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Performance comparison for the decolouration of methylene blue *via* photodegradation between zinc oxide embedded-cellulose nanofibril membranes and aerogels

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Abstract

This paper discussed the comparison of the decolouration efficiency of methylene blue (MB) using developed cellulose nanofibril (CNF) membranes (CMZ) containing 1.6 wt% zinc oxide (ZnO) and aerogels (CAZ) containing 1.6 wt % ZnO as a catalyst. Two forms of scaffolding filled with ZnO were characterized using field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy (FESEM-EDX) to show the distribution of ZnO particles on the surface and proven the embedded particles were successful. The particle size distribution of ZnO was provided by the images of FESEM which is 96.1 ± 4.4 nm and 100.1 ± 4.58 nm for membranes and aerogels respectively. EDX data have shown the presence of ZnO particles. A photocatalysis study with a 26 watt UV lamp was done to show the efficiency of both regenerated cellulose membranes and aerogels in the process of decolouration of an organic dye such as MB which recorded optimum decolouration of 87.6% and 50.3% for membranes and aerogels respectively. A study on the effect of initial pH was also been done to ensure the best condition for the catalysis and shows pH 6 is the most suitable condition for both forms.

Keywords: Cellulose nanofibril (CNF), membranes, aerogels, ZnO and photocatalysis

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1. Introduction

Environmental pollution has been in highlight worldwide for over decades. One of the main issues being raised is water pollution and expected to become worse in the coming decades [1]. Pollution of water sources is contributed by many factors such as the tremendous human population, agricultural activities, modern industrial waste, global change and textiles industries [2][3]. As one of the main sources of water pollution, textiles industries contributed to this issue by demanding increments of textiles nowadays may lead to a huge amount of dyes waste has been released into water sources. Dyes are not only about the colour but their toxicity and mutagenicity create concerns worldwide [4]. Without necessary treatment taken, these dyes are stable and remained in the environment for a long period which can lead to many other consequences such as eutrophication phenomena that threaten aquatic organisms. Furthermore, almost 7105 tons of 10,000 different types and pigments are produced were reported around the globe [5] can lead to many consequences if no action is taken to prevent water resources from being polluted. For that, numerous wastewater technologies such as chemical oxidation, electrochemical treatment, flocculation-coagulation, adsorption and photocatalysis have been developed. Implementation of bi-functional treatment such as a combination of adsorption with photocatalysis might reduce the operational cost, particularly in the decolouration of organic dyes such as methylene blue (MB) [6].

Cellulose has the most abundant resources in the world despite its desirable properties such as being biodegradable, biocompatible, green and containing a huge amount of hydroxyl (OH) groups [7]. Because of its remarkable performance as a scaffolding loading catalyst, it has been used to support heterogeneous catalysts such as silver nanoparticles, palladium nanoparticles, iron oxide nanoparticles and zinc oxide nanoparticles [8].

In the past few years, zinc oxide (ZnO) is among the favourable heterogeneous catalysts because of its non-toxic, cheap, low-corrosion, recyclability and minimum execution properties [9]. When irradiated by UV light, changing of electron energy state from the valence band (VB) to the conduction band (CB) forms electron-hole pairs (h^+) that lead

to the excitation of radical forms for the decolouration of methylene blue (MB) as described below:

$$ZnO + UV\ light \rightarrow h^+ + e^- \quad (1)$$
$$e^- + O_2 \rightarrow O_2^{\cdot -} \quad (2)$$
$$h^+ + OH^- \rightarrow OH^{\cdot} \quad (3)$$
$$O_2^{\cdot -} + H_2O \rightarrow HO_2^{\cdot} + OH^- \quad (4)$$
$$HO_2^{\cdot} + H_2O \rightarrow H_2O_2 + OH^- \quad (5)$$
$$H_2O_2 \rightarrow 2OH^{\cdot} \quad (6)$$
$$OH^{\cdot} + MB \rightarrow CO_2 + H_2O \quad (7)$$

In this study, a comparison of performance via photocatalysis between two forms of regenerated cellulose embedded with ZnO has been done. MB was chosen as a model of pollutant because it is widely used in various industries such as organic dyes as textiles, paint, aquaculture and medicine [5].

2. Materials and methods

2.1. Materials

Commercial zinc oxide (ZnO) powder (average particle size 21±5 nm), methylene blue (MB) and epichlorohydrin (ECH, C_3H_5ClO) were purchased from Sigma Aldrich. Cotton linter with an average molecular weight (Mw) of 90,000 was obtained from Hubei Chemical Fiber Co. Ltd., China. Other chemicals such as sodium hydroxide (NaOH) and urea (CH_4N_2O, 99%) were purchased from R&M Chemicals. All chemicals were analytical grade and used without further purification.

2.2. Preparation of regenerated cellulose membrane and aerogels

The regenerated cellulose membrane was prepared according to a previous report [10]. Briefly, an aqueous solution of NaOH/urea with a weight ratio of 7:12:81 was prepared and frozen at -20°C for at least eight hours. The solution was then thawed to -13°C, after which cotton linter (3.5 g) was added and the solution was stirred vigorously using an overhead stirrer until the linter dissolved. The resulting cellulose solution was centrifuged at 12,000 rpm for 10 min at 5°C to separate unreacted cellulose and air bubbles. Finally, the supernatant was collected and stored at 4°C until further analysis.

Membranes

The cellulose solution membrane was prepared by adding 0 and 1.6 wt% of ZnO in the cellulose solution and labelled as CM and CMZ respectively. The soluble cellulose solution containing ZnO was cast on a glass plate to form a thin layer of membrane and immerse in distilled water as a coagulating bath to regenerate the cellulose. The formed membrane was soaked in another distilled water to remove excess and unreacted chemicals.

Aerogels

The soluble cellulose solution was poured into a beaker and added with 0 and 1.6 wt% of ZnO in the solution and labelled as CA and CAZ respectively. The solution was stirred vigorously until total dissolved. 5wt% of ECH was then added to the solution and continued stirring until a homogeneous solution was achieved. The formed hydrogel was dialyzed in distilled water to remove excess and unreacted chemicals before freeze-drying to get the aerogel forms.

2.3. Characterization of cellulose membranes and aerogels

A square swatch of each cellulose membrane and aerogel was observed under a field emission microscope mapping (FESEM, SUPRA 55VP).

2.4. Photocatalytic activity for decolouration of MB

All MB solutions were prepared according to the initial MB concentrations required. Concentrations were measured using a UV-vis spectrophotometer (OPTIZEN POP) at λmax 662 nm. A calibration curve was constructed using MB solutions with absorbances ranging from 0.1 to 1. Membranes with different concentrations of ZnO were cut to dimensions of 1×1 cm and aerogel dimensions of 1×1×1 cm weighing about 0.4 g. The cut membranes and aerogels respectively were immersed in 100 mL of MB solution (5 mg/L) in a beaker with a magnetic stirrer, which beaker was in turn placed in a chamber walled with aluminium foil and having a lid equipped with a 26-watt UV lamp ($\lambda \leq 390$ nm). The solution was stirred at 250 rpm in the dark for one hour to allow equilibrium between the organic molecules and the catalyst. After that hour, the solution was exposed to light and the photocatalytic activity was measured at five-minute intervals for another 100 minutes using a UV-vis spectrophotometer (OPTIZEN POP). In addition, the effect of pH on the decolouration of MB was studied by adjusting solutions to desired pH values using NaOH and HCl. The amount of decolourized MB was determined according to the following equation:

$$\textbf{Removal Percentage} = \frac{C_0 - Ce}{C_0} \times 100 \quad (8)$$

where C_0 and C_e are the initial and equilibrium concentrations of MB, respectively.

3. Results and discussion

3.1. Characterization of cellulose membranes and aerogels filled with ZnO

The presence of ZnO particles was confirmed using FESEM EDX mapping for particles was done to show the morphology and the distribution of the particles of ZnO on the surface of membranes and aerogels as shown in Fig. 1. Fig 1 (a) shows blank control of cellulose membrane (CM) compared to cellulose membranes embedded with ZnO particles (CMZ) Fig 1 (b) clearly shows the distribution of ZnO on the surface of the membranes which is represented in cyan. The ZnO size particle distribution is 96.1 ± 4.4 nm

presented in histogram Fig 2 (a) was extracted from the FESEM images. In addition, EDX data shows the wt % of Zn in CM is 0.3% compared to CMZ with 24.4% which shows the embedded was successful as shown in Table 1.

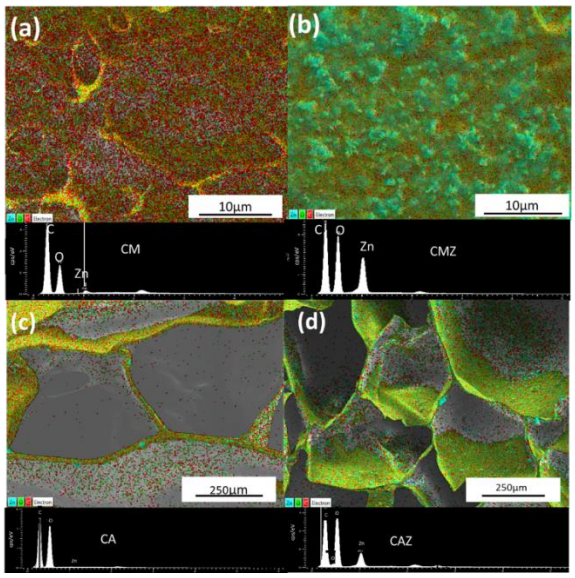

Fig. 1. Particle mapping with EDX which cyan represents Zn, green represents O and red represents C on the surface by FESEM for (a) cellulose membrane, (b) cellulose membrane filled ZnO, (c) cellulose aerogel and (d) cellulose aerogel filled ZnO

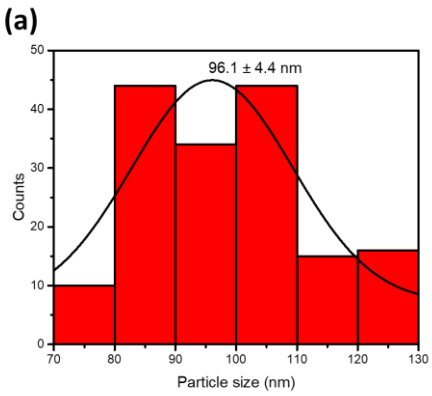

Fig. 2a. Histogram size of ZnO particle distribution on cellulose membrane

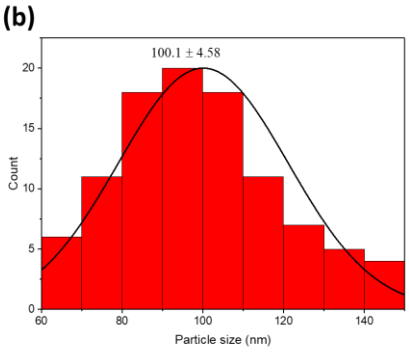

Fig. 2b. Histogram size of ZnO particle distribution on cellulose aerogel

Meanwhile, Fig 1(c) shows blank cellulose aerogel (CA) as blank control in comparison with Fig 1(b) cellulose aerogels filled with ZnO nanoparticles. These images were also proved the successful filling of ZnO on the surface of the aerogel presented by cyan with the size distribution of 100.1 ± 4.58 nm as shown in Fig 2 (b) with wt% of Zn particles in CAZ being 13.4% compared to CA with just 0.1% as shown in Table 1.

Table 1. Confirmation of particles C, O and Zn presence by EDX for CM, CMZ, CA and CAZ

Sample	**wt %**		
	C	O	Zn
CM	61.1	36.8	0.3
CMZ	45.5	30.1	24.4
CA	51.3	48.0	0.1
CAZ	45.3	41.3	13.4

3.2. Efficiency comparison via photocatalysis

ZnO has been proven as a highly potential catalyst for dye degradation in the solar-driven photodegradation process attributed to its low production cost, non-toxic and absorption ability [11]. Therefore, the efficiency of CMZ and CAZ were studied via the photodegradation process which also involved CM and CA as blank control together with ZnO powder to show the capability of ZnO as the catalyst as shown in Fig 2 (a). The graph has been divided into two main regions, the first region represents the initial dark period which also excluded the absorption factor misinterpreted as the photodegradation factor [12]. The second region represents the photodegradation period where samples are exposed to 26 watt UV light ($\lambda \leq 390$ nm). All samples have reached the equilibrium phase at 50 minutes as confirmed at 60 minutes. Compared to ZnO powder; CM, CA, CMZ and CAZ have better absorption in the dark period with CMZ recording the highest % decolouration by 70.9%. After exposure to UV light, ZnO powder excite to be the highest photodegradation performance among all samples because of direct exposure to UV light without any barrier such as cellulose component [13]. At 100 minutes, ZnO powder started to go plateau and achieved its maximum decolouration at 94.7% decolouration. Meanwhile, CMZ has shown better performance with 91.6 % compared to CAZ with just 50.3%. This may be caused by membranes having a higher surface area and better adsorption than aerogels that allow better irradiation of ZnO by UV light.

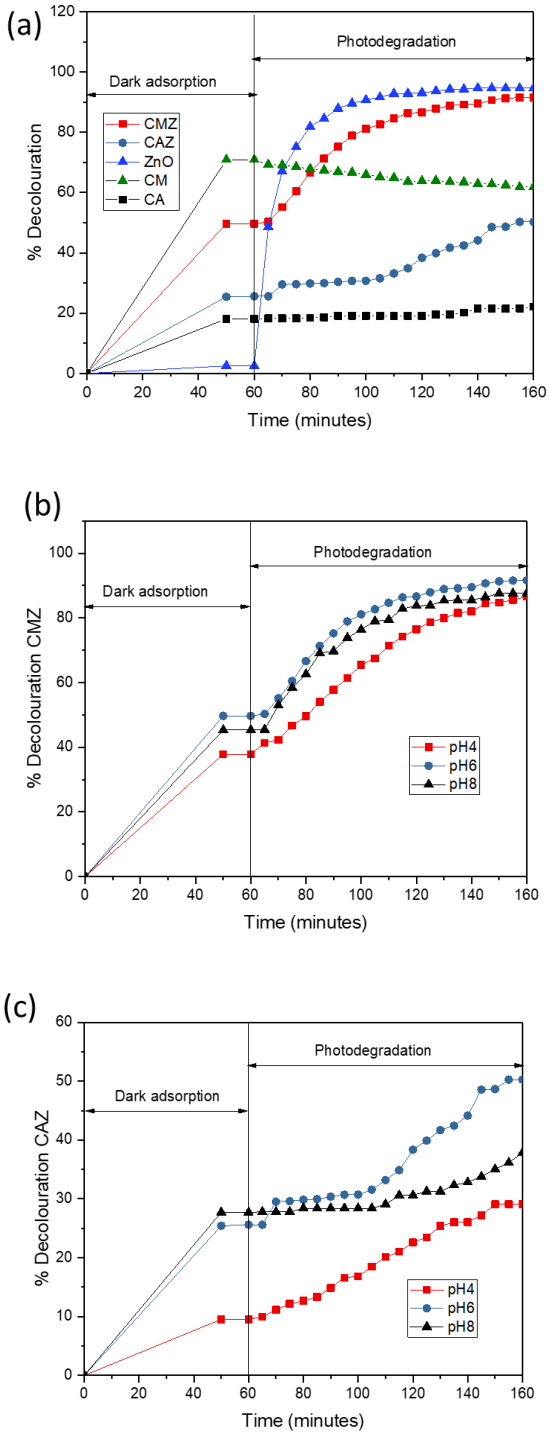

Fig. 3. Photocatalysis study for (a) comparison of % decolouration for ZnO powder, CMZ, CAZ with CM and CA as blank control, (b) effect of initial pH for CMZ and (c) effect of initial pH for CAZ

Fig.3 (b) and (c) illustrated the effect of initial pH in photocatalytic performance by CMZ and CAZ for the decolouration of MB. Initially, increasing the pH shows better performance for both forms may be caused by the formation of greater OH radicals in the alkaline pH range that catalyzed the decolouration [14]. For membranes in Fig. 3(b), pH 4 started at a little bit slower rate upon initiation of UV but manage to catch up starting at 100 minutes with similar decolouration at 86.6% compared to pH 6 with 91.6%. For the record, pH 6 is the initial pH of MB without any pH adjustment. Fig. 3(c) shows pH 6 recorded the highest decolouration with 50.3% compared to pH 4 and pH 8 with 29.1% and 37.8% respectively which is similar to data shown for membranes that no adjustments are needed for photodegradation of both forms.

4. Conclusions

This study has shown a success story of the development of cellulose membranes and aerogel filled with ZnO as a catalyst for the decolouration of MB. Therefore, a comparison between both forms has been studied that shows CMZ has a better performance compared to aerogels. This may be caused by membranes having higher surface area and better liquid penetration compared to aerogels for better irradiation of UV light on ZnO. Other than that, the formed radicals by the excitation of UV light would oxidize the closest MB molecules because of the bigger surface area [15]. This study has proven that regenerated cellulose membranes and aerogels can be a model for scaffolding catalysts for other uses.

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