The Adsorption Ability of Cibacron Red Dye from Aqueous Solution Using Copper Oxide Nanoparticles

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Abstract

This research describes the environmentally friendly production of CuO nanoparticles utilizing watercress plant extract and calcination at 400 C for 3 hours. SEM and TEM were used to analyze the size of nanoparticles. X-ray diffraction (XRD) was used to determine their crystal structure. Energy-dispersive X-ray spectroscopy (EDX) analysis of the created product's structure revealed just copper and oxygen constituents, demonstrating the purity of the synthetic material. The addition of CuO NPs improved the absorption of the dye Cibacron red. At 35 minutes of contact time, quicker adsorption of Cibacron red dye onto CuO nanoparticles was observed. The Freundlich isotherm and kinetic of pseudo-second order with R2 values more than 0.9785 and 0.999, respectively, were the most effective in describing the adsorption process. The thermodynamic parameters were calculated using thermodynamic analysis. It can be concluded that CuO NPs are an effective adsorbate surface for the Cibacron red dye.

Keywords: Adsorption, Cibacron red dye, CuO NPs, X-ray diffraction, green synthesis.

Introduction

The creation of materials with unique size, structure, and content is now possible because of nanotechnology, a critical development in contemporary science. Materials with a diameter of less than a nanometer are produced, processed, and used. Compared to individual bulk atoms and molecules, nanoscale physical, chemical, and biological properties vary. This makes it possible to develop fresh classes of cutting-edge substances and materials that meet the demands of high-tech applications. Numerous businesses and fields, including as the chemical industry, electrochemical photo applications, environmental health, medicine, and energy, are using nanotechnology. Since some time ago, medical institutions have used metal nanoparticles, including gold, silver, and zinc, as therapeutic agents. In energy, biomedicine, and the environment, transitional metal oxides like CuO, TiO2, Fe3O4, ZnO, and NiO NPs have been successfully used as cutting-edge nanomaterials. These nanoparticles' high adsorption abilities considerably improve their applications and performance. There has been increased research into the biological effects of metal nanoparticles. Recently, various researchers began evaluating the biological effects of metal oxide nanoparticles like copper oxide, whereas increased biological and photocatalytic activities superior to those derived from metal nanoparticles have been observed. CuO NPs have shown unique anticancer, antibacterial, and antioxidant activity in addition to the previously indicated use, making them a viable
tool for biomedical applications. Copper oxide nanoparticles have been shown to have potential uses in a variety of fields, including gas sensors, catalysis, solar cells, batteries, food preservation, high temperature superconductors, waste treatment, photovoltaic devices, agriculture, field emission emitters, and dye removal. Dyes, which include all substances used to color textiles, leather, food, and other materials, are regarded as organic pollutants in aqueous systems and may pose a number of risks to all elements of the environment due to their high toxicity, particularly when they are present in high concentrations. Among the components of industrial effluent, organic compounds play a crucial role. Due to the possibility of some organic contaminants causing malignant diseases, there is a high danger of long-term effects. According to World Health Organization (WHO) reports, drinking water contamination is the primary source of the majority of diseases that are spread in underdeveloped nations. As a result, many treatments have been employed by researchers to treat industrial water.

Material and methods

Preparation of Watercress Plant Extract

A plant extract from the watercress has been gathered and cleaned with de-ionized water to remove dust particles. The dry leaves are gently combined in a mixer to create homogenous powders then, 10 g of leaves were pulverized and mixed with 150 ml of de-ionized water, then heated for 30 minutes at 60 °C with stirring. The solution was filtered and stored in the fridge.

Synthesis of CuO Nanoparticles

The green synthesis technique was used to make copper oxide nanoparticles. In accordance, an amount of 200 ml of watercress extract was added slowly (one drop per second) to 0.01 mole of Cu(NO₃)₂ and stirred for 30 minutes. The green powder was precipitated, separated, and washed with deionized water numerous times. The precipitate was dried for an hour at 150°C and calcined for three hours at 400°C. The black powder of copper oxide nanoparticles was obtained.

Adsorption of Cibacron Red Dye on CuO NPs

The equilibrium isotherm of a particular adsorbent serves as a representation of its adsorbent properties while building adsorption processes. In deionized water, a stock solution of cibacron red dye 50 ppm was created. 10 ml of dye solution were combined with 0.01 g of CuO nanoparticles, which were then heated at 298 K for 30 minutes. A UV-visible absorption spectrophotometer measured the dye concentration after filtering the solution as Eq. 1:

\[ Q_e = \frac{(C_0 - C_e)V_{sol}}{m} \]  

Where \( C_0 \) and \( C_e \) are the starting and equilibrium concentrations of Cibacron red dye (mg/L), \( Q_e \) (mg/g) is the equilibrium adsorption capacity, and M is the mass of the CuO nanoparticles (g), \( V_{sol} \) is the volume of cibacron red dye (L).

Characterization of CuO Nanoparticles

The CuO nanoparticles sample was examined using X-ray diffraction (XRD-6000). Transmission electron microscopy was used to examine the
morphology of nanoparticles. Using a scanning electron microscope (SEM), the CuO nanoparticles' form was examined.

Results and Discussion

The X-ray Diffraction of CuO Nanoparticles

The X-ray crystallography was used to determine the structure of nano-synthesized, in which the crystal's atoms cause an incoming X-ray beam to diffract in various directions. According to XRD analysis, the monoclinic CuO (JCPDS 45-0397) planes (110), (111), (200), (-202), (020), (202), (-113), and (022) are allocated to a series of diffraction peaks at 2θ of 32.41, 35.61, 38.81, 48.91, 53.31, 58.21, 61.61, and 66.31, respectively, Fig. 1. Except for these CuO peaks, all of the diffraction peaks can be indexed as conventional monoclinic structures. No other peaks matching to Cu or Cu2O were seen. Using the Scherrer formula, the average crystallite size of CuO crystal size was determined as Eq. 2:

\[ D = \frac{k\lambda}{\beta \cos\theta} \]

where D is the particle size (nm), k is a constant of value 0.94, \( \beta \) is the full-width at half maximum (FWHM) of the peak (in radians), \( \lambda \) is the X-ray wave length 1.5406 Å, as well as 2θ is the Bragg angle (degree). The size of the typical crystallite was determined to be 24nm.

Field Emission Scanning Electron Microscope (FE-SEM)

The surface morphology of pure CuO nanoparticles that had been calcined at 400 °C was examined using FE-SEM. The prepared sample was produced as semi-spherical aggregates with a roughly uniform distribution, according to the SEM analysis. Equal-sized produced nanoparticles' crystal nature is seen in Fig. 2.
Transmission Electron Microscopy (TEM)

The TEM image of CuO NPs is depicted in Fig. 3. The TEM image of nanoparticles in various sizes and shapes is depicted in Fig. 3. The TEM examination aims to comprehend the crystalline properties of the nanoparticles. The particles are determined to be 28 nm in size and to be spherical in shape. The aggregation of tiny nanoparticles into larger ones that have dimensions that match those seen in the XRD study could be the cause of the larger particles.

Energy-dispersive X-ray Spectroscope Characterization

The EDX spectrum of CuO NPs is depicted in Fig. 4. The spectrum has the usual copper and oxygen peaks. The outcomes support the great purity of the produced nanoparticles. Furthermore, the actual estimations derived from the EDX measurement concur with the theoretical computations of the elements. The matrix of the mixed catalyst has effectively dispersed the CuO NPs, as shown in Fig. 5. Additional information suggests typical x-ray mapping images that show the distribution of a CuO catalyst’s elemental components and facilitate the dispersion of the catalyst's elements.
Adsorption Isotherms

The main objective of the adsorption analysis is to ascertain how the dye and adsorption interact in addition to compare the adsorption isotherm with the adsorption data. The Langmuir and Freundlich models were assessed in this study. The following formula \(^{38-40}\) describes the linear Freundlich adsorption process as Eq. 3:

\[
\log(Qe) = \log(k_f) + \left(\frac{1}{n}\right) \log(Ce)
\]

The adsorption capacity, as well as intensity of adsorption, are shown by the Freundlich constants \(K_f\) and \(n\), respectively are depicted in Fig. 6. Calculating \(k_f\) is done using the intercept, while \(n\) is done using the slope. For the CuO isotherm Freundlich, \(1/n\) was determined in this work to be 0.235. Thus, this investigation supported the benefit of physical adsorption \(^{41}\). The adsorption is better fit by the Freundlich isotherm model \((R^2=0.9785)\).
Figure 6. The Freundlich isotherm model plot at 298 K.

The data fits the Langmuir adsorption isotherm (Fig. 7), as can be seen in the Eq. 4, that follows:

\[
\frac{C_e}{Q_e} = \frac{1}{q_{\text{max}}} K_L + \frac{C_e}{q_{\text{max}}} \tag{4}
\]

The maximum capacity of Cibacron red dye is \(q_{\text{max}}\) (mg/g), whereas the Langmuir constant is \(K_L\) (mg/L). The Langmuir isotherm’s key characteristics are outlined and shown by the separation factor, sometimes referred to this as the dimensionless constant (RL) in Eq. 5:

\[
RL = \frac{1}{1 + K_L C_i} \tag{5}
\]

The dye adsorbs best on CuO when the initial dye concentration is \(C_i\) (mg / L), and the RL values are all within the range of (0–1).

Figure 7. The Langmuir isotherm model at 298 K.
**Effect of Contact Time**

To measure contact time and equilibrium time, a series of tests using 0.01 g CuO NPs and 10 mL 50 ppm dye were conducted with a 200 rpm shaker at 298 K. The first 5 to 40 minutes of adsorption are relatively quick. Fast adsorption is made possible by closely associating the active CuO nanoparticles with the dye. As shown in Fig. 8, the nanoparticles’ surface causes the dye adsorption rate to stabilize after 30 minutes.

![Figure 8. Effect of time on the cibacron dye adsorption onto the CuO NPs.](image)

**Effect of Adsorbent Mass**

To test the effectiveness of the adsorbent, different masses of CuO NPs 0.005g, 0.01g, 0.05g, 0.1g, and 0.15g were introduced to 50 ppm of dye. Shaking the mixture at 298 K and 200 rpm took place. The relationship between removal percentage and mass is seen in the graph. Because there are more active sites in nanoparticles, adsorption happens very quickly. Fig. 9, demonstrates the increase in dye adsorption, by boosting the bulk of the CuO NPs.

![Figure 9. Effect of CuO NPs mass on dye adsorption](image)
Effect of Temperature

The effect of temperature on dye adsorption on the surface of CuO NPs was investigated at several temperatures 288 K to 328 K. As the temperature rises, the dye adsorption solution volume grows. As a result, the endothermic process. This shows how the mechanics of absorption and adsorption work. As the temperature increases, the diffusion rate increases, and a strong bond is formed with the adsorbent. In the perforations, the diffusion molecules are absorbed. The right evaluation of thermodynamic parameters is necessary because they provide accurate information on changes in inherent energy caused by adsorption. The adsorption free energy (\(\Delta G^\circ\)), enthalpy (\(\Delta H^\circ\)) and entropy (\(\Delta S^\circ\)) were used to analyze the following adjustments to estimate the adsorption process as Eqs. 6-8 34,40-44.

\[
\ln(K_e) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}
\]

\[
K_e = \frac{Q_e}{C_e}
\]

\[
\Delta G = \Delta H - T\Delta S
\]

\[\text{Figure 10. Van't Hoff plot between ln K and 1/T.}\]

Ke is an equilibrium constant, R is gas constant is 8.314 J/mol K, and T is the temperature in Kelvin (K). According to a van't Hoff plot between ln K and 1/T in Fig. 10, the interaction was endothermic and the \(\Delta H\) was 7.69 kJ/mole determent by slope. The \(\Delta S\) from the intercept, which was 24.38 J/mole, indicating that the adsorbed particles were still moving close to the surface. With a positive \(\Delta G\) value of 0.538 KJ/mol at 293 K, non-spontaneous adsorption is implied.

Dynamics

Adsorbent applications depend on the kinetics of dye adsorption on CuO NPs’ surface adsorbents. The dye analysis discovered that for 0.01 g of the CuO nanoparticle adsorbents, the adsorption equilibrium period was approximately 35 minutes. Additionally, in this research, the following information about adsorption was depicted using classical and kinetic models:

Model of pseudo-first-order as Eq. 9 34,40-44:

\[
\ln(qe - qt ) = \ln(qe) - k_1 t
\]

The equilibrium adsorption capacity, \(q_e\) (mg g\(^{-1}\)), the amount of dye that has been adsorbed after time, \(qt\) (mg g\(^{-1}\)), and \(k_1\) is a pseudo-first-order rate constant (min\(^{-1}\)), are shown in Fig. 11. The pseudo-second-order kinetic model is as Eq. 10 31,32:

\[
\frac{1}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe}
\]
Figure 11. Dynamic of adsorption of dye pseudo-first-order

$K_2$ is the second-order rate constant. The pseudo-second-order model may adequately describe the kinetic information with $R^2 = 0.999$, as illustrated in Fig. 12.

Figure 12. Dynamic of adsorption of dye pseudo-second-order.

Conclusion

Green synthesis and imaging with XRD, SEM/EDX, and TEM were used to create high-quality CuO. According to TEM studies, CuO NPs' particle size ranged from 28 nm. For removing dye from aqueous solutions, the observed adsorption properties are perfect. In both kinetic and thermodynamic experiments, the usefulness of CuO NPs as adsorbers was proven. Langmuir and Freundlich isotherm isotherm models were well-suited to the data. Much better describes the adsorption is the Freundlich isotherm model. The adsorption is non-spontaneous and endothermic, according to thermodynamics. The slope of the van't Hoff plot was used to determine the enthalpy value (7.69 kJ/mole), which represents the physical
properties of adsorption. This adsorption follows pseudo-second order with \( R^2 = 0.999 \).

**Authors’ Declaration**

- Conflicts of Interest: None.
- We hereby confirm that all the Figures in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

**Authors’ Contribution Statement**

A.Q.K. was responsible of design, acquisition of data, organized research idea, and contributed to the paper writing. A. M. F. organized research idea and conducted the revision and proofreading of the manuscript.

**References**


34. Hasanin M, Hashem AH, Lashin I, Hassan SA. In vitro improvement and rooting of banana plantlets
using antifungal nanocomposite based on myco-
قابلية امتزاز صبغة السايبكرون الحمراء من محلولها المائي باستخدام دقائق أكسيد النحاس النانوية

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الخلاصة

يصف هذا البحث الإنتاج الصديق للبيئة لجسيمات النحاس النانوية باستخدام مستخلص نبات الجرجير والحرق عند درجة حرارة 400 درجة مئوية لمدة 3 ساعات. تم استخدام TEM وSEM لتحليل حجم الجسيمات النانوية المحضرة. تم استخدام حيود الأشعة السينية لتحديد الهيكل البلوري. كشف التحليل الطيفي للأشعة السينية المشتتة للهيئة النانوية المشتقة للمادة المنتج التي تم إشاؤها عن مكونات النحاس CuO NPs والأكسجين فقط، مما يدل على نقاء المادة المحضر. استخدمت المادة النانوية المحضرة CuO NPs في امتزاز صبغة Cibacron الحمراء. في 35 دقيقة من زمن الاتزان، لوحظ امتزاز أسرع لصبغة Cibacron الحمراء على الجسيمات النانوية CuO NPs. تم حساب المعلمات ΔG, ΔH, ΔS. يمكن الاستنتاج أن CuO NPs هي سطح ممتز فعال لصبغة Cibacron الحمراء.

الكلمات المفتاحية: الامتزاز، صبغة السايبكرون الحمراء، أكسيد نحاس النانوي، التحليل الطيفي للأشعة السينية، التوليف الأخضر.