Rhodamine B Photocatalytic Degradation using CuO Particles under UV Light Irradiation for Applications in Industrial and Medical Fields

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Abstract: In this paper, the kinetics of photoinduced degradation of rhodamine B (RhB) in aqueous solution utilizing synthesized copper oxide (CuO) particles as catalyst has been studied by measuring the absorbance of the dyes at various time intervals. The CuO particles were fabricated using sol-gel method, and calcined at different temperatures in the range from 450 to 750 °C. The crystallinity of the CuO particles was confirmed using powder X-ray diffraction. The highest RhB degradation efficiency was only 10.9% by the CuO550 upon UV irradiation in 30 min, proving that CuO particles, regardless of their calcination temperature, showed poor photodegradation activity.

Keywords: activation energy, copper oxide particles, photocatalysis, rhodamine B, sol-gel

1. Introduction

Toxic substances, such as synthetic dyes of effluents from textile industries, are often discharged directly to sewage systems, causing contaminations to lakes and rivers. There are a large number commercially available synthetic dyes which were produced in a massive scale. During the dyeing process some amounts of applied synthetic dyes are lost and include in the wastewater as they are well soluble in water1). The dyes absorb most of the sunlight in the UV and visible region, thus they make the water system light impenetrable and high resistivity to aerobic digestion. Moreover, the synthetic dyes, even at trace concentrations, can cause severe risks to living organisms in the aquatic life and the water resources. Finally, it can be dangerous to the entire ecosystem. Therefore, it is important to find a more suitable and efficient wastewater treatment technologies 2-4).

Conventional methods for eliminating dyes such as using liquid membrane 5), ozonation 6), and adsorption 7-10) are expensive and not very effective 11). A promising approach to decompose organic dyes with superior activity is the heterogeneous photocatalysis 12,13) which can be a clean, low-cost, and environmentally friendly remediation method 14,15). Photocatalysis is already a well-known method to degrade environmental pollutants, particularly synthetic dyes 16), because reduction potentials of organic dyes are much lower than the energy of electron of catalyst in the excited state. For example, highly crystallized tungsten trioxide (WO3) loaded TiO2 composite (TiO2/WO3) for efficient photodegradation of methylene blue under visible light irradiation has been reported 17). The ratio of Pt particles on the TiO2/Pt catalyst was determined using transmission electron microscopy (TEM) and X-ray diffraction (XRD). It is similar method that reported by Taira and Einaga 18).

Copper oxide (CuO) has a relatively narrow band gap (1.7 eV) 19) in near infrared, but it can be utilized as a catalyst because it is a p-type semiconductor oxide, cheap, non-toxic, and stable photochemically 20). CuO has been utilized for many applications, such as in electrochemical cells, light emitters, gas sensors, photovoltaic cells, and photoconductive and photothermal materials 20-23). The physical, optical, and chemical properties of CuO nanomaterials depend strongly on their particle size, electronic structure, and surface morphology 19).

CuO particles in nanometer scales show exceptional electronic and optical properties suitable for the
applications. Interestingly, the CuO is metallic in bulk; however, they behave like semiconductors when they appear in nanosized scales 24).

Rhodamine B (RhB) is one of synthetic dyes widely utilized to dye silk, leathers, nylon, cotton, wood, and paper, and due to its fluorescence, it is also used in biotechnology 5). Thus, RhB is one of representative model of the textile dyes 8,9). RhB is an amphoteric dye, but usually considered as basic due to having overall positive charge. It also belongs to the family of Xanthenes dye 25).

In this study, CuO particles was synthesized using sol-gel method and used as catalyst to degrade RhB dye under UV light excitation. The photocatalytic degradation of RhB was investigated across different experimental parameters, such as the catalyst dosage, the initial concentration of RhB dye, and medium temperature to observe their effects on the photocatalytic activity of CuO particles which were prepared at the different temperatures. This study can be further investigated for applications in industrial and medical fields that are environmentally friendly and efficient.

2. Experimental

2.1 Materials

Copper(II) chloride dehydrate with purity ≥99.0% was purchased from VWR Chemicals, BDH. Sodium hydroxide and acetic acid were obtained from Merck (Germany). Double distilled water was used to prepare all aqueous solutions throughout this study. All chemicals used in this study were of analytical grade and without any purification.

2.2 Preparation of CuO particles

The CuO particles were prepared using sol-gel method following the procedures previously reported by Kshirsagar and coworkers 24). Here, 0.2 M CuCl2·2H2O in water was mixed with 1 mL of glacial acetic acid and the mixture was heated to 100 °C with constant stirring. 8 M of NaOH was then added dropwise to the heated solution until the mixture was neutralized (pH reached 7). The mixture turned from green to black. The black precipitate was separated by centrifugation and it was washed with mixture turned from green to black. The black precipitate but usually considered as basic due to having overall positive charge. It also belongs to the family of Xanthenes dye 25).

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2.4 XRD Characterization

The crystallinity of CuO particle was analyzed using XRD (Shimadzu XRD-7000) with Cu Kα reflection mode.

2.5 Particle Size Analyzer

The size distribution of the prepared CuO particles was determined by dynamic light scattering (DLS) using a digital correlator DLS (BI 9000, Brookhaven Instruments Corp) equipped with a diode-pumped laser (532 nm; 10 mW).

3. Results and Discussion

3.1 XRD Characterization of CuO Particles

Figure 1 shows the XRD pattern of CuO particles calcined at different temperatures along with that of commercially available CuO particles for comparison. It can be seen that CuO particles exist in a single crystalline phase with a monoclinic structure, even though the CuO particles were synthesized and calcined at different temperatures from 450 to 750 °C. The set of their 2θ peaks at 35.4, 38.9, 48.7, 53.3, 58.6, 61.4, 66.2, and 67.9° was indexed as (-111), (111), (-202), (020), (202), (-113), (-311), and (220) of CuO 22). The XRD pattern was similar observed for the commercial CuO particles. This results suggested that the prepared CuO particles have the same crystalline phase with the commercial one. Therefore, one can anticipate that all the CuO particles in this study have almost similar photocatalytic activity.

The crystallite sizes of the CuO particles (L) were estimated based on XRD spectrum using Scherrer formula 26):

\[ L = \frac{K\lambda}{\beta \cos \theta} \]  

where \( \lambda \) (0.15418 nm) is the wavelength X-ray beam in
nanometer, $\beta$ is the peak width of the diffraction peak profile at half maximum height (in radians), $K$ is the Scherrer constant (which is normally taken to be 0.9), and $\theta$ is the Bragg diffraction angle. The crystallite size of CuO particles was analyzed to be within 23 to 29 nm for all samples. This value is not necessarily the same as the particle sizes, where the latter were estimated using DLS ranged from 145 to 200 nm.

3.2 Photocatalytic Degradation of RhB

The photodegradation rate of RhB was obtained by fitting the absorbance of the RhB solution as a function of irradiation time. The photodegradation of RhB dye was considered to follow the first order reaction, as represented by Langmuir-Hinshelwood model. This is consistent with the photocatalytic reaction, as usually observed for other organic compounds. The absorption spectra of RhB dye after UV light irradiation up to 30 min in the presence of CuO550 particles as catalyst (see Fig. 2).

The photodegradation rate increased with increasing initial RhB concentration up to 7.5 ppm (see Fig. 3). This can be rationalized by considering that there are more RhB molecules absorbed on the surface of CuO particles and the RhB undergo photodegradation. At higher RhB dye concentrations, the degradation rate becomes slower. This can be explained on the basis that excessive amount of RhB dye being absorbed and immobilized on the surface of the CuO particles results in inefficient oxidation of the synthetic dye with the generated free hydroxyl radicals.

The photodegradation rate of RhB dye is enhanced with CuO particles catalyst dosage (see Fig. 4). The degradation rate is faster at higher dosage of CuO particles because the high dosage of catalyst has a higher probability to absorb the irradiated photons to excite electrons to the conduction band. This leads to the higher concentration of generated hydroxyl radicals responsible to reduce the organic compounds 27). Hence, the results suggested that CuO particles might have a good photocatalytic performance. The commercial CuO particles shows a better photo-degradation rate of RhB compared to the CuO particles synthesized in this study. This highlights the efficient photocatalytic ability as well as inhibition of electron-hole recombination of the CuO particles. It is also important to mention that, in the presence of higher density of particles, the colloidal mixture become more turbid and absorbe the UV light. The larger number of particles in the mixture obviously requires a larger number of irradiated photons, namely higher light power or loner irradiation time. Therefore, under the constant UV light power, large quantities of particles will result in the saturation of photonic efficiency 28). However, this trend was not observed under our experimental conditions, the photodegradation rate of RhB dye should increase, reach a maximum, and decrease with increasing catalyst dosage of CuO particles.

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**Fig. 1.** XRD patterns of CuO particles calcined at different temperatures for 1 hour.

**Fig. 2.** Time evolution of absorption spectrum of 10 ppm RhB using CuO550 as catalyst upon UV light irradiation

**Fig. 3.** Plot of $k$ as a function of [RhB]$_0$ at the same amount of catalyst, i.e. 5 mg of CuO$^{450}$ (■), CuO$^{550}$ (●), CuO$^{650}$ (▲), CuO$^{750}$ (▼) and CuO$^{550}$ (♦) particles. The lines in the graph are only for guidance.

**Fig. 4.** Absorbance [OD] of RhB as a function of wavelength [nm] for different CuO$^{550}$ particle dosage and irradiation time.
3.3 Effect of Temperature on RhB Photodegradation

The effect of medium temperature on photodegradation rate of RhB dye after 30 min irradiation in the presence of CuO particles was investigated at temperature from 25 to 50°C with a constant catalyst CuO mass of 5.0 mg using 10 ppm RhB dye in 10 mL. Our findings suggested that the photocatalytic degradation rate of RhB dye increases with increasing temperature (see Fig. 5).

The experimental data measured at different temperatures were fitted with Arrhenius equation, \( k = A e^{-E_a/RT} \), where \( A \) is the pre-exponential factor attributed to the frequency of successful oxidation reaction of RhB dye, \( E_a \) is the activation energy, \( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), and \( T \) is the absolute temperature. Figure 5 shows the Arrhenius plot, \( k \) against inverse temperature (1/T) of the degradation of RhB dye on the CuO particles under the UV light irradiation. The solid lines shown in Figure 5 are the best fit, from which \( E_a \) of the oxidation reaction of RhB on the different CuO particles was deduced, and the results are summarized in Table 1. It is noteworthy to recall that the photonic activation, namely the generation of electron in the excited state upon photoexcitation, is the core process of photocatalytic oxidation and reduction. Thus, one can neglect the effect of heating. The \( E_a \) should be associated to the potential barrier of the photocatalytic degradation which is a diffusion-controlled reaction. In this sense, one could consider that the activated state should be a well solvated structure formed between the RhB dyes and generated hydroxyl radicals. Thus, the \( E_a \) of the photocatalytic degradation should depend on the diffusion of hydroxyl radicals. The photocatalytic degradation of RhB is controlled by the diffusion and its reaction with hydroxyl radicals on the CuO catalyst surface. It is explained that photodegradation of RhB dye can be optimized when the CuO particles in the colloidal solution were well covered by RhB dye and the hydroxyl radicals were effectively generated on the surface of CuO particles.

Table 1. Deduced activation energy, \( E_a \) for CuO particles on removal of RhB dye

| Sample   | \( E_a \) (kJmol\(^{-1}\)) |
|----------|--------------------------|
| CuO\(^{c}\) | 73.2                     |
| CuO\(^{450}\) | 49.7                     |
| CuO\(^{650}\) | 54.4                     |
| CuO\(^{750}\) | 68.8                     |

4. Conclusion

In summary, the CuO particles have been synthesized at different calcination temperatures using sol-gel method and used as catalysts for photocatalytic degradation of RhB dye in aqueous solutions under UV light irradiation. This system can be considered as a suitable model for wastewater remediation treatment. The highest RhB degradation percentage achieved was only 10.9 % by the CuO\(^{350}\) after UV irradiation for 30 minutes, proving that CuO particles showed poor photocatalytic activity. The interaction between dyes and CuO particles is important in the photoinduced oxidation and reduction. The activation energy of the photodegradation of RhB dye is related to the diffusion-controlled reaction of free hydroxyl radicals. Further research, a higher catalyst dosage and their composite can be developed for applications in industrial and medical fields that are environmentally friendly and efficient.
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