Green synthesis of copper nanoparticles using *Allium cepa* (onion) peels for removal of Disperse Yellow 3 dye

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**Abstract**

Textile effluent contains an enormous range of colors and heavy metals. When transferred directly to the environment without any further treatment, it stupendously harms the environment by disrupting chemical, biological, and nutritional aspects. Due to their unique physical, chemical, and biological characteristics, low cost, and environmentally friendly nature, copper nanoparticles (Cu NPs) have recently received substantial attention for photocatalytic decolorization of wastewater contaminants. The creation of copper nanoparticles using onion peel extract is the major goal of this investigation. The characterization of produced nanoparticles was done using scanning electron microscopy and X-ray diffraction. Using various optimization parameters, the synthesized copper nanoparticles were used to decolorize the Disperse Yellow 3 dye. The chosen dye was degraded to its greatest extent (73.7%) at the ideal experimental conditions (0.01% dye, 0.01 g/L copper nanoparticles, pH 5, and 50°C). The reductions in chemical oxygen demand and total organic carbon were calculated to be 70.22% and 69.23%, respectively. The current study suggests that copper nanoparticles might be used to filter out other toxic dyes from the textile effluents.

**Keywords:** *Allium cepa* (onion) peels; Copper nanoparticles; Scanning electron microscopy and X-ray diffraction, Disperse Yellow 3 dye, Chemical oxygen demand; Total organic carbon
1. Introduction

Water covers 71% of the entire earth, and natural resources of only around 1% of this water are available for the consumption of human beings [1,2]. Water is a universal solvent that finds its various applications in multi-fields like textile, pharmaceutical, food industries, etc. Water after use must be disposed of in a proper way keeping in view the safety of the surroundings [3]. The contaminated water mainly industrial effluent having synthetic dyes is an alarming threat to the environment for the water bodies which are the recipient of it. The safer way in discarding wastewater is after processing it through the appropriate treatment [4,5]. Various physical and chemical means are in use which have to find their limited applications as either they are associated with phase changes or are associated with more toxic end-products [6]. For the treatment of various issues of wastewater and the environment, among the development of different emerging technologies, nanotechnology has emerged as an effective method for detoxification of pollutants, for example, dyes [7–9]. Biosorption has proven to be a potential process with the advantages of high efficiency even with low metal concentrations, no additional nutrient requirements, low cost, easy operation, and potential metal recovery and with no harmful effects on the surroundings [10–12].

Agricultural waste is a universal term, used for organic substances, disposed of by humans in the procedure of agricultural manufacture. It largely consists of plant waste, domestic animals, poultry dung, agricultural and unimportant products giving out waste, and rural household waste [13]. We discarded most of the peels as waste. The peels of fruits and vegetables can be used as effective sorbents. As “waste peels” are renewable resources and industrial waste if these are applied for the treatment of water and wastewater then these peels show a promising source for environmental technology to treat it [14]. The selected waste material is onion. The onion peel is a readily available, cheap, and environment-friendly material for treating wastewater containing toxic metals. During the last few decades, most recent advances in the field of science and nanotechnology have urged the scientific community to explore the true potential of this technique. It is considered that adopting this unique nanotechnology can be advantageous to exploit more efficient and sustainable solutions to the main water-related issues by using properties of novel nanostructured materials [15,16].

Copper nanoparticles (Cu NPs) possess different physicochemical features that include catalytic, magnetic optical, high surface area to volume ratio, heat transfer, antibacterial and biocidal properties [17,18]. Moreover, copper nanoparticles (Cu NPs) participate a pivotal role in the removal of organic pollutants such as phenols, heavy metals, and their derivatives, insecticides, a nitro group containing fertilizers, and pesticides [19,20]. The development of new green synthetic methods using eco-friendly materials, reagents, and non-toxic solvents is highly suggested with the least wastage of energy and raw materials [21]. In this direction, we have planned the utilization of peels of onion which is one of the most abundant kitchen waste materials for the preparation of Cu NPs, and their use for the removal of selected dye.

2. Materials and methods

At first, Cu NPs were initially created synthetically. In the second section, synthesized NPs were used to optimize the experimental parameters for the decolorization of the Disperse Yellow dye (the structure shown in Fig. 1). Onion was collected from the local market. After that, it was cleaned thoroughly to get rid of stuck-on debris. Peels from onions were dried in the shade. The dry bulk was then put through an electrical blender, filtered, and maintained in a vessel that was tightly sealed.

2.1. Preparation of onion peels extract and copper nanoparticles

450 mL of distilled water was added to the reaction vessel along with 10 g of finely powdered peel. The flask was preheated at 65°C–70°C for 20 min. Thereafter, the spinning and filtering processes were carried out for 20 min at 5,000 rpm. It was preserved at 5°C in the refrigerator. The extract was used about a week after preparation [22]. 10 mL of 0.3 M aqueous solution of copper sulphate was placed in a beaker. The 300 mL of copper sulphate solution is then mixed with 30 mL of onion peel extract. After then, the solution was given 3 days to stabilize. After 3 days, brown particles began to accumulate at the bottom of the container, indicating the presence of our desired Cu nanoparticles. To collect the synthesized Cu NPs, the mixture was centrifuged, filtered, and the leftover was cleaned numerous times with water to remove any remaining unattached polymers. The characterization of copper nanoparticles was measured by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2.2. Experimental procedure and mineralization analysis

50 mL of Disperse Yellow 3 dye solution (0.01%) was made and the pH was kept at 6. To homogenize our dye solution, thymol N, N was added as a dispersing agent. It was combined with copper nanoparticles (1 mg), and the flask was placed on a magnetic stirrer at 40°C for 90 min. Every 15 min, a little sample of the reaction mixture was taken from the reaction chamber to determine its λ_{max} using a spectrophotometer. Numerous experimental factors like the dye concentration (0.01%, 0.03%, 0.05%, 0.07% and 0.1% with 10 times dilution), 4–8 pH, Cu nanoparticles dose (0.001–0.01 g/50 mL) and temperature (40°C–70°C) were rectified. All parameters were optimized by using the use of the identical method. One factor was changed once whereas keeping other factors constant [23].

The dye decolorization experiments were performed three times. The absorbance of all reaction samples was monitored by assessing the absorbance at λ_{max}. Decolorization efficiency was calculated using the equation given below.

\[
\text{Decolorization} (\%) = \left(\frac{I - F}{I}\right) \times 100
\]

where \(I\) is the untreated sample absorbance and \(F\) is the treated sample absorbance.
All the tests were repeated three times and were computed by taking their averages and standard error was calculated [24].

Treated and untreated samples were subjected to two water quality parameters such as chemical oxygen demand (COD) and total organic carbon (TOC) [25]. Based on the experimental results, the degradation pathway for treated disperse yellow three dye was proposed and drawn [26].

3. Results and discussion

3.1. Determination of wavelength of maximum absorbance

The maximum absorbance is measured between the wavelength ranges of 350 and 750 nm, often in intervals of 10–20 nm. To calculate the wavelength of maximum absorbance ($\lambda_{\text{max}}$), various dilutions of dye solution were prepared and their absorbance values were recorded. The $\lambda_{\text{max}}$ was found to be 440 nm (as it is given in Fig. 2).

3.2. Characterization of copper nanoparticles using Allium cepa (onion) peel extract

A concentrated electron beam scans the sample’s surface using an electron microscope technique known as the SEM. After this, the image of the sample is produced. Atoms that are present in the sample interact with the electrons to produce signals. An image is produced by combining the location of the beam and the strength of the detecting signal that showed well-organized Cu nanoparticles (Fig. 3). The XRD measurement in Fig. 4 has shown strong and high-pitched peaks, which is an indication of a crystalline face-targeted cubic (FCC) section of synthesized copper nanoparticles.

3.3. Optimization of experimental conditions to decolorize Disperse Yellow 3 dye

3.3.1. Effect of dye concentration

The concentration of Disperse Yellow 3 dye is a compulsory parameter that has to optimize to study its effect on its removal by the Cu nanoparticles [27,28]. The 0.01% dye resulted in the maximum decolorization (59.1%) in 60 min (Fig. 5a). More rise in dye up to the level of 0.05% caused a decrease in the % decolorization of our dye. With the rising in dye level, its uptaking by the catalyst also boosted up for a certain level [29]. The catalytic response is enhanced up to a certain stage of dye and the reaction is repressed with the rise in the number of dye particles. As more dye molecules may cause self-association, hence may cause their agglomeration, which inhibits the approach of dye molecules towards the available catalytic surface, thus reducing the rate of reaction [23,30–32].

3.3.2. Effect of catalyst particles

The catalyst dose is an essential parameter that should be considered important as it is related to the number of lively sites to be had for its catalytic performance. The high amount of the catalyst usually affects dye degradation. To investigate the most suitable catalyst dose, sequences of experiments were done with copper nanoparticles of different concentrations (0.001, 0.005, 0.007, 0.009, 0.01 g/L). It became evident that as we increase the catalyst level up to 0.007g, the maximum % decolorization (62.3%) was observed at 0.007 g/L. Beyond the 0.007 g/L of copper nanoparticles, no increase in dye decolorization was observed, so 0.007 g/L was found to be the best optimum dose of Cu nanoparticles for decolorization of target dye for successive experiments (Fig. 5b). The rising in decolorization value
with the rise in the catalyst amount is because of an enhanced growth within the total energetic surface vicinity; however, elevated level of the catalyst may cause a turbid appearance in its solution. Moreover, the catalytic performance of the catalyst at its elevated level is probably laid low with the response products, subsequently declining the reaction rate [20,32,33].

3.3.3. Effect of pH

It is imperative to observe the pH effect on the removal of the dye because there is the discharge of textile dyeing wastewater occurs at different pH levels [34]. The dye removal efficiency is greatly affected by the solution pH. A minor variation in pH may change the rate of reaction appreciably. Consequently, the optimization of pH is a very important parameter [35]. The alteration in pH varies the surface activity of Cu nanoparticles and modifies the capacity of reactions catalyzed by catalysts [20]. The highest dye removal (67.8%) value using the copper nanoparticles as catalyst was observed at pH 5.0, as shown in Fig. 5c. It is evident that degradation efficiency improves as pH increases. Further, a decrease in the decolorization was impacted by an increase in pH. It is probably due to the abundance of hydroxyl ions and the repulsive pressure among negatively charged surface and anionic dye particles [36]. A catalytic agent performs proficiently at an optimal pH, beyond which no noticeable decolorization can be achieved. The charges of response rise at lesser pH for less acidic contaminants [37]. The experimental results had been consistent with the literature [38].

3.3.4. Effect of temperature

According to the results of the current experiment, the rate of decolorization of dispersed dyes greatly rises to the most favorable temperature, while decolorization activity decreases slightly thereafter [39]. The percentage of decolorization of Disperse Yellow 3 dye was investigated as a function of temperature (40°C–70°C). 90 min were given for the experiment to run. The greatest degree of decolorization (73.7%) was revealed at 50°C. The decolorization (%) of our dye went on to decline above 50°C (Fig. 5d). It might be due to the reduction within the adsorption capability of the catalyst owed to the sintering technique with a boosting of temperature which ends up in decreased catalyst surface area [23]. A better temperature generally delays the adhesion of dye particles on the catalyst floor as it could be a basis for alteration in the three-dimensional alignment of nanoparticles [40].

![Fig. 4. Characterization of Cu nanoparticles by XRD.](image1)

![Fig. 5. Effect (a) concentration of dye, (b) concentration of nanoparticles, (c) pH, and (d) temperature on decolorization (%) of Disperse Yellow 3 dye.](image2)
3.4. COD and TOC measurements

Using copper nanoparticles as a catalyst, the efficacy of quality control measures including COD and TOC was examined. The assessment of TOC and COD was then switched to the dispersed yellow dye solution. It was shown that as the reaction time increased, the elimination (percent) of both water quality measures increased steadily. Decreases in TOC and COD (in percent) by catalytic treatment were originally 69.23% and 70.22%, respectively (Fig. 6). The percent reduction in both these parameters is an indication that our dye molecule was not only decolorized but also degraded as well. These results are supported by literature too [28,41].

3.5. Proposed degradation pathway of Disperse Yellow 3 dye

The sorption process and catalyzed destruction of dyes make up the fundamental possible mechanisms for capped nanoparticles. Electron transport can be used to explain the dye removal reaction. The efficacy of the compounds to donate electrons and the dye molecule to capture them are directly related to the catalytic efficiency of capped Cu-NPs. First, the dye is adsorbed onto the capped Cu-NPs’ surface. Polyphenols (the capping agent) used after adsorption, operate as a potent nucleophilic agent, whilst the dye particle works as an electrophilic agent. The solution’s Cu-NPs serve as a communication link, transporting the electron needed for the degradation of dye particles from the capping agent to the dye molecule [42–44]. Based on the current experimental studies, the proposed degradation pathway of Disperse Yellow 3 dye by synthesized Cu nanoparticles is given in Fig. 7. Here it is evident, that first of all azo linkage was broken, and then rupturing of the benzene ring took place forming various reaction intermediates, which ultimately ended up in the simplest products [26]. An overall proposed degradation mechanism is given in Fig. 7.

4. Conclusions

This environmentally friendly method uses onion peel extract as capping and reducing agents for the formation of metal nanoparticles. It has many benefits, like easy application for a sustainable environment, renewable, and inexpensive. There is no requirement to employ dangerous substances, high temperatures, high pressures, poisonous chemicals, energy, etc. The maximal decolorization (73.7%) of the selected dye was obtained at optimal experimental conditions (0.01% dye, 0.01g/L copper nanoparticles, pH 5, and temperature 50°C). Percent reductions in TOC and COD were determined which were 69.23% and 70.22%, respectively. These sustainably produced copper nanoparticles have shown promising results in the deletion of Disperse Yellow 3 dye. These Cu nanoparticles can be applied for the removal of other synthetic dyes too; hence can help to minimize the hazardous effects caused by synthetic dyes in wastewater.

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Data availability statement

The whole date is present in this manuscript. We invite researchers that are interested to use this reported method(s) to contact the corresponding author (Shumaila Kiran) for support.

Disclosure statement

No potential conflict of interest was reported by the authors.

References


