CATALYSIS

# Enhancing Photocatalytic Activity of Cu<sub>2</sub>O in Degradation of Sulphonic Acid-Based Dye<sup>1</sup>

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Received November 22, 2018; revised November 23, 2018; accepted February 4, 2019

**Abstract**—In the present investigation, we synthesized copper (I) oxide nanoparticles (NPs) by the coprecipitation method. The obtained materials were characterized by X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDXA), field emission scanning electron microscopy (FESEM), Transmission Electron Microscopy (TEM), and the Brunauer–Emmett–Teller (BET)/Barrett–Joyner–Halenda (BJH) Method. Surface areas and the average particle size were evaluated to be around  $4.20 \pm 0.04 \text{ m}^2 \text{ g}^{-1}$  and 28 nm, respectively. Then, Ag/Cu<sub>2</sub>O NPs were synthesized by the same process, examined by X-ray diffraction, and the average particle size obtained was around 118 nm. The photocatalytic degradation of [1,3-Amino phenyl [4-Sulphonic acid ][2,6-Dis azo phenyl] 4,4'sulphato ethyl [6'sulpho] ester of Sulphonic acid ] (COG-423) was investigated with Cu<sub>2</sub>O and TiO<sub>2</sub> NPs, Cu<sub>2</sub>O Microparticles (Micro-Ps) and Ag/Cu<sub>2</sub>O NPs under UV-C irradiation in the presence of hydrogen peroxide as auxiliary oxidant with three parameters including dopant concentration, intensity, and time, as the obtained experimental results showed a good agreement with theoretical values and succeeded to calculate the optimal conditions. Degradation efficiency with Cu<sub>2</sub>O Micro/NPs under UV-C irradiation (32 W), for 30 min. were determined to be 20.0% and 91.4% respectively, while for the synthesized TiO<sub>2</sub> and Ag/Cu<sub>2</sub>O NPs were 99.9%. The photocatalytic activity order was of the following nature: Ag/Cu<sub>2</sub>O ~ TiO<sub>2</sub> NPs > Cu<sub>2</sub>O NPs > Cu<sub>2</sub>O Micro-Ps.

**Keywords:** Cu<sub>2</sub>O NPs, Cu<sub>2</sub>O micro-Ps, [1,3-amino phenyl[4-sulphonic acid[2,6-dis azo phenyl]4,4'sulphato ethyl[6'sulpho]ester of sulphonic acid, Ag/Cu<sub>2</sub>O NPs and photocatalytic degradation

**DOI:** 10.1134/S1070427219010208

### INTRODUCTION

Industrial development in recent years has been one of the most important factors behind an increase in pollutants affecting human life and that of other living organisms. One of the biggest sources of air pollution is wastewater from factories that do not have any proper means to dispose of their waste material, resulting in pollutants being directly released into the environment [1-5]. Therefore, the use of photocatalysts is a new method to remove toxic pollutants and chemicals from the air and sewage [6, 7].

 $Cu_2O$  is a very suitable option for photocatalytic activities [8, 9]. The above compositions of nanoparticles have optical clarity and high absorption coefficient at

wavelengths above 500 nm [10, 11]. This composition as a P-type semiconductor with a band gap 2.0–2.2 eV [12], has unique optical, electronic and catalytic properties [13, 14], with a great potential for use in solar cells [15], electrode tools [16, 17], gas sensors [18, 19], and organic pollutant degradation under UV and visible irradiation [20–22].

Various morphologies of  $Cu_2O$ , including nanospheres and nanowires, have also been synthesized [23–28]. This oxide is known as an efficient, cost-effective, and eco-friendly photocatalyst for the degradation of organic compounds [29–31].

In the photocatalytic oxidation process, free radicals are generated in the semiconductor, leading to the destruction of substances absorbed by the photocatalyst surface.

<sup>&</sup>lt;sup>1</sup> The text was submitted by the authors in English.

Among of the various semiconductors cited in the scientific literature,  $TiO_2$  is the most suitable compound for various environmental applications. This nanocomposite shows band gap absorption in the ultraviolet region only [32]. There are limitations in the  $TiO_2$  synthesis method, such as its high cost, while the synthesis of Cu<sub>2</sub>O and/Ag Cu<sub>2</sub>O NPs, owing to its simplicity, cost-effectiveness, and relatively high efficiency, is a suitable alternative to  $TiO_2$ .

Sha Tao and co-workers synthesized Ag/Cu<sub>2</sub>O NPs with core-shell structure. According to the study, an increase in the photocatalytic properties of nanoparticles was observed in the above-mentioned compound compared to pure copper oxide nanoparticles. This increase occurred in the photocatalytic properties of the larger BET surface area and separation efficiency. Experiments showed that superoxide anion radicals and holes had a vital role in the photocatalytic degradation of methyl orange by Ag/Cu<sub>2</sub>O with a core-shell structure [33].

In addition, Xuexiang Hu and co-workers studied the impact of  $Cu_2O/Ag/AgBr$  compound on alumina. The obtained results indicated photocatalytic activity and high stability in the degradation of organic pollutants under visible light irradiation and the release of metal ions during the degradation of the pollutants [34].

Yang Jianbo et al. successfully synthesized Ag/ Cu<sub>2</sub>O by an affordable solution. They have shown that the formation of the Ag/Cu<sub>2</sub>O microcomposite was significantly influenced by the concentration of the silver nitrate solution, and an increase in its concentration strengthened the optical absorption of the composites. This effect was used for photocatalytic degradation of methyl orange under visible light irradiation. According to studies, this method can be used to decompose sewage waste in industry [35].

The present study investigates the effect of the doping of Ag on  $Cu_2O$  NPs to enhance the photocatalytic activity and degradation efficiency. COG-423 was studied and, finally, the optimum conditions with three parameters including dopant concentration, intensity, and time were calculated. The effect of pH was not investigated because no significant effect was observed in the degradation efficiency within the desired range, but the photocatalyst was synthesized for application in industries because of the uncontrollable effects of pH changes.

# EXPERIMENTAL

**Materials.** Copper acetate was used as a precursor of copper to prepare the catalyst ascorbic acid d: 1.65 g cm<sup>-3</sup>,

both made by SIGMA Co., while Cu<sub>2</sub>O micro-Ps were purchased from RIEDEL Co. All materials were of an analytical grade and used without further purification.

The X-ray diffraction pattern of pure Cu<sub>2</sub>O and Ag/ Cu<sub>2</sub>O NPs was applied by the STOE Model of the STADIP system using the mechanism of light transmission. The morphology and structure of the synthesized nanoparticles with (FESEM) and Ag, wt %, were determined by technique (EDXA) using scanning electron microscopy of TESCAN Model of MIRA3. Absorption values were obtained to calculate the efficiency of the destruction by a UV-vis UVIKON923 spectrophotometer.

The synthesis of  $Cu_2O$  NPs. Copper oxide of 2.00 g was added to 50 mL of distilled water and stirred for about 30 min. At room temperature until a transparent blue solution was reached.

Sodium hydroxide of 8.00 g was added to 40 mL of distilled water, and stirred for 20 min at room temperature. The resulting solution was added drop by drop to the solution of copper acetate to make a colloidal phase. The solution was stirred for 30 min at room temperature to make cupper hydroxide.

Ascorbic acid of 15.6 g was added to 40 mL of distilled water and stirred for 30 min. The solution was added drop by drop to the previous solutions, and a change in color from green to orange indicated the formation of  $Cu_2O$  particles.

The solution was stirred for 45 min, then the filter was washed twice with distilled water, and the prepared precipitate was placed in a vacuum oven at 150°C for 4 h.

The synthesis of  $Ag/Cu_2O$  NPs. Minitab-16 software was used to achieve the accurate % w/w of Ag, which ultimately resulted in 6 and 12% of the abovementioned % w/w.

Silver nitrate, weighing 0.078 g (6%) or 0.157 g (12%) was added to 40 mL of distilled water and stirred for 30 min until the solution became completely transparent. Tri-sodium citrate weighing 0.107 g was added to 25 mL of distilled water and stirred for 30 min. The prepared solution was added drop by drop to the silver nitrate solution and stirred for 2 h at room temperature in order to provide metallic silver. The resulting solution was added drop by drop to a solution of copper oxide in the synthesis process and stirred for 24 h at room temperature, and the solution was filtered and washed with distilled water. Ag/Cu<sub>2</sub>O NPs were, finally, obtained by drying the precipitate in a vacuum oven at 150°C for 4 h.

**Photocatalytic procedure.** In the photocatalytic degradation processes, organic pollutants disappear under radiation and in the presence of oxidants and semiconductors. To study this effect, solutions were prepared as follows:

COG-423 solution (150 mL 200 ppm), 30 mL hydrogen peroxide 0.05 M (as auxiliary oxidant), 0.2 g Cu<sub>2</sub>O (or Ag/Cu<sub>2</sub>O), and 20 mL of distilled water were mixed and placed into the reactor vessel. Photocatalytic degradation efficiency of the catalyst was calculated according to the following general equation extracted from the Beer– Lambert law:

Degradation, % 
$$\frac{A_0 - A_\alpha}{A_\alpha} \times 100,$$
 (1)

where  $A_o$  and  $A_{\alpha}$  are absorptions of the initial and final solutions respectively.

**Experimental design** Experimental design is a method for systematically conducting a series of tests to determine the importance of the process factors, interactions, and their control in achieving an optimal response. The purpose of this procedure is to obtain reliable and appropriate results based on a limited number of observations. For this purpose, experimental design uses statistical tools.

The main instruments in this field are divided into two groups that include design tools and test analysis. In the field of experimental design, there are methods such as full factorial methods based on Latin squares, and in the field of test analysis, variance analysis and its derivatives and regression analysis are the most important tools [36, 37].

There are four types of test analysis:

- Mixture experiments;
- Factorial design;
- Combined design;
- Response surface.

The response surface methodology (RSM) is used to optimize the process of multivariate testing with the minimum number of tests. Test analysis by the minimum number of tests leads to the saving of time, materials, and laboratory work.

If all variables are measurable, the response surface is calculated by the following formula:

$$y = f(x_1, x_2, \dots, x_k).$$
 (2)

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The goal is to optimize *y*.

It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. Proper approximation functions for communication between independent variables and the response surface are essential.

Usually, a second-order polynomial equation is considered a perfect RSM model:

$$y = \beta_0 + \sum_{i=1}^{k} (\beta_i x_i) \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{j=1, i < j} \sum_{i < j} \beta_{ii} x_i x_j + \varepsilon.$$
(3)

In this equation, y is response (photocatalytic effect on amount of destruction),  $\beta_0$ ,  $\beta_{ii}$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  are regression coefficients,  $x_i$  is the coded independent variable and k is the number of variables [38].

Among the several methods of response surface design, the Box–Behnken method studies the variable interaction effect on response, because this technique requires a minimum number of tests to run.

The Box–Behnken design (BBD) is one of the experimental designs for the response surface methodology that was developed by George Box and Donald Behnken. The above plan is one of the second-order equation convertibles based on the combining of the two-level factorial and partial-block equations. In each block, there are a number of points of variable designs and a repeatable central point. The Box–Behnken design, along with RSM, is used to optimize the physical, chemical, and biological processes.

The number of required tests for the BBD method is calculated with the following equation:

$$N = k^2 + k + cp, \tag{4}$$

where k is the number of variables and cp shows the number of repeats in the central points.

Photocatalytic degradation by different catalysts with respect to time has been calculated as following order:  $Ag/Cu_2O \sim TiO_2 NPs (99.99\%) > Cu_2O NPs (91.4\%) > Cu_2O Micro-Ps (20\%).$ 

RSM is used to analyze and optimize photocatalytic degradation. The impact of different variables such as dopant concentration, light intensity, and the duration of irradiation were analyzed by design techniques.

This work uses the Box–Behnken design for 15 tests and used three replicated central points.



**Fig. 1.** The contour plots of (R: response) (a) showing simultaneous influence of dopant concentration and irradiation intensity (w) on degradation, (b) showing the interaction between dopant concentration and time (min), (c) showing the interaction between irradiation intensity and time along the response surface plots of (R: response), (a') showing simultaneous influence of dopant concentration and irradiation intensity on degradation, (b') showing the interaction between dopant concentration and time, (c') showing the interaction between irradiation intensity and time.

The design points, besides the experimental and predicted values of the organic pollutants' photodegradation, are given in the table.

By plots, the experimental degradation data versus predicted values, and the straight-line equation of these amounts,  $R^2 = 0.985$ , was calculated that representing the coordination and compliance between the design methods and experiments.

Figures 1a and 1a' represent the simultaneous effect of dopant (Ag) concentration and UV light intensity on the degradation efficiency of organic pollutants.

According to the figures, an increase in the dopant (Ag) concentration to 6% results in a decrease in the degradation efficiency, and its subsequent increases up to 12%, have an inverse outcome on the process. For example, when light intensity is 32 W and dopant



Fig. 2. Optimal condition of photocatalytic degradation by Ag/Cu<sub>2</sub>O NPs.

concentration is 12%, the degradation efficiency is about 99.9%, while the degradation efficiency is 72.5% when the light intensity and dopant concentration are 32 W and 6%, respectively.

The correlation between light intensity and degradation efficiency is a direct relationship because, in a higher intensity, more crystals are exposed to the light, so more crystalline sites are activated.

Figures 1b and 1b' show the interaction between dopant (Ag) concentration and the irradiation time. According to the preceding descriptions, at lower dopant concentrations, degradation efficiency was inversely related to the concentration, while at higher concentrations, degradation efficiency showed a reverse trend, so that the maximum efficiency was seen when the dopant concentration was about 12%.

The influence of time on degradation efficiency was direct; hence, the degradation efficiency is the maximum at 30 min. because crystals are exposed to irradiation for a longer time, enabling the activation of more crystalline sites.

Figures 1c and 1c' show the effects of both severity and time on degradation efficiency of organic pollutants. These two variables have a similar effect on the degradation efficiency. As already mentioned, by increasing the intensity and time, crystals are exposed to large amounts of light rays for a long period, increasing the number of efficiency of reaction was calculated 99.99% that showed good agreement with experimental results. Table

active crystal sites and degradation efficiency. Figure 2

is shown optimal conditions as per obtained results by

experimental design with Ag%, light and time param-

eters as [12%], [32 W] and [30 min], respectively. The

Run	Blk	Coded levels			Photodegradation %	
		A	В	С	experimental	predicted
1	1	_	0	_		80.831
2	1	_	0	+	01.40	89.244
3	1	_	_	0	81.49	74.004
4	1	+	_	0	72.57	87.319
5	1	+	0	_	87.43	90.146
6	1	0	_	_	89.26	39.615
7	1	+	0	+	50.39 99.99	100.649
8	1	_	+	0	91.04	91.151
9	1	0	+	+	72.49	63.265
10	1	+	+	0	99.99 58.09	98.556
11	1	0	_	+	60.92	47.542
12	1	0	0	0	60.74	50.85
13	1	0	0	0	60.89	50.85
14	1	0	0	0	01./3	50.85
15	1	0	+	_		52.277



Fig. 3. X-ray diffraction pattern of (a) Cu<sub>2</sub>O and (b) Ag/Cu<sub>2</sub>O NPs.



Fig. 4. FESEM imaging of (a)  $Cu_2O$  NPs with resolution of 200 nm, (b)  $Ag/Cu_2O$  NPs with resolution of 1  $\mu$ m, (c) resolution of 100 nm, (d) TEM imaging of  $Ag/Cu_2O$  NPs.

# **RESULTS AND DISCUSSIONS**

X-ray diffraction (XRD) patterns. Figures 3a and 3b show the X-ray diffraction pattern for  $Cu_2O$  and  $Ag/Cu_2O$  NPs respectively. As a result of the doping of Ag on  $Cu_2O$  NPs, a crystalline phase change occurs

from the cubic to the hexagonal form. This means the formation  $Ag/Cu_2O$  NPs prevents  $Cu_2O$  NPs crystal growth.

Figure 3a shows the X-ray diffraction (XRD) pattern of  $Cu_2O$  NPs. In the (XRD) pattern, there are four main peaks at angles of diffraction 36.49, 42.37, 61.45, and

73.4° that correspond to with crystal faces with Miller indices (111), (200), (220) and (311), respectively.

In the Ag/Cu<sub>2</sub>O X-ray diffraction pattern (Fig. 3b), there are four major peaks at angles of diffraction 36.41, 42.33, 61.31, and 73.37° that correspond to crystal faces with Miller indices (111), (200), (220) and (311), respectively. This pattern represents the cubic phase for Cu<sub>2</sub>O NPs.

Two cubic crystalline phases,  $Cu_2O$  and Ag, in the X-ray diffraction pattern of Ag/Cu<sub>2</sub>O NPs were obtained. The diffraction peak width of Ag/Cu<sub>2</sub>O NPs compared to the Cu<sub>2</sub>O crystalline structures represented smaller crystalline structures in Ag/Cu<sub>2</sub>O NPs. As a result of the Ag doping on Cu<sub>2</sub>O NPs, the crystalline phase changed from cubic to hexagonal, preventing the growth of Cu<sub>2</sub>O NPs crystals.

Using the Debye–Scherrer equation (Eq. 5), the mean sizes of  $Cu_2O$  cubic and  $Ag/Cu_2O$  hexagonal nanocrystal were calculated to be 28.21 and 118.07 nm, respectively.

$$B = \frac{k\lambda}{L\cos\theta},\tag{5}$$

where *B* represents the crystal size, k = constant parameter (0.89),  $\lambda = \text{the wavelength of the cathode}$ , L = the full width at half maximum (FWHM) and  $\theta$  is desired peak angle.

**Morphology analysis.** FESEM and TEM imaging were used to observe the morphology of synthesized nanoparticles.

Figure 4a shows the FESEM imaging of  $Cu_2O$  NPs with an appropriate particle distribution. Based on the shape, the average particle size was about 20 nm.

Figures 4b and 4c, reveal the structure and morphology of  $Ag/Cu_2O$  NPs at different resolutions. As shown in the figures, approximately 8% of the total area of  $Cu_2O$ is covered by silver. Average particle size is depicted to be about 118 nm. This size points to the fact that the photocatalyst is nanostructured. The morphology of the synthesized  $Ag/Cu_2O$  NPs was investigated with the help of a transmission electron microscope (TEM) as shown in Fig. 4d.

**Elemental analysis.** The EDXA technique was used for elemental analysis and evaluation of the surface layers of the Ag/Cu<sub>2</sub>O NPs. As indicated by the pattern shown in Fig. 5, there are Ag and Cu elements with 37.79 and 11.56% w/w in the structure of Ag/Cu<sub>2</sub>O NPs, respectively.



**Fig. 5.** Energy-dispersive X-ray analysis results of Ag/Cu<sub>2</sub>O NPs.



**1 ig. 0.** *Cu*<sub>2</sub>O 101 5 hysteresis loop.

The results of imaging and EDXA represent the Ag surface accumulation of Cu<sub>2</sub>O NPs.

**BET–BJH test.** Based on the results of the BET–BJH test, Cu<sub>2</sub>O particle surface area was calculated as  $4.20 \pm 0.04 \text{ m}^2/\text{g}$  and the volume percentage of pores in the three-phase micro, meso, and macro was 21.76, 72.90, and 5.34%, respectively.

Figure 6 shows the Cu<sub>2</sub>O NPs hysteresis loop. If a pore is formed by several parallel plates, a meniscus cannot be formed as long as the vapour pressure of the adsorbate is raised to the saturation vapor pressure. On desorption, the pore is emptied at a relative pressure corresponding to the extend of the capillary, as this will be the effective radius of curvature of the meniscus. Thus, the isotherm has an ascent adsorption branch at a relative pressure of unity and a sloping desorption branch in between relative pressures. Such an isotherm is said to show type B hysteresis. Another type of capillary which may cause to type B hysteresis is an ink-bottle pore with a body, which is quiet wide, ca 1000 Å, that the adsorption

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branch practically coincides with a relative pressure of unity [39].

### CONCLUSIONS

In summary, Cu<sub>2</sub>O and Ag/Cu<sub>2</sub>O NPs were synthesized by the coprecipitation method. Ag/Cu<sub>2</sub>O NPs were obtained by reducing Cu(OH)<sub>2</sub> with ascorbic acid in the presence of Ag three-dimensional crystals. The results showed that doping of Ag in Cu<sub>2</sub>O increased and upgraded the photocatalytic properties, so that the degradation efficiency under optimal conditions (when intensity is 32 W for 30 minutes) was calculated for Cu<sub>2</sub>O Micro-Ps and NPs to be 20.0% and 91.4% respectively, and for Ag/Cu<sub>2</sub>O and TiO<sub>2</sub> NPs about 99.9%.

The XRD analysis showed that the effects of doping changed the crystal phase from cubic to hexagonal. This means the creation of Ag/Cu<sub>2</sub>O NPs prevents the growth of Cu<sub>2</sub>O NPs crystals.

The synthesis of Ag/Cu<sub>2</sub>O NPs is a suitable alternative to  $TiO_2$  on an industrial scale due to functional simplicity, cost-effectiveness, high efficiency and the limitations of the synthesis method of  $TiO_2$  photocatalyst, including its high cost.

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