much attention because it is economical. The use of a photocatalyst in the presence of sunlight can help in reducing dyes, especially methylene blue and methyl orange, and also their mineralization [108–110]. Many studies have considered the use of the desired photocatalyst for cleaning of textile industrial wastewater [111–114].

2.1. Azo Dye. The main problem of pollution in textile industries is water pollution. Methylene blue and methyl orange are among the commonly used dye compounds in the industry, and they are often known as azo dyes because they contain the functional group R-N=N-R, in which N=N is known as azo. The structures of methyl orange and methylene blue compounds are shown in Figure 4. Azo dyes are divided into three groups: mono, di, and tri, and this classification is dependent on the number of azo groups. R and R’ can be aryl and alkyl groups, and as we know it is quite difficult to break down benzene ring; hence, the simplest benzene ring is C₆H₆ in the aryl group.

Studies have shown that the presence of UV radiation helps TiO₂ in removing organic dyes [50, 51].

3. Strategies for Improved Power of TiO₂

3.1. Doping. Doping titanium dioxide with metal elements such as Cr, Co, Cu, V, Mo, V, Ag, Au, Pt, Nb, and Ru and nonmetal elements such as C, N, S, P, I, F, and B increases the charge transfer reaction and thermal stability of the photocatalyst [27]. For example, X. Z. Li and F. B. Li reported the photodegradation of methylene blue in aqueous solutions...
under visible light over AU³⁺ with modified TiO₂ power [115].

3.2. Surface Chemical Modification. Surface chemical modification is essential for increasing the efficiency of photocatalysts, thus preventing the recombination charge (electron and hole (h⁺)) and their further separation, which is performed through two methods: sensitization and coupling. Sensitization, where different groups have used narrow band gap semiconductors to enhance optical absorption properties of TiO₂ nanoparticles in the visible light region, can be used to sensitize TiO₂ materials. Coupling different semiconductors with different energy systems provides another way to improve charge-carrier separation.

3.2.1. Synthesis of Types of GO-TiO₂ Membrane. The use of graphene, especially in the water treatment industry, has increased significantly in recent years due to its perfect mechanical and electrical features as well as high surface area. In the water treatment industry, graphene has been so useful in the removal of organic pollution, bacteria, heavy metals, and dyes, especially azo dyes [116], MB dyes and MO dyes [117, 118]. These dyes are produced, as mentioned before, in textile factories and have to be closely monitored to have standard concentration before being released into the environment [116]. In recent years, the synthesis of GO-TiO₂ membrane for the reduction of dye pollutants, especially azo dyes, has been studied in different cases in the water treatment industry to improve TiO₂.

The GO-TiO₂ membrane can be placed on any texture or on any membrane surface of the water filter. The photocatalytic process is an introduction to membrane properties, such as hydrophilicity, water penetration, and degradation of pollutants, and, as a result, there is a decrease in the odor produced from degradation of organic materials [117].

Studies were performed to achieve two major objectives: (1) studying the absorption ability of the membrane without considering the photocatalytic properties [118] and (2) studying the levels of degradation of organic dyes under UV radiation and considering the photocatalytic properties of the membrane [34, 117–119].

The GO-TiO₂ sheet can be placed on the following:

(1) Anionic perfluorinated polymer (Nafion) [120]
(2) Cellulose acetate [118]
(3) Polycarbonate (PC) [117]
(4) Polysulfone fluoride (PSF) [116]
(5) Poly(vinylidene fluoride) (PVDF) [120]

The polymeric membranes possess excellent chemical resistance, thermal stability, and good membrane formation [121, 122].

The photocatalytic effects of the produced membrane on the removal of organic dyes, especially for removed RB [117], MB [116], and MO dyes [117], which are considered as aromatic compounds, have been studied.

A comparison of hybrid membranes and standard nanomembranes showed that hybrid membranes act 5 times faster than standard nanomembranes in removing pollution [123]. Also, the energy consumption of hybrid membranes is half that of standard nanomembranes. Due to their mechanical and chemical features, these filters have stable photocatalytic activity in the presence of UV radiation [124, 125]. It is worth mentioning that GO is synthesized from natural graphite through Hommer’s methods, similar to previous studies [126]. The TiO₂ microsphere was synthesized by the reported method, with some modifications [127–129].

The LbL (layer-by-layer) method has the ability to form a hybrid membrane. This experiment used a gold coated sensor to determine the mass of TiO₂ and GO during the LbL procedure. The sensor was coated with a base polymer membrane. The sensor was put in a desiccator for drying, after which it was put in DI water. A fixed concentration on the surface of the sensor was at 0 ng/cm² after 15 min, and the DI water was replaced with TiO₂ solution. TiO₂ nanoparticles were adsorbed on the base polymer and, after 2 h, the mass of the nanoparticle slowed down and became stabilized. After that, TiO₂ solution was replaced with DI water for the removal of packed nanoparticles. Next, the TiO₂ coated sensor was soaked in the GO solution [130].

According to Athanasekou et al., the reduced graphene oxide-TiO₂ (GO-TiO₂) was synthesized with GO suspension. GO was prepared according to previous studies, similar to the Hommer method, using LPD (liquid phase deposition) method at room temperature. Among all the membranes, GO-TiO₂ was the best membrane for removing MO under UV, and GO-TiO₂ was the best membrane for removing MB. The hybrid membrane when compared with nanofiltration was better for the removal of pollutants and energy consumption [131].

![Figure 4: Structure of (a) methyl orange and (b) methylene blue.](image)
Membranes are typically made of inorganic (ceramic) materials and a polymeric membrane. Membrane separation is basically on three principles: adsorption, sieving, and electrostatics as shown in Figure 5 [38]. The pore size determines the different membrane types: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Among the membrane processes, UF with polymeric membrane has the efficiency of removing contaminants such as organic pollutants, heavy metal, suspended solid, and different dyes. The polymeric membrane graphene oxide-TiO$_2$ is significantly efficient in the removal of organic pollutants and dye from solution. It has specific characteristics which completely explain some special traits.

4.1. Analysis of the GO-TiO$_2$ Membrane

(i) Membrane analysis through transmission electron microscopy (TEM) and EDX shows the location of TiO$_2$ anatase crystal particles on the surface of GO [137, 138].

(ii) The amount of TiO$_2$ on the surface of GO sheets is determined by thermogravimetric analysis (TGA) [139].

(iii) The amounts of Ti and GO have been studied in the following researches through CS and XPS analysis [140–143].

(iv) The absorption capacity of the GO-TiO$_2$ membrane is determined when different dye solutions are used in water [144, 145].

4.1.1. Porosity of Membrane. Atomic force microscopy (AFM) can record the roughness and surface morphology of polymeric membranes. The overall porosity of a membrane can be calculated using the gravimetric method as presented in [146]

\[ \varepsilon = \frac{W_1 - W_2}{A \times L \times d_W}, \]

where $W_1$ and $W_2$ are the wet and dry weights of the membrane, $A$ is the effective area of the membrane ($m^2$), $L$ is the membrane thickness ($m$), and $d_W$ is the water of density 0.998 g/cm$^3$. Using pure water flux, the porosity of the membrane and the mean pore radius of the membrane ($r_m$) can be calculated using the Guerout–Elford–Ferry equation:

\[ r_m = \sqrt{\frac{(2.9 - 1.75e) \times 8\eta LQ}{\varepsilon \times A \times \Delta P}}, \]

where $\eta$ is the water viscosity (8.9 $\times 10^{-4}$ pas), $\Delta P$ is the operation pressure (3 MPa), $Q$ is the permeated pure water amount ($m^3/s$), $L$ is the membrane thickness ($m$), and $A$ is the surface area ($m^2$) [146, 147].

Atomic force microscopy, field emission scanning electron microscopy, and the Guerout–Elford–Ferry equation applied for pure water permeation rate were used for determination of average pore size. The pore size calculated from the method of Guerout–Elford–Ferry was the highest, and, based on the make-ready sample (FESEM), the pore size calculated was the least in size [148].

4.2. GO-TiO$_2$ Photocatalytic Membrane for Dye Removal. Photocatalytic properties of TiO$_2$ nanoparticles under UV radiation for removal of dye occur according to the following reactions [149]. In the photocatalytic oxidation, TiO$_2$ has to be irradiated and excited in near-UV energy to induce charge separation. On the other hand, dyes rather than TiO$_2$ are excited by visible light followed by electron injection onto the TiO$_2$ conduction band, which leads to photosensitized oxidation. Subsequently, this is followed by electron injection from the excited dye molecule onto the conduction band of the TiO$_2$ particles, whereas the dye is converted to the cationic dye radicals (Dye$^{+}$) that undergo degradation to yield products:

(6) dye$_{ads}$ + $h\nu$ $\rightarrow$ dye$_{ads}$ $^*$ excitation
(7) dye$_{ads}$ $^*$ $\rightarrow$ dye$_{ads}$ $^{\cdot+}$ + TiO$_2$(e$_{cb}$$^-$) electron injection
(8) dye$_{ads}$ $^{\cdot+}$ + TiO$_2$(e$_{cb}$$^-$) $\rightarrow$ dye$_{ads}$ recombination
(9) dye$_{ads}$ $^{\cdot\cdot+}$ $\rightarrow$ degradation
(10) O$_2$ + TiO$_2$(e$_{cb}$$^-$) $\rightarrow$ O$_2$ (electron scavenging)

Anatase crystals which form mesosphere TiO$_2$ can have high mass transfer flux and photocatalytic activity [150–152]. The mesosphere structure of GO-TiO$_2$ has a huge surface area which forms numerous channels for passing water flow and photocatalysts for photocatalytic degradation [153, 154]. It is absolutely obvious that a membrane with high cross flow, removal efficiency, and low cost is suitable for filtration. GO sheets increase the filtration efficiency [154].

According to studies performed in different researches, GO-TiO$_2$ on a base membrane and under UV radiation shows great photocatalytic power in degrading organic materials. Membrane pretreatment, using ethanol and UV radiation, helps in increasing the degradation of MB [117].

The photocatalytic properties of porphyrin TiO$_2$ and graphene TiO$_2$ under visible light and UV radiation have been studied. Porphyrin graphene TiO$_2$ shows 35% higher efficiency than pure TiO$_2$ [155].

GO-TiO$_2$ is used for the degradation of RhB and AO$_7$ dyes under UV radiation within 20 to 30 min. In the absence of UV radiation, GO-TiO$_2$ membrane shows low efficiency,
lower than 15%, in the degradation of RhB and AO7 dyes. The presence of UV radiation increases removal efficiency by 50% [118].

The presence of photocatalysts on a membrane prevents the accumulation of organic materials and macromolecules and therefore allows higher flow to pass through the membrane. Absorption of MO in darkness has minimal effects on the Nafion-GO SULF membrane, but under UV radiations the initial concentration is reduced by 90% [28,118]. Pores size depends on the amount of GO-TiO2 which is placed on the base membrane. GO-10 membrane (membrane having 10 nm pores) shows higher removal efficiency of dyes than other membranes [156].

The application of the method of liquid phase deposition (LPD) for synthesis of GO-TiO2 composites and their stabilization on the integrated membranes is suitable for the removal of industrial dyes. Membranes with 1 m length and 30 monoliths consume less energy than nanomembranes [156].

4.3. Permeation Flux through GO-TiO2 Membrane. Filtration tests on GO-TiO2 membrane with 5%-5 mL/min flow rate, 0.6 nm constant membrane thickness, and 30 mg/L concentration cobalt ion show that the lesser the flow which is passed through, the more the cobalt removed. As the initial concentration of cobalt ion increases from 1 to 9 mg/L, the removal efficiency decreases from 89 to 21%. The high absorption capacity of nanosheets of graphene oxide ammonium for the removal of cobalt could be related to the ammonium functional groups. These absorbents are able to remove 30 mg/L concentration of cobalt ions in 5 min with 90% efficiency [119].

The presence of sulfonic functional group, along with graphene on Nafion membrane, allows more water to pass through it [28, 38, 118–157]. The movement of proton on Nafion membrane can help in separating ion compounds from the water molecule. These effects have been studied by adding the sulfonic functional group to the surface membrane of Nafion [38,109–158].

The thickness of GO-TiO2 membrane could be changed easily by changing the GO-TiO2 mass which is placed on the base. Membrane thickness affects the flow passing through the membrane, meaning that a decrease in membrane thickness allows higher flow to pass through the membrane and decreases the removal efficiency [118].

4.4. Fouling Resistant Membrane. The total fouling resistance of the polymeric membrane (Rf) is calculated from rf and rin. rf is a reversible fouling ratio which describes the fouling caused by concentration polarization, and rin is an irreversible fouling ratio which describes the fouling caused by adsorption or deposition of protein molecules on the membrane surface.

\[
rf = \frac{J_{w2} - J_p}{J_{w1}},
\]

\[
rin = \frac{J_{w1} - J_{w2}}{J_{w1}}.
\]

Rf is the sum of rf and rin, and Jw1 is the permeation water flux (kg/m² h):

\[
J_{w1} = \frac{M}{At},
\]
where \( M \) is the weight of collected permeation flux, \( A \) is the membrane effective area, \( t \) is the permeation time, \( \dot{W}_2 \) is the water flux cleaned membrane, and \( \dot{J}_p \) is the flux of the BSA solution [144]. Hence,

\[
R_T = \left(1 - \frac{\dot{J}_p}{\dot{W}_1}\right) \times 100. \tag{5}
\]

Under special pressure, after the pure water test, the BSA solutions are immediately replaced in the filtration cell for 90 min [159].

4.5. Antifouling Property of GO-TiO\(_2\) Membrane. Since the cost of cleaning normal membranes is too high and, over time, they produce odors because of the accumulation of organic materials, the application of GO-TiO\(_2\) membrane in the water treatment industry seems to have become more widespread. Humic acid as a standard pollutant formed from natural organic materials and carcinogen disinfectants has been studied [160]. In the first phases of filtration, the accumulation of humic acid on the surface of membrane and closing of the pores are really obvious after 30 min [161]. After 2 h, with 7 L/m\(^2\)·h flow rate, a layer of odorous HA cake becomes noticeable [162]. UV radiation reduces the produced odor significantly [118]. The reason is the degradation of humic acid and production of CO\(_2\) and H\(_2\)O under UV radiation; in this state, there is no reduction in the flow which passed through the membrane.

5. Future Work

GO-TiO\(_2\) membrane, because of its significant applications such as high photocatalytic and antifouling property, flux permeation, and removal of organic pollutants, can be potentially used in the degradation of polycyclic aromatic hydrocarbon (PAH) as a low cost membrane in the future.

6. Conclusion

This study was carried out on the characteristics of different polymeric membranes of GO-TiO\(_2\). According to previous studies, this membrane has lots of advantages like the capability of passing flow. Graphene oxide has a number of covalent attached oxygen containing groups such as epoxy, carbonyl, and carboxyl. The existence of these groups makes membrane possess good hydrophilicity. Another good property of this membrane is the existence of photocatalytic TiO\(_2\) semiconductor, which can help in the degradation of the cake layer of the organic material and the reduction of odor. The object is very economical to reduce cost of washing membrane compared to the usual form. Fouling of this membrane because of GO-TiO\(_2\) photocatalytic properties is also reduced from other forms of membranes. This result shows that the GO-TiO\(_2\) polymer membrane could make considerable improvement in the field of water treatment and could have significant effects on the filtration efficiency.

Competing Interests

The authors declare that they have no competing interests.

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