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Denitrification of water using ZnO/Cu as the photocatalyst

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Abstract: The ZnO:xCu photocatalyst was prepared with reacting media, namely, water method followed by wet impregnation to deposit Cu on the ZnO nano particles. X-ray diffraction was used to perform crystallography and the determination of the ZnO:xCu particle size. Fourier transform infrared was employed for the detection of chemical bonds in the synthesized photocatalyst. The nanoparticle morphology was studied by field emission scanning electron microscope. The elemental composition of the synthesized catalysts was evaluated with X-ray fluorescence technique. Diffuse reflection spectroscopy analysis was performed to investigate the light absorption of the ZnO:xCu catalysts. The photocatalytic activity of the prepared ZnO:xCu nanoparticles was studied for the removal of nitrate from the aqueous solution of ammonium nitrate (50 $mg \cdot l^{-1}$) under UV irradiation. Results indicated that the ZnO:xCu photocatalyst has high photocalytic activity to remove nitrate from water. Moreover, complete degradation was achieved after 2.5 h.

Keywords: nitrate removal; photocatalytic activity; ZnO/Cu.

1 Introduction

Groundwater environment is an important drinking water source in the world, yet it is highly unprotected against contamination [1]. Agricultural activities and urban development are a common source of nitrate contamination and these can become harmful to human health [2, 3]. When groundwater is used as drinking water, the presence of high-level nitrates at this source of water can cause such diseases as cancer, especially stomach cancer [1, 4, 5]. According to the World Health Organization (WHO), the recommended nitrate limit in drinking water is 50 mg/l [6]. Hence, there are various methods for reducing nitrate from drinking water, such as filtration, ion exchange, and biological and photocatalytic processes [7–10]. The photocatalytic process, an economic and simple method compared with other methods, has been the subject of many research projects. Various metal oxide semiconductors, such as TiO_2, ZnO, MoO_3, CeO_2, ZrO_2, WO_3, α-Fe_2O_3 and SnO_2, are used as catalysts in the photocatalytic reactions [11–14]. Mechanical stability, non-toxicity, and high photoactivity of ZnO are the main advantages of this material as a photocatalyst [15–17]. Past studies have prepared ZnO using several techniques, such as chemical vapor deposition (CVD) [18], physical vapor deposition (PVD) [19], and magnetron sputtering [20]. However, these techniques are complex and controlling the operating conditions is very difficult [21–24]. ZnO suffers from photochemical corrosion and high recombination rate of photo-generated electron/hole [25]. Cu is a denitrification catalyst, but it draws its activation energy from a photocatalyst and, in fact, Cu is incorporated in oxidation reduction during the process. In the present study, nanocrystalline ZnO:xCu was prepared via reaction in a water medium method followed by wet impregnation for Cu deposition. Past studies used photocatalysts to remove nitrate from water. For example, Li et al. [2] used the Pt-Cu/TiO_2 photocatalyst for nitrate removal from an aqueous solution and found that the higher content of Cu compared with Pt leads to higher nitrate removal rate. Luiz et al. [1] studied a metal-modified TiO_2 photocatalyst to remove nitrate from water and found that 4.4% Zn-TiO_2 has more photocatalytic activity for nitrate reduction. Mori et al. [10] employed $K_xGa_xSn_{8-x}O_{16}$ for aqueous nitrate removal and found that KGaSO has good results in nitrate reduction. In the present work, the nano powders of ZnO:xCu were prepared and characterized, and their photocatalytic activities were measured by the degradation of nitrate in the aqueous solution. The effect of Cu loading on ZnO nanoparticles was also investigated.

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2 Materials and methods

2.1 ZnO:Cu nanoparticle preparation

All chemicals were analytical reagent grade and used directly without any further purification. Double-distilled water was used throughout this study. The ZnO and Cu precursors used were zinc chloride ($ZnCl_2$, Merck, Germany) and copper (II) nitrate [$Cu(NO_3)_2$, Merck, Germany]. Sodium hydroxide (Samchun, South Korea) was used for the precipitation of ZnO from the aqueous solution.

Nanostructure ZnO was prepared by the following method. Five grams of $ZnCl_2$ was dissolved in 100 ml distilled water at 70°C. Meanwhile, 20 g of sodium hydroxide was dissolved in 100 ml distilled water in a separate vessel. Then, 16 ml of the prepared sodium hydroxide solution was added to the $ZnCl_2$ solution. The aqueous solution turned into a milky white colloid without any precipitation. The reaction was then allowed to complete for 2 h. Next, the solution was removed by washing with distilled water for five times, after which and zinc oxide was dried at 100°C for 30 min followed by calcination at 500°C, before it finally changed into powder form [26].

ZnO:xCu was prepared by employing the wet impregnation method. In order to prepare the ZnO:xCu, ZnO nano powder was contacted with a solution of copper(II) nitrate with different concentrations (15, 25, 35 weight percent). The prepared catalysts were labeled as ZnO:15%Cu, ZnO:25%Cu and ZnO:35%Cu. The real Cu loading was measured using XRF technique and is reported in Table 1.

2.2 Nano powder characterization

The grain size and crystallinity of the ZnO photocatalysts were studied by X-ray diffraction (XRD, Bruker AXS, D8-Advance, Germany) using Cu Kα ($\lambda = 1.5406$ Å) radiation in the region of $2\theta = 20°–75°$. In addition, the grain or crystalline size (L) was estimated using Scherrer's formula [27] given by

$$L = \frac{k\lambda}{\beta\cos\theta}, \tag{1}$$

where L is the crystallite size of pure ZnO, k is a constant (=0.94), λ is the wavelength of the X-ray (Cu Kα = 1.54065 Å), β is the true half-peak width, and θ is the half diffraction angle of the centroid of the peak in degree.

The surface morphology of the nano powders was studied using a field emission scanning electron microscope (FESEM) (Hitachi, Japan). The Fourier transform infrared (FT-IR) (Avantes, Avaspec-2048-TEC, Netherland) spectra of the samples were recorded in the range 4000–400 cm^{-1} on an FT-IR spectrometer; these are then used for the detection of bonds between the photocatalyst and active phase (Cu). Furthermore, for the elemental analysis and composition of ZnO:xCu catalysts, the X-ray fluorescence (XRF, Bruker AXS, D8-Advance, Germany) technique was employed. In addition, the light absorption of catalysts was evaluated with diffusive reflectance spectroscopy (DRS) analysis.

Table 1: Summarized properties of the synthesized ZnO:xCu photocatalysts (impurities are not given).

Photocatalyst	Band gap energy (eV)	Composition (wt%)	
		ZnO	Cu
ZnO:15%Cu	3.3	95.6	3.4
ZnO:25%Cu	3.8	91.3	6.8
ZnO:35%Cu	4.1	87.1	10.2

2.3 Measurement of photocatalytic activity

Ammonium nitrate powder (NH_4NO_3) was dissolved in distilled water at 50 $mg \cdot l^{-1}$ concentration. The ZnO:xCu photocatalyst was added into 5 ml ammonium nitrate solution and a high pressure mercury lamp (125 W) was used as the light source. The averaged intensity of UV irradiance was 6.8 $mW \cdot cm^{-2}$ by measuring with a UV irradiance meter (Camspec, USA). The solution was bubbled with air during irradiation. The UV-Visible spectrophotometer technique was used to measure the concentration of nitrate. The solution was sampled every 30 min and analyzed with this technique at 410 nm wavelength. To interpret the results, a simplified empirical pseudo first-order reaction rate was assumed for the photocatalytic degradation of nitrate [28, 29]

$$\ln\left(\frac{C_0}{C}\right) = kt, \tag{2}$$

where k is the apparent constant of the reaction rate, and C_0 and C are the initial and final concentrations of nitrate in the solution, respectively.

3 Results and discussion

3.1 Characterization of the nano powder

Figure 1 shows the XRD patterns of the ZnO:xCu nano powders. As can be seen, the main peaks are in $2\theta = 32°$,

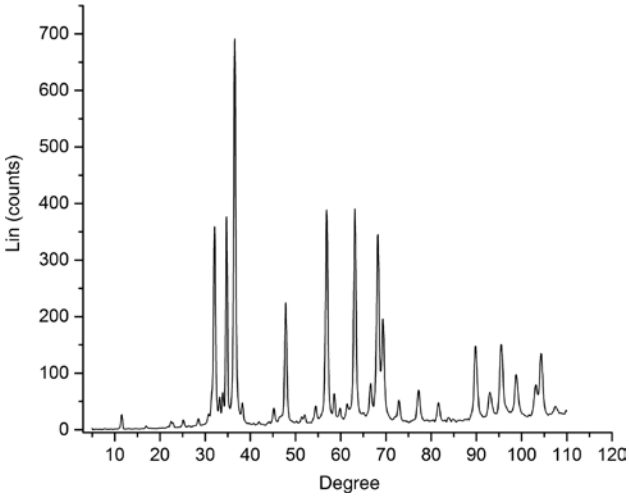

Figure 1: XRD pattern of the ZnO nano powder.

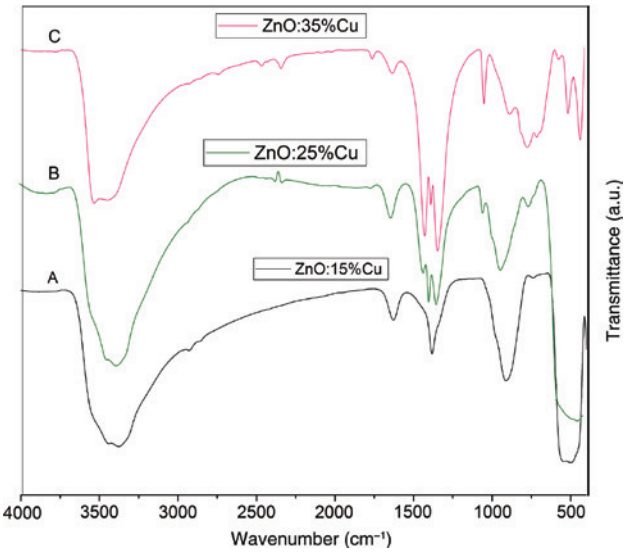

Figure 2: FT-IR spectra for (A) ZnO:15%Cu, (B) ZnO:25%Cu and (C) ZnO:35%Cu.

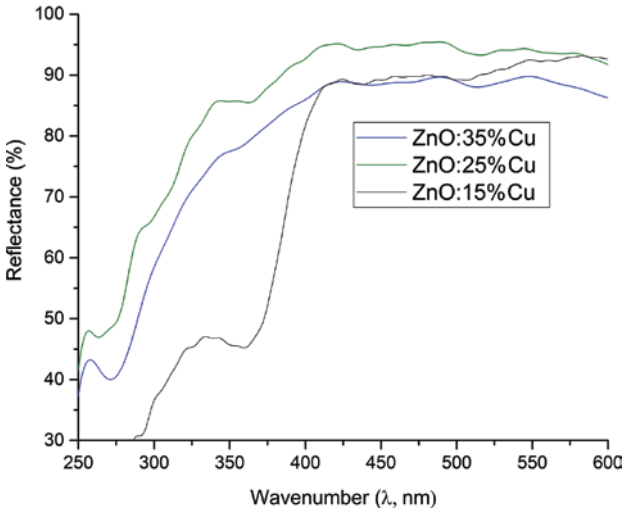

Figure 3: DRS results for the synthesized ZnO:xCu photocatalysts.

34°, 38°, 47°, 56°, 66° and 69°, thus indicating the presence of ZnO crystals. The crystallite size of ZnO:xCu with different weight percent of Cu can be measured according to Figure 1, and Scherrer equation. So, average crystallite size of ZnO:xCu is 45 nm.

The FT-IR spectra of ZnO:15%Cu, ZnO:25%Cu and ZnO:35%Cu are shown in Figure 2. Peaks around 3383–1330 cm^{-1} are assigned to normal polymeric O–H of H_2O in Cu–Zn–O lattice which may belong to moisture included in the atmosphere [30]. The medium to weak bands at 1500–707 cm^{-1} are attributed to the microstructural features that change with the addition of Cu into the Zn–O lattice. Furthermore, stretching bonds at 542, 498, 434, 506 and 427 belongs to the ZnO compound [30].

As mentioned above, the DRS technique was used to evaluate the light absorption and the band gap of the synthesized photocatalysts. The calculation of band gap according to the DRS method can be performed using the Planck equation given by [31]

$$E_g(eV) = \frac{hc}{\lambda}, \quad (3)$$

where h, c and λ are the Planck constant, speed of light and the wave length, respectively. DRS results for ZnO:xCu are shown in Figure 3. As it can be seen, ZnO:15%Cu has the lowest band gap energy (3.3 eV) and ZnO:35%Cu has the highest band gap energy with 4.1 eV energy.

XRF analysis was used to measure the elemental composition of ZnO:xCu photocatalysts. According to the XRF results shown in Table 1, ZnO:15%Cu has 95.6% ZnO and 3.4% (weight percent) Cu, ZnO:25%Cu contains 91.3% ZnO and 6.8% Cu, and ZnO:35%Cu composition is 87.1% ZnO and 10.2% Cu.

3.2 Morphology of the ZnO:xCu photocatalysts

FESEM micrographs were used for observing the morphology of ZnO:xCu photocatalysts. Figure 4 shows the FESEM images of ZnO:xCu nano powders. According to the FESEM micrographs, the particle size of the ZnO photocatalyst is 47 nm, which is in good agreement with the XRD results. The FESEM images indicate that the Cu-incorporated/ZnO nanoparticles exist in a single homogeneous form with narrow size distribution.

3.3 Determination of the photocatalytic activity of ZnO:xCu nano powders

The degradation of 5 ml of nitrate solution (50 mg/l) that came into contact with different synthesized photocatalysts under UV irradiation was studied, in order to investigate the photocatalytic activity of ZnO:xCu photocatalysts. Figure 5 shows changes in the concentration of nitrate solution with time upon coming into contact with the ZnO:15%Cu, ZnO:25%Cu and ZnO:35%Cu photocatalysts. Results of the determination of photocatalytic activity indicate that ZnO:25%Cu has the highest and ZnO:15%Cu has the lowest photocatalytic activity. The lower photocatalytic activity of ZnO:15%Cu is due to the low concentration of Cu. In fact, Cu has a key role in the degradation of nitrate in the solution, such that

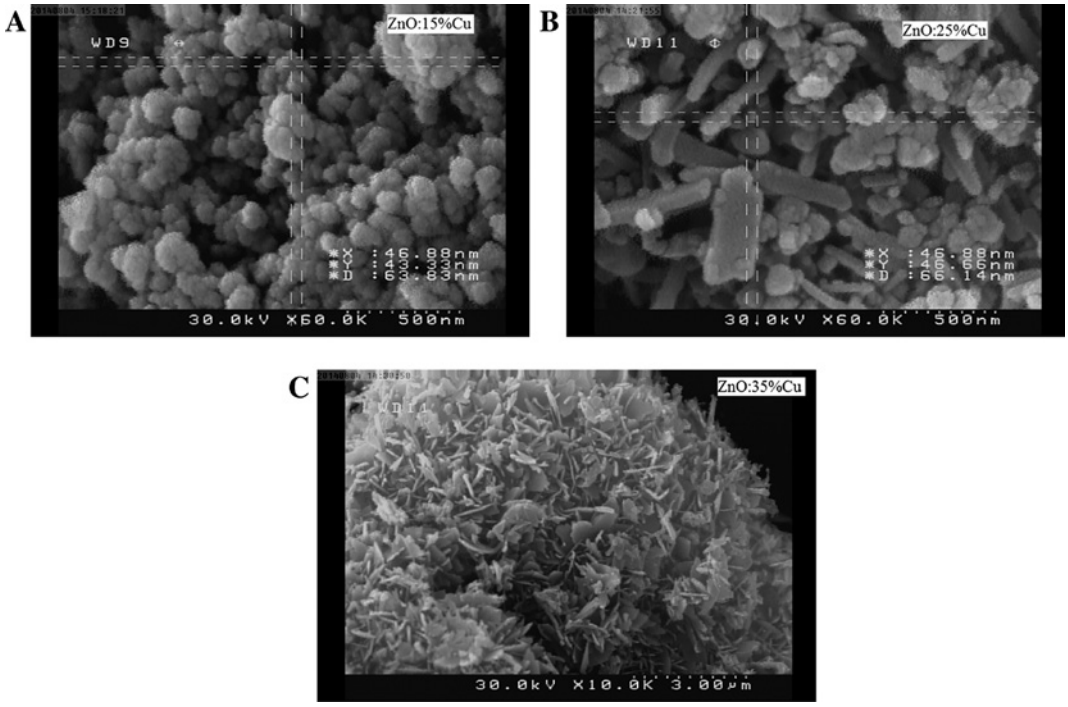

Figure 4: FESEM images of (A) ZnO:15%Cu, (B) ZnO:25%Cu and (C) ZnO:35%Cu.

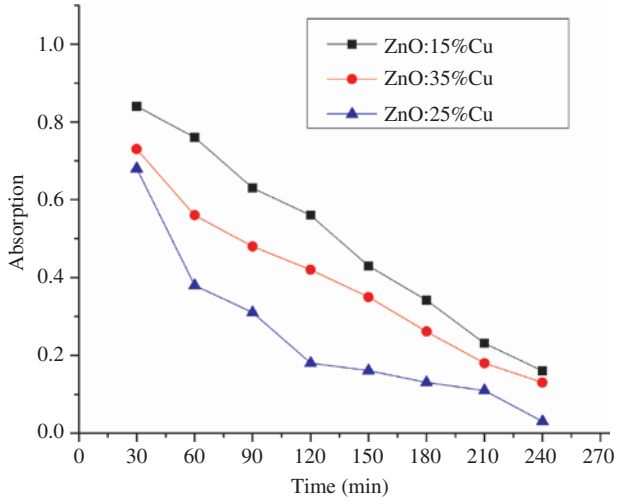

Figure 5: Concentration of nitrate in the aqueous solution based on UV-Visible light.

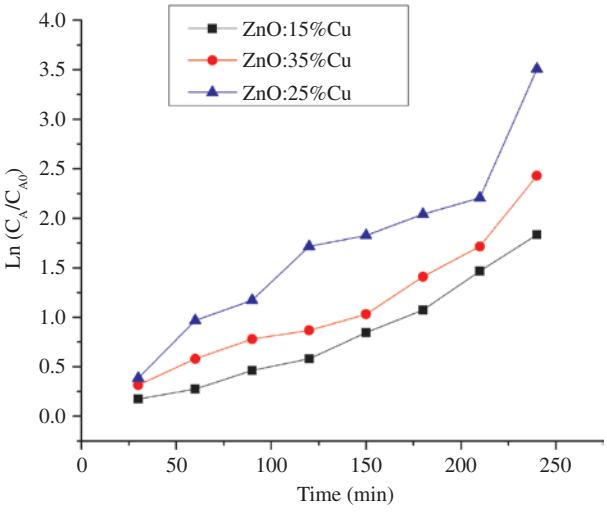

Figure 6: Changes in concentration of nitrate for the ZnO:xCu photocatalysts.

when Cu concentration is high, photocatalytic activity becomes lower due to the decrease in the active sites for activation. The apparent constant rate of reaction k (min^{-1}) is calculated according to Figure 6 and Equation (2). The results are compared with those from a similar work [32] in Table 2. The lowest degradation rate is for ZnO:15%Cu with $k = 7.8 \times 10^{-2}$ and the highest degradation rate is for ZnO:25%Cu with $k = 1.22 \times 10^{-1}$. A higher value for k in the referenced work (TiO_2 doped with Zn) is due to the addition of formic acid as the electron donor, which helped to improve photocatalytic efficiency [32]. A possible mechanism for photocatalytic degradation of nitrate is shown below [2]:

$$ZnO{:}Cu \rightarrow ZnO{:}Cu\,(e^- + h^+)$$

$$H_2O_{ads} + h^+ \rightarrow {}^{\cdot}OH + H^+$$

$$Cu + NO_3^- \rightarrow NO_2^- + Cu^{\delta+}$$

$$NO_2^- + 2H^+ \rightarrow NH_3 + H_2O$$

Table 2: Apparent rate constants (k) for the pseudo first-order reactions of different photocatalysts.

Sample type	k	References	Temperature (°C)
ZnO:TiO_2	0.266 mg N (mg C min)$^{-1}$[a]	[33]	20
ZnO:15%Cu	7.8×10^{-2} (min)$^{-1}$	This work	30
ZnO:25%Cu	1.22×10^{-1} (min)$^{-1}$	This work	30
ZnO:35%Cu	8.9×10^{-2} (min)$^{-1}$	This work	30

[a]N is nitrate and C stands for formic acid.

$$Cu^{\delta+} + e^- \rightarrow Cu$$

Due to the absorption of light and electron-hole generation, the ZnO:xCu photocatalyst can activate the Cu active phase to change NO_2^- to NH_3 according to the above mechanism.

4 Conclusion

A ZnO:xCu photocatalyst was prepared with reaction medium method, namely, water medium followed by wet impregnation for the deposition of Cu on the ZnO nanoparticles. XRD and FT-IR analyses demonstrated the formation of ZnO:xCu photocatalysts. In addition, according to XRD results, there exists only a single crystalline of ZnO nanoparticle loaded by Cu element where ZnO particle size is about 45 nm. Furthermore, FESEM images reveal the formation of ZnO:xCu particles in a single homogeneous phase with an approximate size of about 47 nm. The activity of the synthesized photocatalysts were evaluated for the denitrification of potable water, and the results indicated that ZnO:25%Cu has the higher photocatalytic activity compared with other catalysts. In conclusion, Cu loading has some optimum value for the best photocatalytic efficiency. However, further research is needed to study the stability of the newly formulated photocatalyst and investigate in detail the effect of Cu on the mechanism of nitrate photodegradation.

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