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Effect of various zinc oxide nanoparticles in membrane photocatalytic reactor for Congo red dye treatment

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ABSTRACT

The utilisation of titanium dioxide (TiO_2) in a coupling system membrane photocatalytic reactor (MPR) has been widely investigated. However, there have been very few studies regarding the zinc oxide (ZnO) photocatalyst in MPR, although it has been shown to provide better efficiency than TiO_2 in certain cases, mainly for dye photodegradation. In this study, the influence of ZnO nanoparticles in MPR has been investigated for Congo red (CR) dye treatment. Four types of ZnO were synthesised via the precipitation of oxalic acid and zinc acetate solutions. The X-ray diffractometry (XRD) and transmission electron microscopy (TEM) results showed that precipitation is a valuable method for producing the smallest particle size (7–30 nm) of ZnO without any agglomerations, especially under stirring conditions in the presence of PVP (ZnO-PVP-St). As expected, the ZnO-PVP-St presented the great potential in MPR in terms of the highest photodegradation efficiency and lesser membrane flux decline, which was supported by the FESEM results. From the EDX analysis, it was confirmed that the small amount of ZnO-PVP-St did not pass through the membrane pores to the final stream. It was believed that the other remaining ZnO was reused in the photocatalytic reactor, for the continuous process of MPR. Due to the effective surface area of ZnO-PVP-St and adsorption of UV light, the optimum photocatalyst loading for the system was 0.3 g L^{-1} under 20 mg L^{-1} dye concentration and pH 7 of the initial CR dye solution.

1. Introduction

Coupling membrane technology with photocatalytic degradation system, the membrane photocatalytic reactor (MPR) is an advanced alternative to the conventional treatment method. In the coupling system, photocatalytic degradation acted as the pretreatment process where it can reduce the membrane fouling and flux decline. Membrane filtration replaced the sedimentation process in conventional methods, and acted as a barrier to the photocatalyst and some molecules/ions from being transported in the final stream. MPR consumption can save energy and reduce the installation size since it does not require additional operations such as coagulation, flocculation and sedimentation [1]. In addition, other advantages of this system include simple configuration, better process control, good efficiency, continuous process (photocatalyst and the product can be separated at the same time) and the potential reuse of the photocatalyst [2]. Generally, the catalysts used in coagulation, flocculation and sedimentation cannot be used again.

To date, MPR has attracted much attention due to their advantages. However, almost all of the previous studies were focused on the utilisation of titanium dioxide (TiO_2) as the photocatalyst, due to its effectiveness [3–5]. Recently, Hairom et al. [6] reported the utilisation of zinc oxide (ZnO) nanoparticles in MPR for industrial dye wastewater treatment using UF and NF membranes [6]. They found that the chemical properties of the effluent and nanofiltration (NF) membrane performance were improved in the presence of their ZnO via precipitation methods. In addition, they concluded that ZnO nanoparticles have great potential in MPR for dye treatment. ZnO is already known to be an effective photocatalyst due to its strong excitation binding energy and advantages [7,8]. However, it is very rarely used in MPR. In 2006, Kanade et al. [9] claimed that the characteristics of ZnO powder are dependent on its size and methods of preparation. The statement was supported by a recent report [10] which confirmed that the photocatalytic activity of ZnO nanoparticles is very sensitive to precursors and synthesis process conditions. Therefore, it can be concluded that the preparation of ZnO may influence the photocatalysis

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performance in MPR and subsequently affect the characteristics of the membrane during the filtration process [6]. In order to investigate the impact of the issue in MPR, this study intends to investigate the effect of various types of ZnO via precipitation methods in MPR.

Precipitation process is the production of a solid in solution through a chemical reaction between the reactants. The solid formed in a liquid solution is called a precipitate. Typically, the precipitate will remain in suspension as the force of gravity is not sufficient to bring the solid particles down to the bottom. Therefore, the solid can be obtained through processes such as filtration, centrifugation, etc. The advantages of these processes are the fact that they are simpler routes, inexpensive, energy saving (room temperature) and produce good yields with uniform shapes and sizes. Previously, three different conditions of precipitation method were studied by Behnajady et al. for producing ZnO nanoparticles [10]. They observed that the reaction between zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and oxalic acid ($H_2C_2O_4{\cdot}2H_2O$) in ethanol solvent under ultrasonic radiation obtained the best performance for ZnO in the photocatalysis process. Kanade et al. reported the effect of solvents (water, methanol and ethylene glycol) on the precipitation synthesis of nano-sized ZnO using zinc acetate and oxalic acid under vigorous stirring at room temperature [9]. They found that the same percentage, 90% of ZnO was obtained from zinc oxalate for all of the different solvents. Hence, this study attempts to synthesise ZnO nanoparticles through the reaction between zinc acetate and oxalic acid in water solvent under stirring conditions and ultrasonic radiation at room temperature.

One of the serious problems faced in the synthesis of nanoparticles is 'agglomeration'. Agglomeration is the process resulting from the Ostwald ripening and Vander Waals interactions between nanoparticles when the particle growth is not controlled [11]. Agglomeration can be prevented by stabilising them electrostatically in suitable phases to achieve the selected size [12]. A current trend in view of reducing the agglomeration is capping the nanoparticles using polyvinyl pyrrolidone (PVP) as a stabilising agent [13,14]. PVP is a water-soluble polymer, consisting of an N-vinyl pyrrolidone monomer that can form a bond with the Zn ions on the growing particles, leading to prevention of the aggregation of nanoparticles. Furthermore, it has been reported that PVP not only controls the shape and particle size, but also improves the luminescence properties of several nanoparticles [15,16]. Therefore, the effect of PVP in the precipitation of ZnO was also studied in this report. The main objective of ZnO production is to obtain much smaller ZnO nanoparticles without any agglomeration via a simple method. This is essential in order to acquire a better performance of photocatalysts in MPR.

Most of the MPRs for dye purification described in the literature have used pressure-driven membrane processes including microfiltration (MF) [17,18], ultrafiltration (UF) [19,20] and nanofiltration (NF) [21,22]. However, severe membrane fouling is observed in the case of MF and UF membranes when a suspension photocatalyst was applied in MPR [23]. In addition, the lower quality of permeate was obtained since small particles/molecules/ions can pass easily through the membranes during the both microfiltration and ultrafiltration [6,23]. Thus, an NF membrane was used in this work in order to ensure the effectiveness of the MPR system and the quality of permeate.

Congo red (CR) dye was used in this study as the model of synthetic dye. This is because CR was frequently used in the dyeing process for many industries such as textiles, leather, food, paper, printing, pharmaceutical, cosmetics, etc. However, the waste water produced from these industries involving CR has contributed to serious environmental issues due to its natural aesthetic, where the colours can be seen even at low concentrations [24]. The reactive azo CR dye, which is also difficult to biodegrade, was not affected by the conventional treatment. Therefore, pollution caused by industries involving CR may become a huge problem in the future without proper pollution control.

2. Materials and methods

2.1. Synthesis and characterisation of ZnO nanoparticles via the precipitation method

Here, 0.15 M solution of oxalic acid dehydrate (purchased from R&M Marketing, Essex, U.K) was added slowly to 0.1 M solution of zinc acetate dehydrate (purchased from R&M Marketing, Essex, U.K) (molar ratio of oxalic acid to zinc acetate is 1.5) at room temperature (25 °C) under four different conditions:

(i) vigorous stirring without PVP (ZnO-St),
(ii) ultrasonic radiations without PVP (ZnO-Us),
(iii) vigorous stirring in the presence of PVP (ZnO-PVP-St) and
(iv) ultrasonic radiations in the presence of PVP (ZnO-PVP-Us).

For the preparation of ZnO-PVP-St and ZnO-PVP-Us, 0.015 g/L PVP (purchased from R&M Marketing, Essex, U.K.) was added to the mixture after 5 min of reaction. The precipitate obtained was filtered and then calcined in the furnace (Nabertherm model, Germany) under 550 °C (3 h) in order to remove impurities. Commercial ZnO purchased from Sigma Aldrich, USA was used for comparison purposes. Physical and chemical properties of the nanoparticles were characterised with X-ray diffractometry (XRD) (Bruker AXS GmbH model) and transmission electron microscopy (TEM) (CM12 Philips model).

2.2. Membrane and its characterisation

Polypiperazine amide NF membrane (GE Osmonics®, Trisep® TS40, USA) was used in this study. The characteristics of the membranes are tabulated in Table 1. The new membrane sample was immersed in reverse osmosis (RO) water over-night before it was used in the reactor. Morphology of the membrane surface and cross-sections were observed with field emission scanning electron microscopy (FESEM; Gemini, SUPRA 55VP-ZEISS) equipped with an energy dispersive X-ray (EDX) analysis system. For the cross-sectional analysis, small pieces of the membranes were soaked in an appropriate amount of liquid nitrogen for 4–5 h. The samples were fractured and dried in an oven under 60 °C. The dried samples were coated with gold to generate the electrical conductivity. Afterwards, observation of the prepared samples was carried out with the microscope at 3 and 10 kV. Analysis of the element intensity on the membrane surface was conducted with the EDX system.

2.3. Congo red dye

Congo red (CR) dye powder (molecular weight: 696.66 g/mol) was obtained from R&M Chemicals, United Kingdom (U.K.) and

Table 1
Characteristics of the NF membrane.

Membrane	Characteristic
MWCO[a]	200 Da
Na_2SO_4 rejection[b]	99%
NaCl rejection[b]	10–40%
pH tolerance[a]	2–12
Standard operation pressure[a]	2–14 bar
Hydrophobicity[b]	Hydrophilic
Contact angle (°)[b]	39.0 ± 1.5

[a] Information obtained from manufacturer.
[b] Value obtained from experimental measurements.