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Solar-light-harvesting degradation of aqueous ammonia by CuO/ZnO immobilized on pottery plate: Linear kinetic modeling for adsorption and photocatalysis process

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ABSTRACT

The present study involves the photocatalytic degradation of ammonia by CuO/ZnO photocatalyst. The CuO/ZnO photocatalyst was prepared by an economical and easy method and immobilized over rough surface of pottery plate. The photocatalytic activity of this photocatalyst was investigated under solar irradiation. Also, the morphology and microstructure properties of the prepared photocatalyts have been characterized by FESEM, FT-IR, UV–vis and PL analyses. The characterization results revealed that the CuO particles sufficiently loaded over ZnO. It also was found that an appropriate amount of CuO loading (5 wt. %) could greatly increase the photocatalytic activity. According to the optimum conditions, 77.2% ammonia removal from synthetic wastewater was achieved within 240 min solar irradiation time. Additionally, the photocatalytic activity of the CuO-ZnO/pottery plate decreased with increasing initial ammonia concentration from 85 to 510 mg/L. Linear model was applied to explain relation between adsorption and photocatalytic process in ammonia removal. This model was able to predict adsorption and photocatalytic data with non-significant differences with experimental results.

1. Introduction

Nowadays, water pollution is becoming a worldwide issue for the researches and the global environmental safety community [1]. Effluent streams, especially those from industries, are so hazardous and toxic that traditional treatment methods are not effective enough to remove them [2–4]. Recent studies have shown that photocatalysis has great potential in wastewater purification [5,6]. Ammonia is an essential feed stock for a wide range of downstream nitrogen based products such as urea. When ammonia is released into air and water, it causes some environmental problems. The harm caused by ammonia in water is very serious, and at high concentrations it has undesirable effects on plants, animals and human life [7].

Various semiconductors have been utilized for the photocatalytic removal of pollutants [8–10], among which, titanium dioxide (TiO_2) and zinc oxide (ZnO) with the same band gap (3.2 eV) are most widely used as photocatalyst [11,12]. They have a high resistance to photo-corrosion, good stability in aqueous media, and low cost as well as environment-friendly features [13]. The application of ZnO has some limitations such as absorption of small amounts of photons in the visible region, high recombination rate of photogenerated electron–hole pairs, and difficulty in supporting powdered ZnO on some materials [14–16]. Activation of ZnO under visible light can facilitate the development of promising processes for the purification of wastewater. So, to harvest maximum energy of the sunlight, excitation of ZnO by both UV and visible light is essential. Doping ZnO by metals [17] and metal oxides [18] broadens the absorption spectrum of this semiconductor toward visible light region, as new energy levels are formed between its valence and conduction bands [15,19,20]. CuO is a metal oxide and p-type semiconductor which enhances the visible light absorption of ZnO and also acts as a co-catalyst for wastewater purification [21].

Recently, some researchers have focused on the photocatalytic potential of CuO/ZnO composite. For instance, Ghosh and co-workers have reported on driven p-CuO/n-ZnO composite as visible-light, stable, efficient and recyclable photocatalysts for degradation of organic dyes [22]. Also, Shirzadi and Nezamzadeh have investigated the photodegradation of Mefenamic acid in aqueous solution by CuO/ZnO photocatalyst [23].

Many researchers have researched the photocatalytic degradation of ammonia in aqueous solution under UV light [24,25]. Since photocatalysts are often applied in the form of suspension or slurry

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that are practically difficult due to problems of separation and recycling the photocatalyst particles [26], it is better for photocatalyst particles to be immobilized on a certain support. ZnO can be immobilized onto a solid support such as sand, clays, polymer films and glass [27–29]. Therefore, thin film reactor is suitable for the degradation of ammonia from industry's wastewater under solar radiation [30]. In Middle East countries like Iran, the highest level of global solar radiation is received about nine months of the year. On the other hand, the nominal capacity of ammonia industry in Iran is about 11,400 tons per day (3 million and 430 thousand tons per year) which produces the large amount of ammonia wastewater [31].

Based on the above facts, we reported that the p-type CuO could be coupled with n-type ZnO to enhance the photocatalytic activity for the ammonia degradation under solar light irradiation. CuO/ZnO photocatalyst was coated over pottery plate and the photodegradation rate was examined in a thin film photoreactor. The factors contributing to the high activity of the catalyst are discussed in the following context.

2. Materials and methods

2.1. Materials

The Pottery plates used as support were purchased from traditional workhouse in Hamadan province. These plates were made from clay and shaped in 15*15 cm^2 and thickness 1 cm. Copper nitrate trihydrate (98%) and absolute ethanol (99.5%) were provided from Sigma Aldrich and used without further purification. ZnO powder was obtained from Merck Co. All solutions were prepared using distilled water produced in our laboratory.

2.2. CuO/ZnO photocatalyst preparation

CuO/ZnO photocatalysts with nominal CuO loadings of 0–10 wt.% were prepared by the simple method. Briefly, copper nitrate trihydrate was added to distillate water (20 mL). ZnO was added to the ethanol solution and stirred for 30 min. For achievement to a uniform slurry, the ZnO solution was sonicated for 15 min. In the following, the aqueous copper nitrate was added to the ZnO slurry and resulting suspension was stirred for a further 15 min. The photocatalyst solution was dispersed on the pottery supports and dried overnight at 70 °C in air. CuO/ZnO photocatalyst was obtained by calcination of the $Cu(OH)_2$/ZnO at 450 °C for 2 h.

It should be noted that to estimate how much oxides were loaded over the pottery plate, the prepared suspension containing 2 g of catalyst powder was dispersed over a pottery plat. In the following, the drying plate was weighed and subtracted from initial value of plate. The difference between these values was the weight of photocatalyst which immobilized on the pottery plate. In this method of catalyst preparation, about 1.85–1.96 g photocatalyst particles with a layer of 15.75 μm thickness was formed on each plate. Also, according to the high mechanical stability of CuO–ZnO/pottery plate, the catalyst loss weight after purification process was neglected. Fig. 1 presents the photograph of the pottery plate and its coated by ZnO and 5 wt.% CuO/ZnO.

2.3. Characterization, equipment and operating condition

Field emission scanning electron microscopy (FE-SEM) images were obtained with a MIRA3 Tescan electron microscope operated at 20 kV, with Au/Pd alloy coated samples. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Avatar-370 spectrometer at room temperature. The UV–vis diffuse reflectance spectra (DRS) were obtained on a Perkin Elmer Lambda 900 UV–vis spectrophotometer by using BaSO4 as the matrix. The photoluminescence (PL) spectra were obtained on a Hitachi F7000 fluorescence spectrophotometer at an excitation wavelength of 300 nm. In addition, an EcoTech Marine vectra aquarium DC water pump with flow rate 200 gph and maximum head 6.5 m used for circulation of ammonia wastewater. Also, a 36 mm planetary geared DC motor with voltage 6–36 V and speed 3.5–1500 rpm was used for mixing solution.

In this work, the operating parameters involved pH, CuO content and ammonia concentration that affected catalyst efficiency were investigated by ranges of pH (3–12), CuO (0–10 wt.%), and initial ammonia concentration (85–510 mg/L).

2.4. Photoreactor tests

The schematic diagram of the thin film photoreactor made for ammonia degradation is shown in Fig. 2. Eight pottery plates with a width of 15 cm and a length of 15 cm were used for immobilizing the photocatalyst. The plate's arrangement was in four rows and two columns on a glass frame. The setup was posited in 45° from ground surface. The initial solution was collected in a plastic tank with 20 L volume. Mechanical stirrer with 60 rpm was used for stirring the ammonia solution. For creating uniform falling film of ammonia solution over catalyst surface, we used a series of valve distributors. The ammonia solution was being transformed by a water pump with flow rate of 2 L/min to the top of photoreactor.

All the experiments, under solar light irradiation were carried out in the campus of Razi University, Kermanshah, Iran (latitude 34823.3050 N, longitude 4786.6950 E) in June 2015, between 11

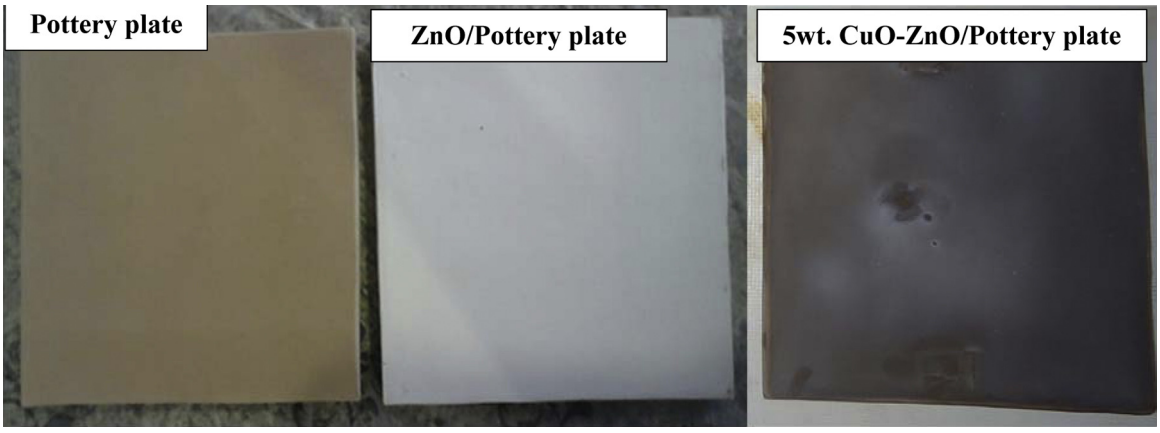

Fig 1. Digital photograph of the pottery plate, ZnO and 5 wt.% CuO/ZnO photocatalysts coated over support.