

Research Article

Decoloring Methyl Orange under Sunlight by a Photocatalytic Membrane Reactor Based on ZnO Nanoparticles and Polypropylene Macroporous Membrane

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Decoloring methyl orange (MeOr) under sunlight was conducted in a photocatalytic membrane reactor (PMR). Zinc oxide nanoparticles (ZnO NPs) were suspended in the solution or immobilized on the membrane. The membrane was modified by grafting 2-hydroxyethyl methacrylate (HEMA) to enhance the adsorption of ZnO NPs on the hydrophobic membrane surface and improve the membrane permeability. The results show that the water fluxes through the modified membranes are higher than that through the unmodified membrane. After introducing ZnO NPs to the membrane, the water fluxes still rise with the immobilization degree of ZnO NPs. For the PMR with ZnO NPs in suspension, the photocatalytic decoloration percent (PDP) was over 98.2% after 40 min under sunlight. For the PMR with ZnO NPs immobilized on the membrane, the max of PDP was 74.3% after 6 h under sunlight, and maintained at 72% after repeated uses for five times. These results demonstrate that photocatalytic membrane reactor (PMR) based on ZnO NPs and polypropylene macroporous membrane (PPMM) could be applied in decoloring dyes.

1. Introduction

Dyes, widely used in industries, like textiles, paper, rubber, and plastics, have led to severe environmental contamination due to the toxic and colored wastewater poured into water bodies, which seriously worsens the quality of water, inhibiting sunlight penetration and reducing photosynthetic reaction.

Conventional treatment methods for dye removal, such as ozonation, bleaching, hydrogen peroxide/UV, and electrochemical techniques, were found to be nondestructive and inefficient, because most dyes have complex aromatic molecular structures that resist degradation [1]. They are stable to light, oxidizing agents, and aerobic digestion. The motivation for more efficient treatment processes has inspired environmental scientists and engineers to explore the technique of combining pressure-driven membrane filtration and heterogeneous photocatalysis [2–6].

Recently, heterogeneous photocatalysis employing semiconductor photocatalysts (TiO₂, ZnO, and adulterate or complex semiconductor) has demonstrated their efficiencies in degrading a wide range of toxic organic compounds into relatively innocuous end products, such as carbon dioxide and water [5]. Photocatalytic oxidation of various harmful organic dyes and inorganic pollutants in industrial wastewater has been carried out by nanosemiconductors under UV light due to their high photosensitivity and nontoxicity [7, 8].

ZnO NPs have great photocatalytic activity under sunlight, which can effectively absorb photons in the UV region from the sunlight [9] and have shown higher photocatalytic efficiencies for the degradation of several organic pollutants [10, 11]. It is known that many adulterate or complex semiconductors have shown great photocatalytic activity under solar light [12, 13]. Compared with these semiconductors, the advantages of ZnO NPs are simple synthesis process (only one step by chemical depositing method) and low cost.

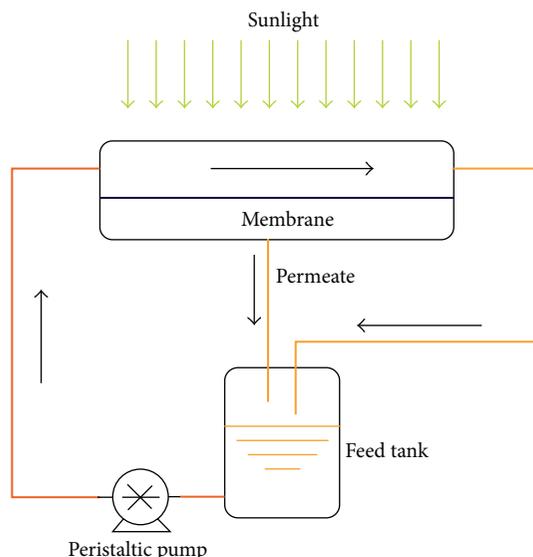


FIGURE 1: A schematic diagram of the photocatalytic membrane reactor (active membrane area is 2700 mm²).

On the other hand, membrane process is widely applied in many industries. The process has several main advantages, such as low energy consumption, low chemicals consumption, low maintenance costs, and easy scale up [14].

Photocatalytic membrane reactors (PMRs) are of hybrid processes in which photocatalysis is coupled with a membrane process, and the permeation of solutes through the membrane and photocatalytic reaction occurs simultaneously. As a low-cost, environmentally friendly, and sustainable treatment technology, the PMRs for wastewater treatment using semiconductors have shown a great potential [15, 16]. Although UV light has been commonly employed in the photocatalytic studies, worldwide efforts are underway to make use of sunlight for environmental protection and water purification [17], because sunlight consists of about 5–7% UV light, 46% visible light, and 47% other irradiation [18], and additionally it is inexhaustible (Figure 1).

In the present work, to improve the membrane permeability and to enhance the adsorption of the semiconductors, hydrophilic surface modification of polypropylene macroporous membrane was carried out. Grafting 2-hydroxyethyl methacrylate (HEMA) onto the membrane surface was performed according to previous work [19, 20]. ZnO NPs were one pot fabricated by direct precipitation; their photocatalytic activity for environmental application was carefully investigated by using decoloring methyl orange (MeOr) under sunlight.

2. Materials and Methods

2.1. Materials. Benzophenone (BP), 2-hydroxyethyl methacrylate (HEMA), methyl orange (MeOr), Zn(NO₃)₂, and oxalic acid were used as purchased from Lingfeng Shanghai Reagent Co. Ltd. Polypropylene macroporous membranes (PPMMs) with a porosity of 45–50% and an average

pore diameter of 0.10 μm were prepared [21], and benzyl dithiobenzoate (BDTB) was synthesized according to the literature [22].

2.2. Synthesis of ZnO NPs. ZnO NPs were synthesized by direct precipitation with oxalic acid as the precipitator [23] with minor modification. 12.7 g Zn(NO₃)₂ and 10.0 g oxalic acid were dissolved in 50 mL distilled water separately. Then the two solutions were mixed slowly under stirring during which the white precipitate produced immediately. After this, the precipitate was washed with distilled water and ethanol for three or four times, dried at 90–100°C, and finally calcined at 450°C for 3 h to achieve ZnO NPs.

2.3. Surface Modification of Membrane. The used method and experimental setup for the membrane surface modification were described in [19].

2.4. Photocatalytic Membrane Reactor. The permeation properties of the unmodified and modified PPMMs were examined in a stirred dead-ended ultrafiltration test cell connected to a 2 L feed tank [24]. The volumetric flux was determined through the timed collection of permeate, and the relative flux was described by the following equation:

$$\text{Relative flux} = \frac{J_{0,m}}{J_{0,u}} \times 100\%, \quad (1)$$

where $J_{0,u}$ and $J_{0,m}$ are the pure water fluxes through the unmodified and modified membranes. $J_{0,u}$ varied from 250 to 450 Lm⁻²h⁻¹, and as a result, the relative flux was adopted to eliminate the differences between the unmodified membranes.

The PHEMA grafted PPMMs were submerged in the ZnO NPs ethanol dispersion for 24 h; ZnO NPs were physically adsorbed on the membrane surface [24]. The immobilization degree (ID) of the ZnO NPs on the membrane is calculated by the following equation:

$$ID = \frac{(W_2 - W_1)}{W_1} \times 100\%, \quad (2)$$

where ID refers to the immobilization degree of ZnO NPs on the membrane surface, % (wt), and W_1 and W_2 the respective weights of PHEMA grafted membranes before and after the immobilization of the ZnO NPs. All the results are the average values of three parallel experiments.

The photocatalytic decoloring MeOr with ZnO NPs suspended is investigated. 0.05 g ZnO NPs were added to 200 mL 10 mg/L MeOr aqueous solution, stirred for 30 min in the dark to achieve the adsorption–desorption equilibrium, and then exposed to the sunlight with stirring (Wuhu, Anhui Province, China, July 2010) (the light intensity was determined by a UV power meter, LS123, Shenzhen Linshang Technology Co. Ltd.); the photocatalytic reaction was conducted within the light intensity of $90 \pm 15 \text{ mW/cm}^2$; then pure water was added to the reacting solution to compensate the evaporation during its exposition to sunlight. The solution was sampled at intervals of 5 min, and the samples were centrifuged for 10 min.

The PMR with ZnO NPs immobilized on the membrane surface is similar to [24]. The membrane (GD = 36.0%, ID = 6.2%) was sandwiched in the cross flow PMMA reactor (each of the PMMA plate is 20 mm in thickness), the total weight of the immobilized ZnO NPs is about 0.05 g; 200 mL 10 mg/L MeOr aqueous solution was pumped into the reactor circularly by a peristaltic pump with the reactor exposed to the sunlight, and the cross flow velocity was kept at 0.15 m/s [25]. At the end of each run, the membrane was taken out, flushed with pure water for three times, then dried and stored in air for a period of time (as shown in Figure 6). After that the next run started.

The supernatant of the effluent was measured by the UV-Vis spectrophotometer (UV-2450, Shimadzu, Japan) at 464 nm (the maximal adsorption wavelength of MeOr). The photocatalytic decoloration percentage (PDP) is calculated by the following equation:

$$PDP = \frac{A_0 - A}{A_0} \times 100\%, \quad (3)$$

where A and A_0 correspond to the UV absorbance of the feed and the filtrate, respectively.

2.5. Characterization. The crystalline structures of ZnO NPs were examined by X-ray powder diffraction on an X-ray diffractometer (XRD) (XRD-6000, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$) at a scanning rate of $0.05^\circ/\text{s}$. Surface morphology of the membranes was observed by field emission scanning electron microscopy (FESEM) (Hitachi 4800, Japan), and the surface hydrophilicity was determined by water contact angle measurements (OCA20, Germany) [26].

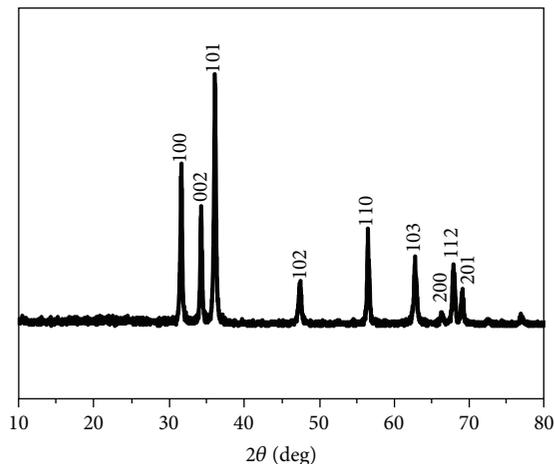


FIGURE 2: XRD pattern of ZnO NPs.



FIGURE 3: FESEM image of the ZnO NPs ($\times 15000$).

3. Results and Discussion

3.1. Characterization and Permeation of the Membranes. XRD is used to investigate the changes of crystalline nature of the prepared ZnO NPs (Figure 2). Most of the diffraction peaks could be attributed to the hexagonal wurtzite structure of ZnO (JCPDS card 36-1451) [27]. It can be observed that no diffraction peaks from other phases of ZnO or impurities, suggesting that the obtained ZnO is of high purity. The average crystallite size for ZnO NPs calcined at 450°C was calculated at $26.6 \pm 4.8 \text{ nm}$ according to the Scherrer formula [28].

Figure 3 presents the FESEM images of the ZnO NPs, which reveal that the surfaces are rough and porous, indicating that the ZnO NPs aggregate due to large specific surface area and high surface energy.

The surface morphologies of the unmodified, the PHEMA grafted, and the ZnO NPs immobilized membranes were observed by FESEM (Figure 4). Compared with the unmodified PPMM with high porosity (Figure 4(a)), the surfaces of the PHEMA grafted PPMMs are gradually covered with polymers; as the grafting degree increases (Figures 4(b) and 4(c)), the membrane pores are plugged and the surface porosity reduces with GD increasing. It can be clearly observed that ZnO NPs have been introduced to the

TABLE 1: Relative water flux (%) through PHEMA grafted and ZnO NPs immobilized PPMMs with different GD. The average water flux for the membranes is $400 \pm 25 \text{ Lm}^{-2} \text{ h}^{-1}$.

GD, % (wt)	Water contact angle on PHEMA grafted PPMMs, °	Relative water flux, %	
		PHEMA grafted PPMM	ZnO NPs immobilized PPMM
0.00	90	100	113
1.00	72	120	124
4.48	54	118	143
6.89	43	115	—
8.21	35	116	136

—: The membrane was broken after ZnO NPs immobilization. The error margin is within $\pm 10\%$.

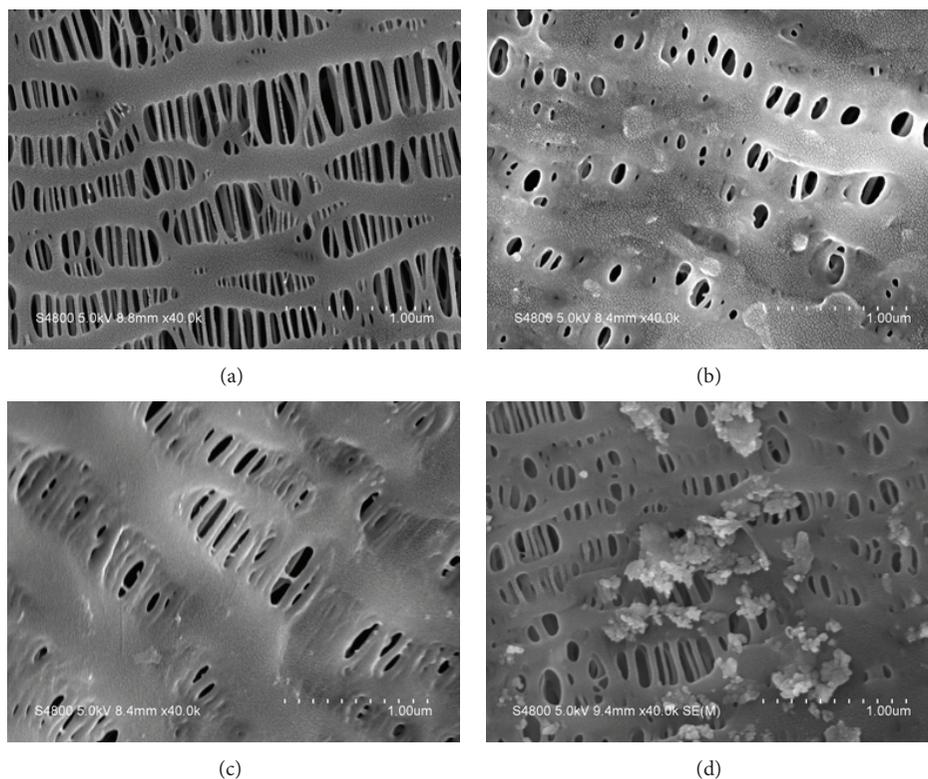


FIGURE 4: FESEM images ($\times 40000$) of (a) the unmodified, and (b)-(c) PHEMA grafted PPMMs with GD = 2.40 and 4.05% (wt), respectively; (d) ZnO NPs immobilized PPMMs with GD = 36.0% (wt), ID = 6.2% (wt).

membrane surface from Figure 4(d). The ZnO NPs appear in large clusters, instead of being evenly distributed. The immobilization degree of ZnO NPs immobilized PPMMs with different GD of PHEMA was shown in Supplementary Material (See Supplementary Material available online at <http://dx.doi.org/10.1155/2013/451398>). The result verified that the grafting of polyHEMA can enhance the adsorption of ZnO NPs on the hydrophobic membrane surface.

Variation of the relative water fluxes through PHEMA grafted and ZnO NPs immobilized PPMMs was investigated (Table 1). The relative water flux goes up after PHEMA grafted on the PPMMs due to the membrane surface hydrophilicity increasing (Table 1) [29]. For the PHEMA grafted membrane with a GD of 4.48% (wt), the relative water flux reaches the maximum value of 118%; after that, the relative water flux decreases slowly.

Membrane permeability in the filtration of aqueous solution is mainly determined by two factors: one is the membrane structure, such as membrane thickness, pore size, and porosity; the other is the membrane surface hydrophilicity. When DG is low, the hydration of PHEMA chains results in a decreased resistance to water permeation and thus improves the water fluxes. For the membranes with a high DG, the graft layer is thick and the expanded PHEMA conformation in aqueous circumstance tends to cover the membrane pores, and consequently the water fluxes decrease [30, 31].

It can also be found in Table 1 that after the immobilization of ZnO NPs on the membrane surface, the membrane permeability continues to increase and the relative water flux rises to 143%. The coating of ZnO NPs on the membrane causes the decrease of water contact angle, because hydrophilic ZnO NPs anchored to the membrane [32, 33],

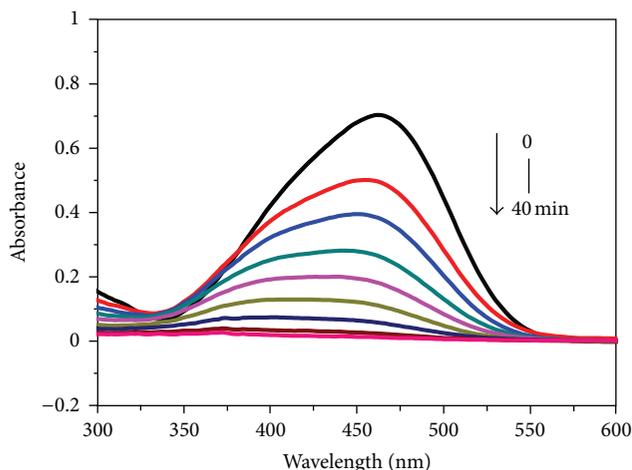


FIGURE 5: UV-Vis spectrum of MeOr under sunlight, using the photocatalytic membrane reactor with the ZnO NPs in suspension.

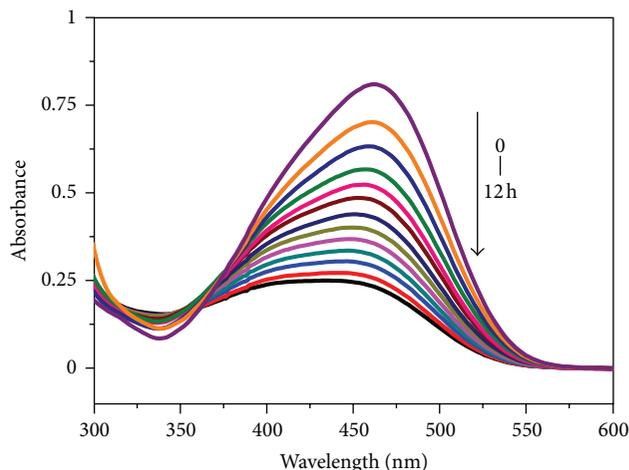
leading to the increase of the membrane surface hydrophilicity and hence increases the membrane permeability.

For the filtration of the dye solution, it was observed that the relative water fluxes were similar to those of the pure water fluxes, that is, the dyes could not be rejected by the membranes, and as a result, the filtrate was returned to the feed tank for the improvement of dyes decoloration. Membranes just acted as barriers for the ZnO NPs.

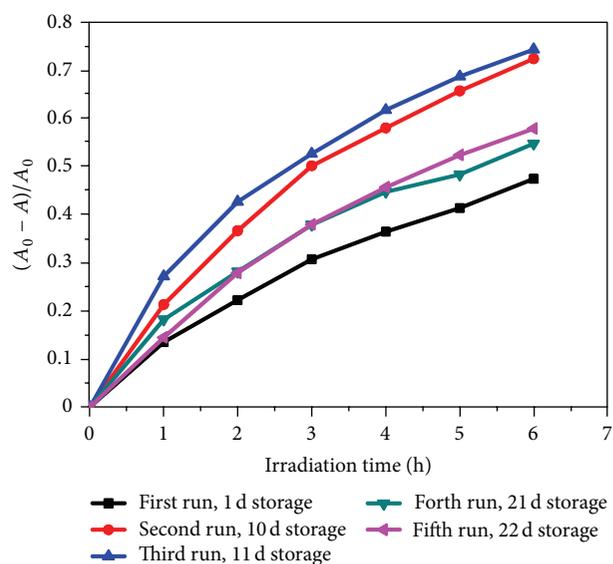
3.2. Photocatalytic Decoloring MeOr under Sunlight. In order to examine the performance of ZnO NPs in decoloring dyes in wastewater, photocatalytically decoloring MeOr was carried out in a photocatalytic membrane reactor under sunlight. The catalysts were suspended in the solution or immobilized on the membrane.

Figure 5 shows that MeOr is nearly completely decolorated after 40 min sunlight (ZnO NPs were suspended in the solution). The result shows that ZnO NPs prepared in the present work are highly effective in decoloring dyes in water and wastewater. The mechanism of ZnO NPs catalyzed decoloring reaction is as follows. ZnO NPs are excited by absorbing the photon with more energy than the band gap, resulting to the photoinduced electron-hole pairs. The peroxy radical anions are reacted by the electron and oxygen, and the hydroxyl radical is reacted by the hole and water. Hydroxyl radical can further decompose and remove organic molecules, namely, organic photodegradation [34]. Figure 5 also shows that the peak position is blue-shifted along with reaction time, which may be attributed to the deamination products of MeOr [35, 36].

The photostability of ZnO NPs photocatalysts is an essential factor to promote heterogeneous photocatalysis technology for practical applications. In this research, hybrid membrane is derived from coating ZnONPs on the PHEMA grafted membrane. The photocatalytic reaction was conducted within the light intensity of $90 \pm 15 \text{ mW/cm}^2$ for each run to eliminate the differences in light intensity. After each run, the membrane was taken out of the reaction chamber,



(a)



(b)

FIGURE 6: Decoloring MeOr in the PMR with the ZnO NPs immobilized on the membrane surface. (a) UV-Vis spectrum of MeOr at 1 h intervals (1–12 h) for the first cycle; (b) photocatalytic experiments for 5 cycles.

flushed with pure water and dried in air. UV-Vis spectrum of MeOr at 1 h intervals (1–12 h) for the first cycle is depicted in Figure 6(a), which shows that MeOr was decolorated slowly. The photostability of ZnO NPs immobilized membrane for the decoloring MeOr is shown in Figure 6(b), which indicates that the ZnO NPs immobilized on polypropylene membrane can photocatalytically decolor MeOr by 47.4%, 72.4%, 74.3%, 54.7%, and 57.8% after 6 h sunlight irradiation from the first to the fifth run, respectively. The PDP of the first run is the lowest, but those of the second and the third run reach the highest.

The reason may be that the active point of ZnO NPs was covered because of the agglomeration. After the first run, the agglomeration configuration of ZnO NPs became

a little dispersive and the MeOr can enter into the interstice between ZnONPs. In addition, the transparency of membrane increased after the first run, and the loosely adsorbed ZnO NPs were washed off (however, this could not be determined due to the trivial gravity changes), causing an increase in sunlight penetrating, hence the PDP ascends.

PDPs of the fourth and fifth run are between those of the first and the second run, showing that PDPs of the two runs slightly decrease, compared with those of the second and the third run. This phenomenon may be resulted from the deactivation of the photocatalysts, which is due to that many MeOr molecules were adsorbed on the membrane surface after being used for three times [37]. The PDP maintains at a very high level of about 55% in the fifth run, which means that after being used for five cycles, the PDP is still 8% higher than that of the first run. This result confirms that the catalysts were not photocorroded during the photocatalytic decoloration of the pollutant molecules under sunlight. After being used for five times, a lot of ZnO NPs were also visibly adsorbed on the membrane surface, suggesting that they are not easy to wash off.

These results demonstrate that PMR with ZnONPs immobilized on the polypropylene macroporous membrane surface can be reused for several times without weakening the photocatalytic activity, exhibiting potential application for continual and long-time reactions [38]. Generally, the immobilized ZnO NPs are stable for repeated uses [34]. Therefore, the ZnONPs can be regarded as ideal photocatalysts for environmental friendly purification on industrial scale under sunlight.

Figure 6 shows that the PDPs are much lower than those of the PMR with ZnO NPs in suspension (Figure 5), which may be attributed to the following reasons: (1) the active area of ZnO NPs decreased; (2) 3/4 of the sunlight was absorbed by the PMMA reactor, which was characterized by a UV power meter; consequently, a more effective reactor with little absorption of the sunlight should be adopted.

It is well known that the polymeric membranes are not promising materials for application in the PMRs due to their susceptibility to damage by irradiation and hydroxyl radicals [24]. However, in the present work, sunlight was employed to decompose the dye; the damage effect was infinitesimal, and as a result, the mechanical properties were not presented.

4. Conclusions

Decoloring methyl orange in a photocatalytic membrane reactor was conducted via coupling zinc oxide nanoparticles and polypropylene macroporous membrane under sunlight. Poly(2-hydroxyethyl methacrylate) was grafted on the membrane surface to enhance the physical adsorption of zinc oxide nanoparticles on the membrane and to improve the membrane permeability.

The poly(2-hydroxyethyl methacrylate) modified membrane with a grafting degree of 4.48% (wt) has the maximum value, the relative flux is 118%; after the immobilization of zinc oxide nanoparticles on this membrane surface, it reaches 143%, improved by 25%.

The photocatalytic decoloration percent of methyl orange is 98.2% under 40 min sunlight irradiation in the photocatalytic membrane reactor with the ZnO NPs in suspension; and in the photocatalytic membrane reactor with the ZnO NPs immobilized on the membrane, the photocatalytic decoloration percent of methyl orange decreases greatly; it reaches 74.3% under 6 h sunlight irradiation. Overall, after repeated uses for five times, it is still 8% higher than that of the first run. These results demonstrate that the immobilized ZnO NPs are stable for repeated uses.

Nomenclature

BDTB:	Benzyl dithiobenzoate
BP:	Benzophenone
GD:	Grafting degree
ID:	Immobilization degree
FESEM:	Field emission scanning electron microscopy
HEMA:	2-hydroxyethyl methacrylate
PHEMA:	Poly-2-hydroxyethyl methacrylate
MeOr:	Methyl orange
PDPs:	Photocatalytic decoloration percents
PMR:	Photocatalytic membrane reactor
PPMM:	Polypropylene macroporous membrane
RAFT:	Reversible addition-fragmentation chain transfer
ZnO NPs:	Zinc oxide nanoparticles.

Authors' Contribution

B. Hu contributed to the preparation and characterization of ZnO NPs and membrane surface modification. X.-M. Wu contributed to the synthesis of the chain transfer agent. J. Zhou, corresponding author, contributed to the conducting photocatalytic membrane reactor and photocatalytic decoloring of dye.

Acknowledgments

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