Adsorption of Congo Red (Acid Red 28) Azodye on Biosynthesized Copper Oxide Nanoparticles

MADIHA BATOOL¹, MUHAMMAD ZAHID QURESHI¹, FARWA HASHMI², NIDA MEHBOOB² and WALID M. DAOUSH^{3,4,*}

¹Department of Chemistry, Government College University, Lahore, Pakistan

²Lahore College for Women University, Lahore, Pakistan

³Department of Production Technology, Faculty of Industrial Education, Helwan University, Cairo, Egypt

⁴Department of Chemistry, College of Science, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh, Kingdom of Saudi Arabia

*Corresponding author: E-mail: wmdaoush@imamu.edu.sa

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A green synthesis of copper oxide nanoparticles and its removal efficiency of azodye were studied. Biosynthesis of stable copper oxide nanoparticles were preformed using *Aloe barbadensis* leaf extract as a size and shape-directing agent for preparing of spherical copper oxide nanoparticles by calcination at 400 °C. The leaf extract of *Aloe barbadensis* was prepared in deionized water. The produced copper particles were calcined at 400 °C to produce copper oxide nanoparticles. The characterization of copper oxide nanoparticles was performed by XRD, SEM, FTIR, UV spectroscopy. The XRD analysis showed that the average particle size was between 5-30 nm. The shape of the copper oxide nanoparticles was spherical and cubic. EDX of the synthesized nanoparticles showed the composition consists of 68 % copper. The UV-visible spectrum analysis confirms an absorption peak at 200-400 nm of the produced CuO nanoparticles. The FTIR analysis of the copper oxide particles indicate the presence of the organometallic Cu-O bond between Cu and O. The obtained copper oxide was used as a removing agent of Congo red dye. The effect of variables like concentration, time, pH, adsorbent dosage were studied. It was observed from the results that the maximum dye removal occurs at pH of 4, the concentration of nanoparticles was 1 mg/L and the maximum time for dye removal was 120 min. The Langmuir isotherm model was calculated to study the adsorption efficiency of the Congo red dye on the produced copper oxide nanoparticles. The kinetics of pseudo second order is followed by adsorption. The calculated sum of square was 0.012 and $r^2 = 0.98$. it was observed that the model fit the best and straight line with r^2 value of 0.991 and probability value of $1.6E-5$. The nanoparticles remove 70 % of the Congo red dye from its solution. This showed that the copper oxide nanoparticles has efficient capacity of azodye degradation.

Keywords: *Aloe barbadensis*, Green synthesis, Copper oxide particles, SEM, XRD, FTIR spectroscopy, UV-visible spectroscopy.

INTRODUCTION

Nanotechnology deals with the manipulation of matter at low size normally less than 100 nm [1]. Recent development in the field of science and nanotechnology has led to a new concept of synthesizing nano-sized particles of desired size and shape. Wastewater characteristics such as dyes, detergents, etc. [2] used in the process are the parameters that have caused a serious effect on health. In this study, a Congo red azodye is removed from its aqueous solution by copper oxide nanoparticles [3].

Recently, there is a scope to develop new methods for the synthesis of nanoparticles which should be required inexpensive, less drastic reaction condition and ecofriendly [4]. Copper

oxide nanoparticles have attracted much attention of researchers due to its application degradation and biomedical properties [5]. Metallic nanoparticles can be prepared by the chemical and physical method. These methods have certain flaws like toxic chemicals and also dangerous to the environment [6]. Developing research in green chemistry employed prominent part in nanotechnology to gain benefit to the society [7]. Nanoparticles have dye degradation property due to increase surface area and mass ratios. Therefore, the need for the development of a reliable, biocompatible, benign and eco-friendly process to synthesize nanoparticles [8]. Green synthesis has been engaged in synthesis of highly stabilized nanoparticles [9]. Copper nanoparticles were synthesized by leaf extract of Aloe vera plant. Phenolic content in plant extracts dissolved in water,

degradable and used to catalyzed synthesis of the nanoparticle as capping and reducing agent [10].

Nanoparticles show unusual structural, electrical, optical and magnetic properties [11]. Several clinical trials are being conducted to further evaluate the use of Aloe vera gel for a variety of disorders [12]. Aloe vera juice is commonly used as an ointment and skin abrasions. Functional groups in aloe vera contain, carboxymethyl (-O-CH₂-COO-) and sulphony (-O-CH₂-CHOH-CH₂-O-CH₂-CH₂SO₃-) groups [13]. This ancient plant may offer deeper healing abilities. It contains antioxidant vitamins A, C and plus vitamin B12, folic acid and choline and eight enzymes [14]. These chemicals salicylic acid and anthraquinones (aloin, emodin, aloetic acid, anthranol, cinnamic acid, anthracene) are responsible for the reduction of copper [15,16].

Polyphenols in Aloe vera plants leaves extract like aloin can act as chelating, capping and also reducing agents for nanoparticle formulation [17]. This is a one-step processes in which no surfactants and other capping agents used [18].

In this work, a new method is performed for the synthesis of copper oxide nanoparticles by using Aloe vera extract as an inexpensive size and shape-directing reagent using a less drastic and eco-friendly reaction condition. XRD, SEM, FTIR, UV spectroscopy were performed to analyze the copper oxide nanoparticles. The obtained copper oxide nanoparticles were used to remove the Congo red acid dye from its aqueous solution. The effect of different variables like concentration, time, pH, adsorbent dosage were studied. The Langmuir isotherm was calculated to study the adsorption efficiency of the red acid dye on the copper oxide nanoparticles.

EXPERIMENTAL

All the chemicals in this present study are analytical grade and purchased from Sigma Aldrich Co LTD, China. The Aloe vera leaves were collected from the nearby botanical garden of the Government College University of Lahore, Pakistan.

Preparation of plant leaf extract: To prepare the leaf extract of Aloe vera plant, leaves (25 g) were thoroughly washed, dried and finely chopped. The finely chopped leaves were allowed to boil for 5 min at 80 °C with 100 mL of de-ionized water in a 250 mL Erlenmeyer flask and then cooled down to room temperature. The resulting solution is passed through a filter paper to remove any solid particles and then again filtered through a Whatman filter paper of pore size 0.2 µm. The filtrate is stored at 4 °C as a stock for the synthesis of CuO nanoparticles [19].

Green synthesis of CuO particles: A copper sulphate (CuSO₄·5H₂O) solution of 50 mL (99.99 % purity, Aldrich) was added to 25 mL of the Aloe vera extract in a 100 mL Erlenmeyer flask with constant stirring on a hot plate at boiling [20-22]. Colour change of the reaction mixture was observed from deep blue to green and then dark greenish after stirring for 24 h. The obtained solution is centrifuged at 10,000 rpm for 10 min. at room temperature (using Beckman centrifuge with a Beckman JA-17 rotor) and the mixture is collected after discarding the supernatant [23]. The collected nanoparticles are allowed to dry in a watch glass. The powder was calcined at 400 °C for 2 h. The obtained black powder was collected for characterization.

Characterization of the CuO particles: The chemical composition, particle morphology, size and shape of the produced copper oxide nanoparticles were investigated by SEM supported by EDAX unit of model (JSM-6480), XRD of model (XPERT-PRO), FTIR spectrophotometer of model (PRESTIGE 21) and UV spectrophotometer (DB-20).

Preparation of the dye: Solution consists of 1000 ppm of Congo red was prepared by dissolving the dye in 1 L distilled water. Different concentrations of dyes were prepared from the stock solution. A diluted solution consists of 100 ppm was prepared from 1000 ppm by dilution [24]. After that 150, 200, 250 ppm solutions were prepared. The catalytic activity of CuO nanoparticles were examined by the degradation of the Congo red dye. About 10 mg of the prepared CuO nanoparticles was added into 50 mL of Congo red dye solution. Hydrogen peroxide (50 µL) was also added into the mixture solution to retain the adsorption equilibrium. The solution was stirred for 50 min. A mixture of 3 mL was taken out after 10 min interval time. The removal efficiency of the dye was calculated according to the change in the colour by using the following equation:

$$\text{Decolourization (\%)} = \frac{A - B}{A} \times 100 \quad (1)$$

where A and B are absorbance of the dye solution without and with nanoparticles respectively.

Dye removal process: Hydrogen peroxide (50 mL) is used as an oxidizing agent of the Congo red dye. Congo red (Direct Red 28) having a chemical formula of C₃₂H₂₂N₆O₆S₂Na₂: and molecular mass of 696.66 g/mol. The concentration of CR in each aqueous solution was measured by UV-visible spectrophotometer) at λ_{max} = 500 nm.

The decolorization of Congo red dye at room temperature was studied. Amount initially taken was 20 mL dye solution and 4 mL of Aloe vera green synthesized copper nanoparticles [18]. The time interval was noted gradually during reaction. The removal % of decolourization was calculated and draw graphically.

The Langmuir isotherm and the kinetics of the dye degradation were studied to determine the adsorption. reaction order of the Congo red azodye on the surface of the CuO nanoparticles by using the ANOVA program.

RESULTS AND DISCUSSION

Synthesis and characterization of CuO nanoparticles: Colour changes of the copper salt solution after the addition of the Aloe vera extract indicates the formation of nanoparticles of copper oxide. The green colour solution was turned into dark brown, indicated for the formation of copper oxide nanoparticles [25].

Fig. 1 shows the XRD patterns of the obtained nanosized powder before and after calcination at 400 °C. It was observed from the pattern (Fig. 1a) that the produced nanosized powder before calcination consists mainly of Cu and its low oxidation state oxide Cu₄O₃. Two types of peaks were observed the first one (111 and 200) of Cu and the second one (112, 200, 103, 202, 004 and 301) of Cu₄O₃. However, it was observed from the pattern of the calcined powder (Fig. 1b) five peaks were observed at 202, 004, 220, 224 and 206 of the CuO crystal

Fig. 1. XRD pattern of the produced copper and copper oxide nanosized particles by using Aloe vera extract, where (a) CuO before calcination and (b) CuO after calcination at 400 °C

structure according to the JCPDS card number (01-071-0251). XRD pattern confirmed that calcined CuO nanoparticles are highly crystalline with a tetragonal crystal structure. The average size of the particle was calculated according to the Scherrer equation was between 5-30 nm [16].

Fig. 2 shows SEM images with EDAX compositional analysis of the calcined CuO nanosized powder. It was observed that the average particle size of the produced CuO particle was in the range between 80 and 120 nm with a spherical particle shape (Fig. 2a and b). It was also observed from the EDAX compositional analysis that particle is consists mainly of Cu and O as well as too small contents of Al and S elements remained from the copper sulphate solution (Fig. 2c) [26].

Fig. 2. Different magnifications of SEM images with EDX analysis for the prepared copper oxide nanoparticles

Several plants extract sources used in literature to produce copper oxide with different particle size as listed in Table-1. *Magnolia kobus*, *abutilion* and *Ecliptiaprostrata* leaves extracts were used as precursors of biogenic synthesis of copper oxide

TABLE-1
PLANT PRECURSORS USED FOR THE FABRICATION
OF COPPER OXIDE NANOPARTICLES WITH
DIFFERENT PARTICLE SIZE

Plant species	Extract	Size (nm)	Ref
<i>Mangoliakobus</i>	Leaves	100-150	[12]
<i>Abutilion</i>	Leaves	40-84	[13]
<i>Ecliptiaprostrata</i>	Leaves	40-60	[15]
<i>Cassia auriculata</i>	Leaves	23	[14]
<i>Syzygium aromaticum</i>	Clove	40-100	[24]
<i>Aloe barbadensis</i>	Leaves	20	[29]
<i>Aloe barbadensis</i>	Leaves	15-35	[28]
<i>Aloe barbadensis</i>	Leaves	5-30	Current study

nanoparticles which having ranges of average sizes 120, 65 and 40-60 nm respectively [12,13,15]. In another study *Cassia auriculata* and *Syzygium aromaticum* are used to fabricate copper oxide nanoparticles [14-26]. In comparison the *Aloe barbadensis* leaves extract used in present and previous studies to produce copper oxide with average particles size ranges between 5 and 30 nm according to the XRD analysis with a uniform particle distribution as investigated by the SEM [27-29].

Fig. 3 presented FTIR of the calcined copper oxide at 400 °C. The band observed at 1100 cm^{-1} , indicated the Cu-O bond stretching of copper oxide nanoparticles. The peak was observed in the range of 4000-400 cm^{-1} . The bands at 3450, 2860, 1650, 1100 and 800 cm^{-1} indicate the O-H stretching of the alcohol, the C-H stretching of the alkene, the C=C stretching of aromatic ring, the C-O stretching of alcohol and the Cu-O of the CuO respectively [26].

Fig. 4 shows the UV-visible spectra of the prepared CuO nanoparticles. It was observed that an absorption peak was appeared at arange of 200-300 nm confirmed the formation of copper oxide nanoparticles.

Removal of Congo red dye by adsorption on CuO nanoparticles: The hydrogen peroxide H_2O_2 was added as an oxidizing agent releasing the hydroxyl radical in the oxidation media. The catalytic activity process is mainly depending on the formation of super oxide anion radical and hydroxyl radicals [26]. The degradation of the Congo Red (Direct Red 28) is takes place according to the following chemical equation [16]:

Fig. 3. FTIR spectrum of stabilized copper oxide nanoparticles after calcination at 400 °C

Fig. 4. UV-visible spectrum of the produced copper oxide nanoparticles

Decolourization and equilibrium of dye removal

Dye removal rate: Fig. 5 shows the effect of the removal time on the decolourization % of Congo red dye by using the copper oxide nanoparticles. It was observed the optimum maximum time of dye removal was observed 120 min with 70 % of colour removal.

Effect of pH: The pH effect on the decolourization of copper oxide nanoparticles was also studied (Fig 6). It was observed from that the decolourization % is strongly affected by the pH of the solution. The decolourization % is increased by increasing the pH of the solution in the acidic range. The maximum decolourization of 70 % was observed at pH 4. This effect may be due to the formation of more positive ions in the solutions.

Fig. 5. Effect of time on the decolourization of Congo red dye by using the CuO nanoparticles

Fig. 6. Effect of pH on the removal (%) of Congo red dye by using the CuO nanoparticles

Effect of dye concentration: Fig. 7 shows the effect of initial concentration of Congo red dye on the decolourization efficiency. The data was collected from several experiments using different concentrations of dye. It was observed that by increasing the dye dosage the decolourization efficiency

Fig. 7. Effect of dye dosage on the removal (%) by using the CuO nanoparticles

(%) was increased and the maximum amount of removed dye is 73 % at dye concentration of 20 mg/L. However, by increasing the dye dosage higher than 20 mg/L the decolourization % of the dye was decreased.

Effect of CuO nanoparticles content on the dye removal:

Fig. 8 shows the effect of the CuO nanoparticles amount on the dye removal %. It was observed from the results that the number of copper oxide nanoparticles depicted positive results on decolourization % and the maximum decolourization % was reached by using 1 g of the CuO nanoparticles. It was also observed that the overdosage of nanoparticle showed no effect on the decolourization % of the dye.

Fig. 8. Effect of copper oxide nanoparticles content on the removal of Congo red dye (%)

As mentioned above the biosorption of azodyes were investigated as function of pH, temperature and removal time. In comparing between the current result and previous reports in the literature, copper oxide nanoparticles have efficient degradation potential (65, 99.8, 92 % respectively) of other azodyes like acid blue 129, malachite green [18,23,25]. Congo red dye removal by copper oxide nanoparticles also investigated in literature for an optimum condition of temperature, pH and initial dyes concentration [17,22,27] as listed in Table-2. The current study has been carried out by using copper oxide nanoparticles for degradation of Congo red dye, observed a reaction parameters were initial pH, temperature, time 4, 60-80 °C, 120 min respectively with maximum degradation of 70-75 %.

TABLE-2
OPTIMUM CONDITIONS USED FOR REMOVAL OF AZODYES BY COPPER OXIDE NANOPARTICLES

Dye	Time (min)	pH	Temp. (°C)	Degradation (%)	Ref.
Congo red	90	4-11	60	90	[16]
Acid blue 129	30	1-8	25	60-65	[18]
Congo red	120	7	50	86	[25]
Congo red	120	5-7	20	81.2	[27]
Acid blue 129	30	1-8	25	99.8	[18]
Malachite green	75	7.4	25	92	[26]
Congo red	120	4	60-80	70-75	Current study

Langmuir isotherm and kinetic study of dye degradation: The removal of dye Congo red by copper oxide nanoparticles follow pseudo second order reaction rather than first order one (Fig. 9) and the data is given in Table-3.

Fig. 9. Pseudo second order kinetics for the degradation of Congo red acid azodye (where $y = a + b^2X$)

TABLE-3
PARAMETERS OF SECOND ORDER KINETICS OF DEGRADATION OF CONGO RED ACID AZODYE AT 25 °C

Parameter	Value	Parameter	Value
K_2	0.689	t/q_t slope	0.029
q_e	14.9	Intercept	1.65
r^2	0.980	Standard error	0.0013
Sum of square	0.012		

Langmuir equation is a two-parameter equation study. A fixed number of sites is available on the surface. This study reveals that the adsorbents have adsorbed efficiently at a fixed rate and only specified adsorbents are present at reaction place. The reaction takes place on adsorbents is equally effective. The Langmuir equation can be written as follows:

$$Q_e/q_m = B C_e / (1 + C_e/q_m) \quad (3)$$

In the equation q_m is adsorption capacity in unit mg/g. C_e is concentration of adsorbent at equilibrium. q_e is difference of initial and equilibrium concentration of copper oxide nanoparticles. Langmuir isotherm constant is K_L . Langmuir constant provide the binding affinity. The values of isotherm q_m and constant K_L can be calculated by plotting a graph between C_e/q_e and C_e . The characteristics of a Langmuir isotherm can be examined in terms of equilibrium parameter (K_L) can be calculated by formula

$$K_L = 1/(1 + bC_e) \quad (4)$$

By plotting a graph between (C_e/q_e) and C_e a straight line proves Langmuir isotherm model. The linearity of Langmuir isotherm (Fig. 10) indicates a strong attraction of Congo red dye depredated by the adsorbent copper oxide nanoparticles [28]. The parameters of Langmuir equation are listed in Table-4 and the resulted values of c_e and c_e/q_e are listed in Table-5. The ANOVA and statistics of Langmuir curve are listed in Tables 6 and 7.

Fig. 10. Langmuir isotherm for the adsorption of Congo red dye on the CuO nanoparticles

TABLE-4
PARAMETERS OF LANGMUIR ISOTHERM AT 30 °C

K_L	q_m	R_L	r^2
0.6	80	-0.03	0.991

TABLE-5
VALUES OF c_e AND c_e/q_e FOR LANGMUIR ISOTHERM WITH RESPECT TO ADSORBENT CONCENTRATION (where $q_e = C_0 - C_e$)

C_0	C_e	q_e	C_e/q_e
20	1.4	18.6	0.07
40	3.2	36.8	0.08
80	6.3	70.7	0.091
100	9.1	90.9	0.12
120	12.4	107.6	0.115
140	16.3	123.7	0.134

TABLE-6
 C_e/q_e ANOVA DATA OF LANGMUIR ISOTHERM

DF	Sum of square	Mean square	F	Pro $\geq F$
Model	1	0.002	608.6	1.6E-5
Error	4	1.83E-5		
Total	5	0.002		

TABLE-7
STATISTIC CALCULATIONS OF C_e/q_e OF LANGMUIR ISOTHERM

Parameter	Values
Number of points	6
Degree of freedom	4
Residual sum of square	1.8394E-5
Precision	0.99673
Adj.R-square	0.99184

Conclusion

In conclusion, it was reported in this study an ecofriendly fabrication method of CuO nanoparticles using leaf extract of Aloe vera plant. The SEM investigations confirmed spherical shape of copper oxide nanoparticles, XRD data predict range of nanoparticles size between 5-30 nm by Scherer equation. The copper oxide nanoparticles have the ability to degrade the Congo red azodye. In the present study, Congo red dye was removed 70-75 % by nanoparticles and observed optimum

condition were noticed like (pH = 4), contact time 120 min, adsorbent by copper oxide nanoparticles dosage of 1 mg/L. The degradation of Congo red dye followed pseudo-second order kinetics rather than first order. Langmuir isotherm was drawn between C_e and C_e/q_e which proved linear isotherm. The calculated sum of square of kinetic curve was 0.012 and observed $r^2 = 0.980$ from graph. Langmuir isotherm model fit best and straight line graph drawn with r^2 value 0.991 and probability 1.6E-5. It was concluded that copper oxide nanoparticles keep efficient degradation capacity of the Congo red dye.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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