Assessment of Rhodamine B Dye Removal by ZnO Nanodisks under Visible Light

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Abstract. The organic dye from the textile and dye industries are highly hazardous to aquatic living and human. They cause serious damage to the surrounding environment. Zinc oxide (ZnO) photocatalyst has attracted much attention because of its high efficiency applications, especially in organic dyes removal, for instance Rhodamine B (RhB) dye. The precipitation method was used to synthesize ZnO nanodisks (NDs) by using zinc acetate dehydrate, aluminium sulphate and ammonia hydroxide as precursors. The X-ray powder diffractometry (XRD) shows that the as-synthesized particles consisted of ZnO and zinc aluminium carbonate hydroxide hydrate (ZnAlOHCO₃) phases. The diffraction peaks matched with the Joint Committee on Powder Diffraction Standards (JCPDS) No. 98-002-7791 and No. 98-010-5856, respectively. The morphology of ZnO NDs was clearly observed by scanning electron microscope (SEM). An average diameter and thickness of ZnO hexagonal disk were 2.12 µm and 74.9 nm, respectively. The UV-Visible spectroscopy showed that the photodegradation efficiency of ZnO NDs in removal of RhB dye in aqueous solution was 39% under visible light illumination of 5 hours. The possible photodegradation mechanism was studied by the examination of active species e.g. •HO, •O₂ and h⁺ through adding their respective scavengers such as methanol, benzoquinone and potassium.

1. Introduction

ZnO is a II-VI group direct semiconductor with wide bandgap (3.3 eV) in the near-UV spectral region and large binding energy (60 meV) at room temperature [1, 2]. It exhibits in a wide range of nanostructures such as nanodisks [3, 4], nanorods [5, 6], nanobelts [7, 8], nanowires [9, 10], nanorings [11]. The variety of nanostructures of ZnO make its unique and possessed remarkable performance in photonics, sensors, photovoltaic devices and photocatalysts applications [12]. Particularly, ZnO photocatalysts have been received much attention for wastewater treatment such as removal of organic – inorganic pollutants [13-19], antibacterial [20, 21] and water splitting [22].

As the preferred growth direction of ZnO is in [0001], ZnO nanorods (NRs) will be formed under normal synthesis condition particularly when no foreign catalyst is used [23]. The application of ZnO NRs as photocatalyst for organic pollutants removal is widely studied because of its simplicity, low
cost, nontoxic, high degradation efficiency, and excellent stability in nature [24-25]. Nevertheless, using ZnO NDs as photocatalyst is relatively less known and explored although this nanomaterial was used as building blocks in lasers, sensors and photonic crystal [26-27]. As compared to NRs, ZnO NDs have large (002) polar surface (disk surface), which either terminated by positively charged Zn$^{2+}$ or negatively charge O$^{2-}$. The present of this polar surface might be able to enhance the photocatalytic performance under visible light illumination. This is crucial for realization of ZnO nanomaterials as photocatalyst because the energy of incoming solar spectrum consists of less than 4% ultraviolet (UV) light but more than 50% visible light [28]. Thus, it is necessary to investigate the photocatalytic activity in organic dye removal of ZnO NDs by using visible light illumination.

In this work, the photocatalytic performance of ZnO NDs in organic dye removal under visible light irradiation was studied. ZnO NDs were synthesized via precipitation method [29]. Aluminium sulphate was used as surface directing agent in order to obtain the disk-like nanostructures. In addition, Rhodamine B (RhB) was used in this study. It represents one of the most important dyes, which has been extensively used in the textile industry due to its high chemical stability. Hence, the decomposition of RhB dye is a challenging task in waste water treatment.

2. Materials and Methods

ZnO NDs were synthesized via precipitation method according to the method described in Ref. [23]. In this process, zinc acetate dehydrate (99.99%, Merck, product number 108802), aluminium sulphate (98%, Systerm, product number A1831-90) and ammonia hydroxide (25%, Merck, product number 105432) were mixed in de-ionised water and stirred at 60 °C for 2 hours. White precipitate was formed and settled down on the bottom of the beaker. The precipitate then was rinsed with de-ionized water and centrifuged to separate the precipitate and solution. Lastly, the white ZnO powders were dried in an oven at 100 °C for 8 hours. The X-ray diffraction (XRD) patterns of the ZnO NDs were recorded using X-ray diffractor (Bruker Advanced X-ray Solution D8 Diffractometer. The morphology of particles was clearly observed by using field-emission scanning electron microscope (FESEM, 35VP Supra Carl-Zeiss) and high resolution transmission electron microscope (HRTEM, Tecnai G2 20 S-TWin).

Photocatalytic activity of ZnO particles was studied by monitoring the intrinsic absorption peak of RhB dye. The concentration of RhB solution was fixed to 5 ppm for all experiments. The aqueous suspension (250 ml) of RhB and photocatalyst (ZnO NDs) were placed in a visible chamber. Visible light irradiation was provided by a lamp with the strongest emission at wavelength \(~\sim\) 555 nm, placed at a distance of about 20 cm above the sample’s surface. The photodegradation of RhB solutions using NDs as photocatalysts was recorded by UV-VIS spectrometer (Carry 50). The photodegradation efficiency (PE) was calculated by using following equation:

\[
PE (\%) = \frac{C_o-C_t}{C_o} \times 100
\]

where \(C_o\) and \(C_t\) are the concentration of the RhB dye solution at the initial and time \(t\), respectively.

The scavenger study was carried out to find out the main reactive species that responsible for the degradation of dyes. In this study, potassium iodide, methanol, benzoquinone were used as scavengers for \(h^+\), ‘OH, ‘O$_2$’, respectively.

3. Results, Discussion

3.1 Structural and morphology of ZnO NDs

The ZnO NDs were synthesized using ammonia hydroxide, aluminium sulphate and zinc nitrate acetate as precursors. The growth mechanism of ZnO was discussed by Thein et al [23]. The XRD pattern of the as-synthesized particles is shown in Figure 1. It is matched with diffraction peaks of JCPDS No. 98-002-7791, indicating that the particles were hexagonal wurtzite ZnO [24]. The XRD at
31.18, 33.91, 35.69, 46.85, 56.05, 62.32 and 67.44 are correspond to (010), (002), (011), (102), (110), (103) and (112) crystal planes of hexagonal ZnO structures, respectively. Furthermore, ZnO NDs also exhibited extra peaks at 11.63, 23.01, 33.91 and 38.73 which were contributed from zinc aluminium carbonate hydroxide hydrate (ZnAlOHCO₃, JCPDS No. 98-010-5856). The phase percentage of zinc oxide and zinc aluminium carbonate hydroxide are 81% and 19%, respectively. The present of aluminium is further verified by EDX analysis, i.e. 7.05 at % aluminium was detected in the ZnO NDs as shown in Fig 2(a). The source of aluminium was come from aluminium sulphate. The complex agent, i.e. Al₂(SO₄)₃, was used to suppress the preferential growth of ZnO in [0001], allowing the growth in six symmetric direction ±[1̅0̅0], ±[1̅0̅1], ±[0̅1̅1] to form hexagonal structure [23]. Figure 2(b) shows the morphology of ZnO hexagonal NDs with the diameter of 2.12 µm and thickness of 74.9 nm.

Figure 1. X-ray diffraction pattern of a) ZnO NDs, b) ZnO JCPDS No. 98-002-7791 and c) ZnAlOHCO₃ JCPDS No. 98-010-5856.

Figure 2. (a) EDX spectrum and (b) SEM image of ZnO NDs

3.2 Photocatalyst study

RhB belongs to the oxygen-containing heterocyclic xanthene dyes family. The RhB contains two key components: chromophores and auxochromes. The chromophores are light absorbing group in the molecule. Figure 3(a) shows the characteristic absorption peak of RhB dye is 554 nm. This is due to the n →π transition of the chromophores, C=N, C=C groups, for instant [25]. To achieve this transition, the RhB molecule need to be excited by high level of energy. Hence, it is neither degraded in the dark in the presence of a photocatalyst nor under illumination of visible light in the absence of a photocatalyst [26]. On the other hand, auxochromes are functional groups of molecule attached to chromophores group such as -NR, -COOH. These functional groups do not absorb radiation itself but
has a shifting effect on main chromophore peaks. Figure 3(b) shows the absorption peak was shifted from 554 nm to 542 nm after 5 hours irradiation of visible light. The longer time RhB dye is exposed under visible light, the more blue shift present in the absorption peak; For instant, the peak shift at 542 nm was preferred to N,N-diethyl-N’-ethylrhodamine [27, 28].

The photodecomposition of RhB molecules by ZnO NDs mainly occurred at auxochromes groups under visible light illumination. This phenomenon is called the deethylation path way [29-31]. As a result, the photodegradation efficiency of RhB aqueous solution of ZnO NDs increased gradually and reached 39% after 5 hours (Fig 3(b)) irradiation of visible light. The first-order kinetic is used to describe the absorption rate base on absorption capacity [32]. The linear form of first-order rate was given by equation (2) [33].

\[ \ln(C_t) = \ln(C_0) - Kt \]

where K is the first-order rate constant. Figure 3(c) showed the linear plot of \( \ln(C_t/C_0) \) against time preferred the first-order kinetic of discoloration of RhB/ZnO solution with the rate constant of 0.098 min \(^{-1}\). Figure 3 (a) Absorbance spectra, (b) degradation efficiency and blue shift of RhB solution and (c) first-order kinetic plot of ZnO NDs under visible light irradiation

### 3.3 Scavenger study and photo-degradation mechanism

The scavenger study was carried out to find out the main reactive species responsible for the degradation of RhB dye in aqueous solution of ZnO NDs. Methanol is used as a diagnostic tool of •OH radical mediated oxidation mechanism [34]. The presence of potassium iodide from a solution provide iodide ion as a scavenger which reacts with \( \text{h}^+ \); that can be used to identify the involvement of hole in the direct oxidation of organic substrate. On the other hand, benzoquinone can be used to detect the superoxide anion due to their ability to trap this ion radical by an electron transfer mechanism [35].

Figure 4(a) shows the scavenger study of RhB with the present of ZnO NDs under visible light irradiation. The photodegradation efficiency of RhB solution in ZnO NDs went down dramatically from 38.65% to 34.19%, 26.55% and 1.88% when methanol, potassium iodide and p-benzoquinone were added into the solution, respectively. When •OH scavenger, methanol (Me) was put into the degradation systems, there was no significant changes occurred on dye degradation except for the hypochromic shift of the absorption band. Hence, •OH radicals were not the major oxidation species in this process. Moreover, it is known that there is limited \( \text{h}^+ \) arises on the surface of ZnO NDs under irradiation of visible light because of its wide bandgap. Thus, the low degradation rate in the presence of potassium iodide (KI) may be due to electron transfer between KI and two dye molecules [36]. Electron transfers between KI molecules make the dye radical ions return to the ground states and result in the small degradation efficiency, 0.066 min \(^{-1}\) of rate constant as shown in Figure 4(b). It means that \( \text{h}^+ \) was not the main factor causing the discoloration of dye. Besides, p-benzoquinone (BQ) was used to examine the role of •O\(_2\) radical. The great influence of BQ on degradation efficiency was only 1.88% after 5 hours illumination of visible light. This is due to the ability of BQ to quench •O\(_2\) radical and inhibited the degradation of RhB dye. Figure 4(b) shows that the •O\(_2\) radical was the main species scavenger in dye photodegradation oxidation reaction with the slowest rate constant 0.007 min \(^{-1}\).
Figure 4. (a) The degradation efficiency with (b) rate constant of RhB by ZnO NDs and scavenger agents under visible light.

![Figure 4](image)

Figure 5. Photocatalyst mechanism of ZnO NDs in degradation of RhB under visible light

Base on the understanding of ROS in photocatalytic process, the mechanism is illustrated in Figure 5. In this strategy, the ZnO NDs were not able to absorb light directly [29, 30, 37]. Instead, the dye molecules acted as a sensitizer by absorbing the visible light and achieved excited state (Eq. 3). This excited dye (Dye*) injected an electron to the conduction band of ZnO NDs in Eq. 4-5. These injected electron on the conduction band can reduce the molecular oxygen to yield the oxidizing species such as H$_2$O$_2$, 'O$_2^-$' and 'OH radicals (Eq. 6 - 8). These active radicals degrade the RhB dye via N-deethylation process into N,N-diethyl-N'-ethylrhodamine, N,N-diethylrhodamine, N-ethyl-N'-ethylrhodamine, N-ethylrhodamine [27]

\[
\begin{align*}
\text{Dye} + h\nu \text{ (visible)} &\rightarrow \text{Dye*} \\
\text{Dye*} &\rightarrow \text{Dye}^+ + e^- \\
\text{ZnO} + e^- &\rightarrow \text{ZnO}^- \\
\text{'ZnO}^- + \text{O}_2 &\rightarrow \text{ZnO} + \cdot\text{O}_2^- \\
\cdot\text{O}_2^- + \text{H}_2\text{O} + e^- &\rightarrow 2\text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + e^- &\rightarrow \cdot\text{OH} + \text{OH}^- 
\end{align*}
\]

4. Conclusion

In summary, ZnO NDs were able to degrade RhB dyes under visible light irradiation. It achieved 39% photodegradation efficiency after 5 hours of light exposure. The result also showed that photodegradation of RhB dye followed the first-order kinetic. Based on the scavengers study, the 'O$_2^-$' free radicals were known as the major agent of the discolorations of RhB via utilizing of ZnO NDs. The degradation mechanism of photo-oxidation reaction of RhB dye by ZnO NDs was proposed attributed to the free radicals produced from photoelectrons originated from optically excited RhB dye.
molecule itself. The scavenger test is an excellent probe to investigate the mechanism of the photocatalytic degradation of organic pollutants, and provides much help on the design of novel visible-active photocatalyst.

Acknowledgements

The authors would like to thank Ministry of Higher Education, Malaysia for providing the research funding to conduct this project.

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