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Influence of zinc oxide nanoparticles in the nanofiltration of hazardous Congo red dyes

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HIGHLIGHTS

- ZnO nanoparticles synthesised via precipitation method under various conditions.
- Influence of ZnO nanoparticles in the nanofiltration of CR was investigated.
- Membrane performances improved with ZnO-PVP-St addition in the solution.
- ZnO interaction was influenced by the preparation methods and agglomerations.

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ABSTRACT

Zinc oxide (ZnO) nanoparticles were produced via a simple and green precipitation method under stirring conditions (ZnO-St) and under ultrasonic radiation (ZnO-Us). The nanoparticles properties were characterised with X-ray fluorescence (XRF), X-ray diffractometry (XRD) and transmission electron microscopy (TEM); and compared with commercial ZnO and no ZnO. Their influence in the nanofiltration (NF) of hazardous Congo red dyes was studied in order to provide the fundamental understanding in the interacting effect of ZnO and NF membranes. The membrane performances were significantly improved after the addition of ZnO in the dye solution in descending order as follows: ZnO-Us > ZnO-St > commercial ZnO > no ZnO. It is believed that the preparation method, agglomerations and the morphology of nanoparticles influence their interaction with dye molecules and membrane surfaces. Membrane characterisations using contact angle, X-ray fluorescence (XRF), Field Emission Scanning electron microscopy (FESEM) and Energy Dispersive X-ray Analysis (EDX) confirmed that ZnO nanoparticles have great potential for fouling mitigation in industrial NF application.

1. Introduction

Recent developments in the area of integrated membrane-photocatalytic nanoparticles [1,2] have led to a renewed interest in the use of nanoparticles during membrane filtration. Data from several reports have shown that the addition of nanoparticles in NF systems has led to a reduction in the membrane fouling flux with an increased total removal of colour and unwanted elements of wastewater dyes [3]. ZnO nanoparticles, in particular, would be of interest due to their higher reactivity, surface area, photosensitivity, chemical stability, non-toxic nature, and low cost [4]. Along with its stable wurtzite structure and wide bandgap (3.4 eV) compound semiconductor, ZnO has been mainly used as a catalyst for dye treatment [5,6]. Similarly within a photocatalytic membrane reactor, nanoparticles can be used as the photocatalyst to degrade the dyes while they are being separated and recycled at the same time through the use of membranes [7,8]. Therefore, the influence of such nanoparticles on membrane performance is an important issue in this research area. However, there are very limited detailed studies concerning the influence of ZnO nanoparticles on the performance of NF membranes in the dye wastewater treatment field. Thus, this study aims to analyse the influence of the presence of ZnO nanoparticles on the rejection and flux performance of the NF membrane.

It should be noted that the characteristics of ZnO are dependent on its size and preparation methods [9]. Recent reports [10,11] have confirmed that the photocatalytic activity of ZnO nanoparticles is

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very sensitive to precursors and synthesis process conditions. Therefore, the performances of ZnO nanoparticles may be influenced by the method of synthesis. To date, various methods have been implemented for the production of ZnO nanoparticles such as sonochemical [10,12], precipitation [9,11], electrolysis [13] and hydrothermal synthesis [14]. Among these methods, precipitation has been recognised as the preferable technique since it provides a simpler route, is more economical and occurs at moderately low temperatures. However, very few studies involving the synthesis of ZnO nanoparticles via the precipitation method have been published. In addition, there have been several studies which have shown that the size and characteristics of ZnO nanoparticles varied, but were improved under ultrasonic conditions [10,15,16]. The ultrasonic radiation method has gained much attention among researches due to it being green, low cost, rapid, and preservative free technique [16,17]. Data from several reports have revealed that the photocatalytic efficiency of ZnO synthesised via the ultrasonic method was better in comparison to commercially available ZnO [10,15]. Therefore, the influence of ZnO nanoparticles synthesised via preparation methods under different conditions (ultrasonic radiation and vigorous stirring) and their effect on the performance of the NF membrane were also examined.

Since Congo red (CR) dye was frequently used in the dyeing process for many industries, it was used as the model of synthetic dye in this study. It is also known as 3,3′-([1,1′-biphenyl]-4.4′-diyl) bis (4-amino-1-aminonaphthalene sulphonic), with molecular formula $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight of 696.7 g mol^{-1}. The complex structure would causes wastewater containing CR difficult to biodegraded, contaminated, high organic content and high colour concentration [18,19]. Moreover, CR has also been known as a highly toxic substance, unpleasant and suspected to be mutagenic and carcinogenic. These negative features will lead to a variety of hazards that pose a significant risk to the environment and human health. Therefore, the treatment of CR dye effluent is very important. The overall objective of this study is to provide preliminary understanding of the influence of ZnO nanoparticles during the nanofiltration of Congo red dye. The output from this study will help to provide the fundamental understanding in the interacting effect of ZnO and NF membranes if they are applied within a membrane photocatalytic reactor for the treatment of hazardous dyes.

2. Materials and methods

2.1. Congo red

Congo red powder (λ_{max} = 510 nm) received from R&M Chemicals, United Kingdom (U.K.) were used as the model of synthetic dye. It is a benzidine-based anionic diazo dye, contains of coupling tetrazotised benzidine with two naphthionic acid molecules as illustrated in Fig. 1. Appropriate amount of CR powder was dissolved in reverse osmosis (RO) water for preparing 20 mg L^{-1} dye solution. The pH was adjusted by adding either hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions, obtained from R&M Chemicals, U.K. The solution pH was measured using a microprocessor pH meter (Sastec ST-PHS3BW Model).

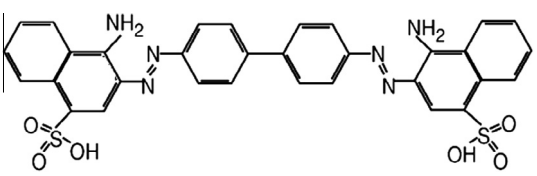

Fig. 1. Molecular structure of Congo red.

2.2. Synthesis of ZnO nanoparticles by precipitation method and their characterisations

ZnO nanoparticles were prepared according to Kanade et al. [9] and Behnajady et al. [11]. A 0.15 M solution of oxalic acid dehydrate (R&M Marketing, Essex, U.K.) was added slowly to a 0.1 M solution of zinc acetate dehydrate (R&M Marketing, Essex, U.K.) under room temperature with two different conditions: vigorous stirring and ultrasonic radiations. The precipitate obtained was filtered and calcined in the furnace (Nabertherm model, Germany) at 550 °C for 3 h to remove impurities. Commercial ZnO (Sigma Aldrich, USA) was used for comparison purposes. The nanoparticle properties were characterised with X-ray fluorescence (XRF) (PANalytical model), X-ray diffractometry (XRD) (Bruker AXS GmbH model) and transmission electron microscopy (TEM) (CM12 Philips model).

2.3. Membrane and experimental set-up

Polypiperazine amide nanofiltration (PA-NF) membrane (GE Osmonics® HL, Trisep® TS40, USA) was used for this study due to its effectiveness [20,21]. Its specifications and properties are summarised in Table 1. The membrane were immersed in RO water over-night before use, for elimination of conservation products. A stirred cell (Sterlitech™ HP4750, USA) with 14.60 cm^2 of effective membrane area was used for the NF run. In order to prevent membrane compaction throughout the experiments, the NF membrane was wetted out for 30 min under 5 bar (using nitrogen gas) by circulating RO water. 20 mg L^{-1} CR treatment was carried out under pH 9 with the addition of 1.0 g L^{-1} ZnO. The schematic diagram of the experimental set-up was shown in Fig. 2. The mixed CR solutions-ZnO were stirred for 30 min in order to reach adsorption–desorption equilibrium of the ZnO. Subsequently, the

Table 1
Characteristics of the PA-NF membrane.

Membrane	Characteristic
Pore size/molecular weight cut-off (MWCO)[a]	200 Da
Na_2SO_4 rejection[b]	99%
NaCl rejection[b]	10–40%
pH tolerance[a]	2.0–11.0
Standard operation pressure[a]	2.0–14.0 bar
Hydrophobicity[b]	Hydrophilic
Contact angle (°)[b]	39.0 ± 1.5

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

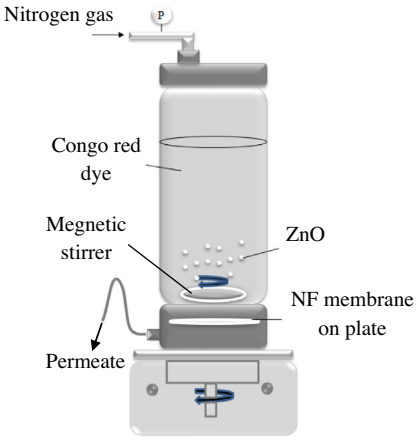

Fig. 2. Schematic diagram of stirred cell rig.