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Citrus paradisi fruit peel extract mediated green synthesis of copper nanoparticles for remediation of Disperse Yellow 125 dye

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ABSTRACT

In the present research work, low cost and eco-friendly copper nanoparticles were prepared by a reduction method using grapefruit (*Citrus paradisi*) peels extract as the reducing agent. The nanoparticles were characterized by using UV-visible and scanning electron microscopy (SEM) techniques. The absorption peak at 525 nm in UV-visible spectrum indicated the nature of copper nanoparticles. SEM analysis showed the morphology and structure of copper nanoparticles. The nanoparticle size ranged from 56 to 59 nm. The synthesized copper nanoparticles were utilized for the decolorization of Disperse Yellow 125 dye following the optimization of reaction conditions concentration of dye and copper nanoparticles, concentration of dye and copper nanoparticles, pH, reaction time and temperature. The targeted dye was decolorized 73.5% at 0.01% concentration of dye, 0.05% copper nanoparticles concentration, and 6 pH at 50°C. The experimental results showed that COD and TOC removal efficiencies were 75.56% and 77.23%, respectively. The degradation pathway of the target dye was also studied.

Keywords: Green synthesis; Copper nanoparticles; *Citrus paradisi*; Disperse Yellow 125 dye Decolorization; Mineralization; Degradation

1. Introduction

The rising global population in urban areas is one of the driving factors for the need to secure water. Water is used as a solvent in a variety of industrial operations. The used water is disposed of into the main water body by the industries without any prior treatment [1]. Heavy industrialization has resulted in the production of hazardous waste, which is posing a negative impact on health and environment [2]. The presence of pollutants such as heavy metals, salts, pharmaceuticals, aromatic compounds, and textile dyes in wastewater streams is a major global environmental challenge because a majority of them are toxic and particularly threatening for living organisms [3,4]. Several biological and physiochemical methods such as aerobic and anaerobic biological treatment, membrane filtration, adsorption, etc. have been conventionally implemented for the removal of various environmental pollutants [5–8], but each of them has certain drawbacks, which turned the

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focus of researchers towards a more effective way to reduce toxic pollutants up to the maximum level. Nanotechnology is found to be an economically feasible and viable option for efficient environmental remediation [9,10]. Scientists are synthesizing nanoparticles via various ways such as physical and chemical approaches, but these approaches are mostly associated with ecological issues and noxiousness [11]. The synthesis of nanoparticles by biological means is a greenway as it is found to be eco-friendly and associated with less toxic effects [12].

The cheapest approach is the conversion of agro-waste material into a beneficial one that can be used for environmental remediation. These agro-waste materials are used to prepare metal or metal oxide nanoparticles to remove disperse dyes from textile wastewater [13]. For the removal of dyes, scientists used different physical and chemical methods including coagulation, flocculation, membrane filtration, and adsorption [3]. Nanotechnology opens up a tremendous field of new applications beneficial to the ecosystem. Recent studies have shown that disperse dyes contribute to the remediation of textile wastewater polluted by harmful effluents with the help of copper nanoparticles [14,15].

Grapefruit (*Citrus paradisi*) is a citrus tree in the hotter region. The taste of its fruit is sour to semisweet, somewhat bitter. Grapefruit is rich in vitamin C, pectin, and lycopene. It lowers the cholesterol level in human beings. Grapefruit seeds extract and oil possesses anti-microbial activity [16]. Grapefruit peels act as the best reducing agent to synthesize metal/metal oxide nanoparticles such as gold, silver, nickel, etc. The synthesized nanoparticles could be used for the treatment of industrial effluents especially textile effluents [17].

The nanoparticles find their catalytic applications in many organic reactions such as hydrogenation, hydration reactions of organic molecules having double bonds, oxidation–reduction reactions, and environmental remediation applications [18–20]. Copper nanoparticles (Cu-NPs) play a key part in removing toxins such as heavy metals, phenolics, stimulants, and other agrochemicals. Copper nanoparticles (Cu-NPs) are low cost than other noble metals such as silver, platinum, and gold [21]. Copper nanoparticles have a particular chemical, catalytic, physical, optical, antimicrobial properties, and large surface area [22].

Keeping in view the above-stated benefits of agro-waste materials in the synthesis of metal nanoparticles, the present study was planned to synthesize copper nanoparticles using peels of grapefruit and the application of synthesized copper nanoparticles in the removal of hazardous disperse yellow dye 125 from water.

2. Materials and methods

The current study was committed to establishing a safe methodology to prepare copper nanoparticles (Cu-NPs) and bio-degradation of disperse yellow 125 dye. The experimental work was carried out in the Dept. of Applied Chemistry, GC University, Faisalabad, Pakistan. First, copper nanoparticles (Cu-NPs) were synthesized via a greener approach, which was then used for the remediation of disperse yellow 125 dye (structure given in Fig. 1. below), following the optimization of experimental parameters.

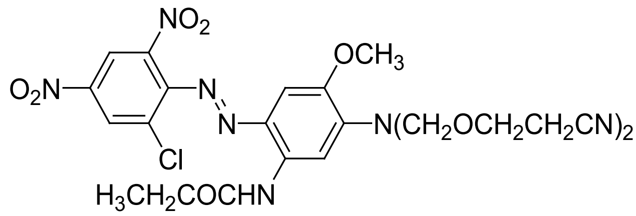

Fig. 1. Structure of disperse yellow 125 dye (C.I.110175).

2.1. Sample collection

Citrus paradisi (grapefruit) peels were collected from the local fruit market of Faisalabad, Punjab, Pakistan. These peels were washed thoroughly with distilled water, ground, sieved, and stored in an airtight container.

2.2. Preparation of aqueous extract of Citrus paradisi (grapefruit) peels

About 10 g of finely powdered *Citrus paradisi* (grapefruit) peels were taken in 450 mL of distilled water in a measuring vessel. The mixture was covered with aluminum foil for complete sealing and heated at 65°C for 15 min. The reaction mixture was cooled and centrifuged at 5,000 rpm for 15 min and was filtered. The extract was stored at –4°C for the next usage. The aqueous extract was used within a week to avoid any contamination [23].

2.3. Preparation of copper nanoparticles (Cu-NPs)

100 mL of aqueous solution (0.1 M) of anhydrous copper sulfate was taken in a reaction vessel and 100 mL of *Citrus paradisi* (grapefruit) peels extract was added into it. The pH of the reaction mixture was adjusted to 4 using 0.1 M NaOH/0.05 M H_2SO_4. The reaction vessel was put on hot plate and heated at 70°C for 20 min. After that, the reaction mixture was left for 72 h. After 3 d, brown precipitates were formed at the bottom of the reaction vessel which indicated the presence of copper nanoparticles (Cu-NPs). These particles were then centrifuged about 5,000 rpm for 15 min, filtered and the residue was washed with double distilled twice to get rid of any impurity to yield the stable copper nanoparticles (Cu-NPs) [23].

2.4. Characterization of nanoparticles

Copper nanoparticles were characterized by scanning electron microscopy (SEM) and X-ray diffraction technique (XRD).

2.5. Scanning of λ_{max}

Different solutions of disperse yellow 125 dye were prepared at different concentrations (0.01–0.05% w/v) in distilled water and then diluted up to 50 mL. Thymol N (1%) was added as a dispersing agent, which makes the solution homogeneous. The pH of this solution was maintained using 1 M NaOH/0.5 M H_2SO_4. These series of dye solutions were used to scan λ_{max}.

2.6. Experimental procedure

50 mL of dye solution (0.01%) was prepared in distilled water and pH was adjusted to 6 using 1 M NaOH/0.5 M H_2SO_4. Nickel nanoparticles (1 mg) were added into it and the reaction vessel was placed on a hot plate at 40°C for 90 min. The progress of the reaction was assessed by taking out a small amount of sample from the reaction vessel after every 15 min and noting its absorbance at λ_{max} using a spectrophotometer [24].

Disperse Yellow 125 dye concentration was varied from 0.01 to 0.05% w/v with 10 times dilution and copper nanoparticles (Cu-NPs) concentration was changed from 0.001 to 0.009 g/L. pH was varied from 4 to 8 and temperature from 40°C to 70°C. All parameters were optimized using the same methodology. One parameter was varied at a time while other parameters remained the same.

2.7. Chemical analysis

All the tests were carried out thrice. The process performance was examined using UV-vis spectroscopy by measuring absorbance at 450 nm. The effectiveness of decolorization (%) of all parameters was assessed using the formula given below:

$$\text{Decolorization}\left(\%\right)=\frac{\left(I-F\right)}{I}\times 100 \quad (1)$$

where I shows the absorbance of the untreated dye sample and F is the absorbance of the treated dye solution.

2.8. Mineralization study

Dye solutions were assessed through different water quality parameters such as COD and TOC [25].

To calculate COD, digestion vials were used. 3.5 mL of catalyst solution (solution of silver sulfate in concentrated sulfuric acid), 1.5 mL of digestion solution (solution of potassium dichromate in acidified mercuric sulfate), and 2.5 mL of dye sample were added into vials. A blank sample having all material instead of a dye sample was also prepared in deionized water. The vials were put in an oven for 110 min at 150°C. Then vials were chilled and their absorbance values were noted at 600 nm.

To find out TOC value, 1.6 mL of concentrated H_2SO_4, 1 mL of potassium dichromate solution (2 N), and 4 mL of treated dye solution were added in a vial. The same sample having all materials except dye solution was prepared which served as blank. The digestion vials were kept in the oven for 90 min at 110°C. Then vials were chilled and their absorbance values were noted at 590 nm.

The blank sample absorbance was deducted from the absorbance of the sample for the precise estimation of the sample.

The following formula was used to find out COD and TOC values:

$$\frac{\text{TOC}}{\text{COD}}=\text{SF}\times A \quad (2)$$

where SF indicates standard factor; A indicates absorbance; whereas standard factor can be calculated as follows:

$$\text{Standard factor}=\frac{\text{Conc. of standard}}{\text{its absorbance}} \quad (3)$$

2.9. Degradation study

The degradation of disperse yellow 125 dye was evaluated in different steps with the breakage of bonds and the formation of new compounds [26].

2.10. Statistical analysis

The data were collected in triplicate and the values were computed as an average of triplicate using standard error of means [27].

3. Results and discussion

The research work was aimed at a low cost and eco-friendly methodologies for degradation of disperse yellow 125 dye. At the first stage, stable copper nanoparticles (Cu-NPs) were prepared using *Citrus paradisi* (grapefruit) peels. The second stage involved the use of these stable copper nanoparticles (Cu-NPs) for decolorization of disperse yellow 125 dye following the optimization of experimental factors.

3.1. Part one: preparation of copper nanoparticles (Cu-NPs) using Citrus paradisi (grapefruit) peels

The copper nanoparticles were characterized by SEM. The size and morphology of copper nanoparticles (Cu-NPs) were monitored by SEM and the results of the pictures clarified sphere-like the structure of copper nanoparticles having 56–59 mm diameter as shown in Fig. 2a [28]. XRD patterns obtained for the CuNPs synthesized using grapefruit peels aqueous extract is shown in Fig. 2b. The intense peaks (111, 200, 220) are present in the graph, which indexed a crystalline face-centered cubic (FCC) phase of copper nanoparticles.

3.2. Part two: measurement of "λ_{max}" for disperse yellow 125 dye understudy

The solution's strength could be measured by the determination of its quantity to be adsorbed. The wavelength of maximum absorption (λ_{max}) was calculated using a UV-Visible spectrophotometer. Dye solution was prepared in water. Thymol N (1%) was added as dispersing agent to make the solution homogeneous to avoid any suspension to ensure compliance with the Beer–Lambert law. For it, a range of wavelengths was selected in the visible region. The graph was plotted for the measurement of λ_{max}. The λ_{max} was found to be 450 nm (Fig. 3).

3.3. Optimization of experimental conditions for decolorization of disperse yellow 125 dye

In this section, the research was carried out with disperse yellow 125 dye solution to optimize various experimental parameters (concentration of disperse yellow 125 dye,

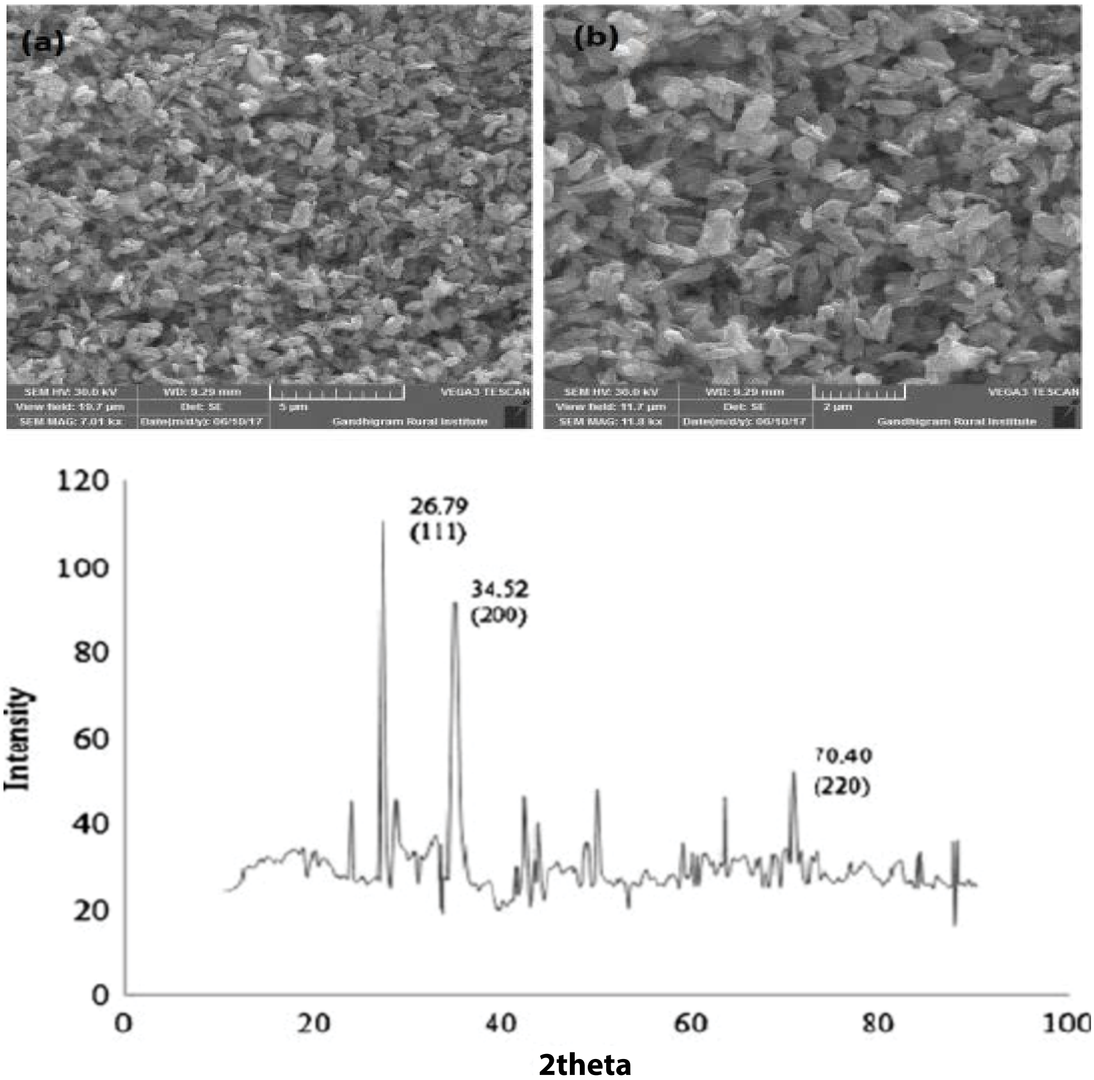

Fig. 2. (a) SEM images of synthesized copper nanoparticles and (b) XRD pattern of FCC phase of copper nanoparticles.

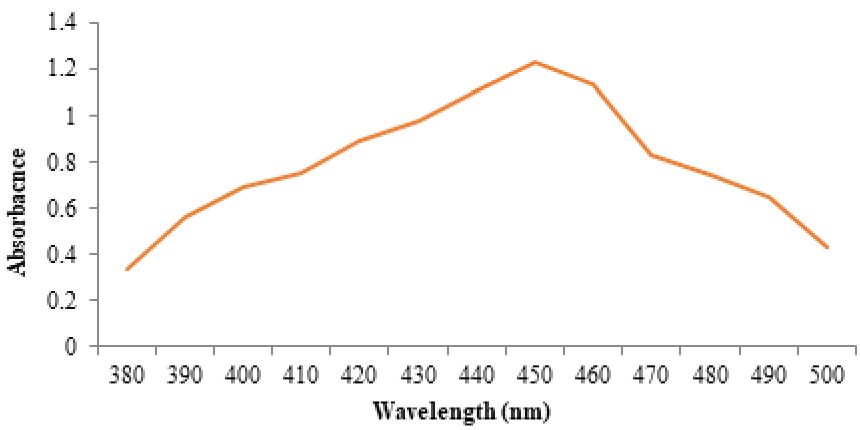

Fig. 3. Scanning of λ_{max} of disperse yellow 125 dye.

catalyst dose, reaction time, pH, temperature), which affect the rate of decolorization of disperse yellow 125 dye.

3.3.1. Optimization of the concentration of disperse yellow 125 dye

The concentration of a dye is a necessary parameter for catalytic treatment [29]. It has been found that by raising the initial concentration of dye increases the amount of adsorbed dye as well; thus, it can be said that the removal of dye is affected by its initial concentration [30,31]. The quantity of substrate is the most important factor for the treatment of effluents having dyes. Different concentrations (0.01%–0.05%) of disperse yellow 125 dye were taken in the current study. Maximum decolorization (63.4%) of disperse yellow 125 dye was achieved at a 0.01% level. Further increase in the concentration of dye resulted in the subsequent decrease in its decolorization (Fig. 4a). Dye molecules act as a substrate for copper nanoparticles catalyst. More number of dye molecules may cause their self-association causing turbidity of the dye solution. Moreover, more substrate concentration may act as an inhibitor for a catalytic site, hence retarding the reaction rate. It was also noted that the bio-degradation is decreased when the concentration of disperse yellow dye was increased due to the turbidity of the solution and the substrate acts as an inhibitor. When disperse yellow dye concentration is maximum, the effectiveness of the catalyst reduced [32,33].

3.3.2. Effect of catalyst dose

The amount of catalyst greatly affects the dye decolorization [34]. The rate of decolorization of dye is increased when the concentration of the catalyst is enhanced. The reason behind this is that when we increase the quantity of the catalyst, the number of active sites is increased [35]. A wide range of experiments was performed. It was noted that when catalyst concentration was raised in range 0.001–0.005 g/L, the percentage of dye decolorized was raised from 30.6% to 68.9% (Fig. 4b). So 0.005 g/L catalytic dose of copper nanoparticles (Cu-NPs) is found to be its optimal concentration of catalyst for decolorization of targeted dye. When active sites of catalysts are fully saturated with dye molecules, then no further increase in reaction rate could be observed. The increased quantity of catalysts might cause turbidity of the solution resulting in a decrease in reaction rate [36,37].

3.3.3. Effect of pH change

The pH of the dye solution is a key parameter as it effects on ionization rate of dye and it can change the nature of charges on the surface of the adsorbent. It is noted that the pH of the aqueous phase is the crucial parameter, which affects the surface charge of an adsorbent [38]. A series of catalytic experiments were performed with varying pH from 4 to 8, keeping the optimized variables constant. As pH was raised from 4 to 6, the decolorization of the dye understudy went on the increase from 54.1% to 73.5%. A further rise in pH up to 8 resulted in a gradual decline in the decolorization of dye. At very low pH, due to protonation of dye molecules, less number of dye molecules gets adsorbed on the catalytic surface. The attractive forces between positively charged catalytic surfaces and negatively charged target dye molecules are probably more at pH 6, hence maximum catalytic efficiency was observed (Fig. 4c). Moreover, catalysts possess an optimum pH value for their maximal catalytic potential [39]. pH level above the optimum one may cause denaturation of the catalyst [40].

3.3.4. Effect of temperature

Experiments were carried out to assess the effect of temperature on decolorization of disperse yellow 125 dye using an optimal dose of copper nanoparticles (0.005 g/L) as a catalyst at a temperature range of 40°C–70°C. On increasing the temperature from 40°C to 50°C, the efficacy of dye decolorization raises from 68.7% to 77.4%, showing a dependency of the catalytic action of copper nanoparticles on temperature (Fig. 4d). When the temperature was further increased up to 70°C, the decolorization of dye was decreased up to 54.7%. So, 50°C was found to be the optimum temperature for the maximal decolorization of disperse yellow 125 dye by copper nanoparticles. The possible reason is that catalysts have several active sites to catalyze reactions. Catalysts show their maximum catalytic activity at a particular temperature only. The temperature beyond the optimal one may cause an irreversible change in the three-dimensional structure of catalysts, hence losing their catalytic activity. It is evident from the decrease in decolorization (%) of dye understudy with a further rise in temperature (Fig. 4d) [37]. The increase in temperature may cause a change in the three-dimensional structure of catalyst, hence affecting its binding ability for dye [41].

3.4. Mineralization study

The quantity control factors such as chemical oxygen demand (COD) and total organic carbon (TOC) for the treatment of disperse yellow 125 dye with the help of copper nanoparticles (Cu-NPs) catalyst were used to calculate the mineralized performance. The disperse yellow 125 dye solution was put to check COD and TOC. Percentage reductions in COD and TOC were calculated at different contact time intervals from 10 to 70 min. It was noted that as the contact time was increased from 10 to 50 min, the percentage reduction of both these factors was increased (Fig. 5). The further rise in contact time up to 70 min resulted in the decline in percentage reduction of COD and TOC (Fig. 5). A literature survey showed that the products of a reaction may decrease the reaction rate as they may act as inhibitors [42]. High values of COD and TOC removals revealed that Cu-NPs not only degrade our targeted molecules but also significantly mineralized it as well as reaction byproducts produced during catalytic reaction [43].

3.5. Dye degradation study

According to heterogeneous reactions, the dye molecules are initially adsorbed onto the active sites of Cu-NPs owing to their surface area [44]. Disperse Yellow 125 dye belongs to the class of azo dyes. First, the degradation of

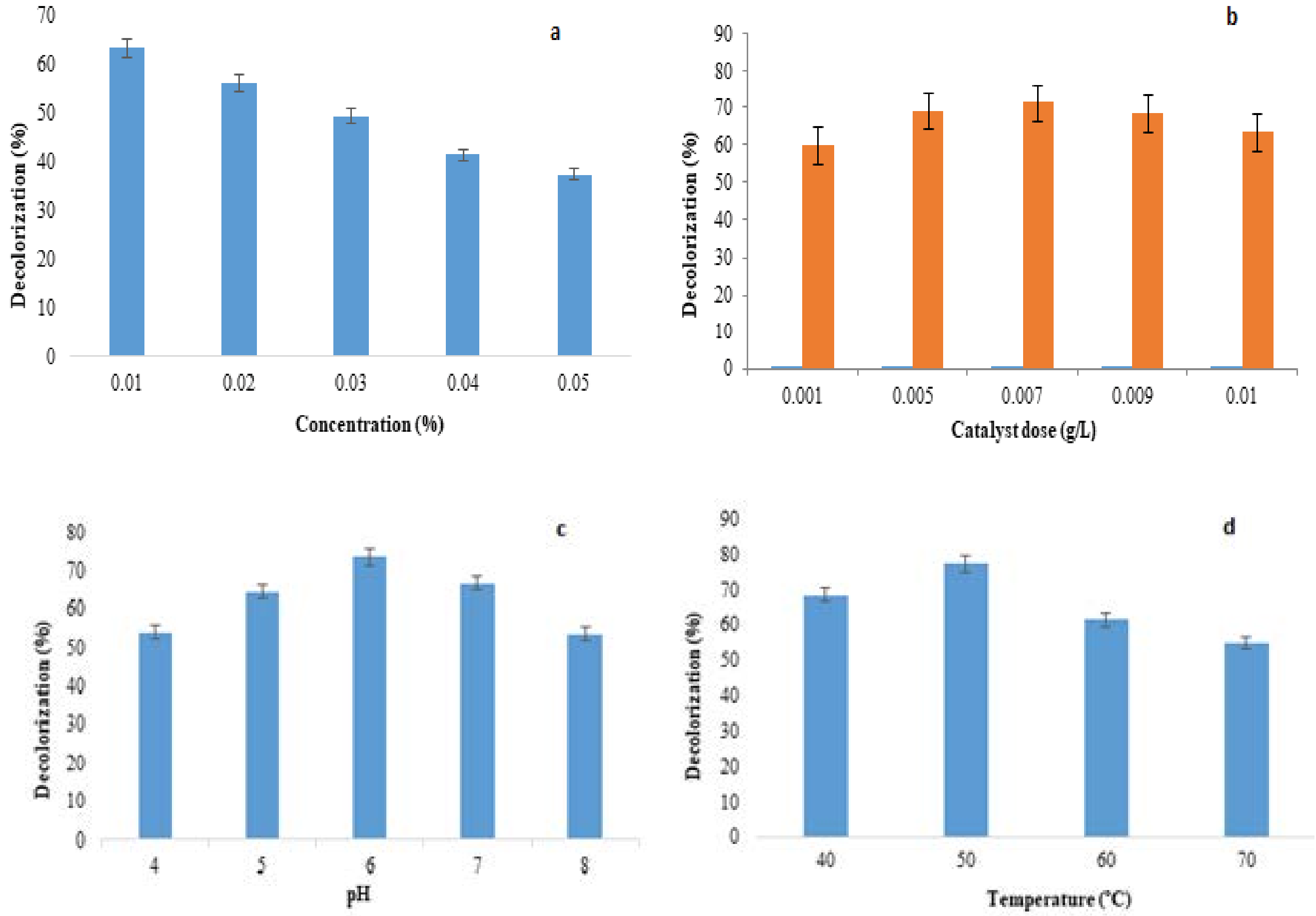

Fig. 4. Effect of dye concentration (a), concentration of catalyst (b), pH (c), temperature (d) on decolorization (%) of disperse yellow 125 dye using copper nanoparticles as a catalytic agent.

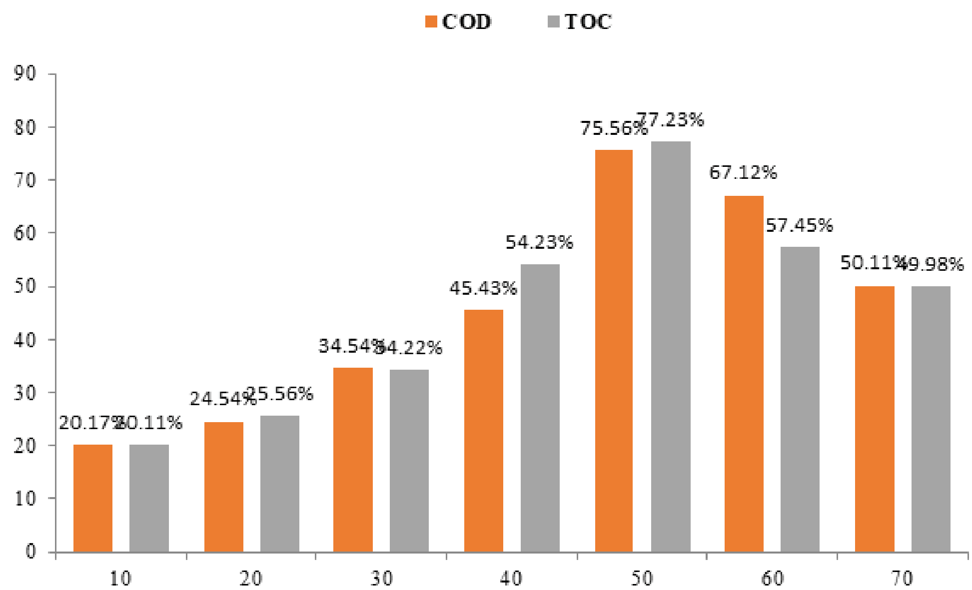

Fig. 5. Effect of catalytic treatment contact time on water quality control factors.

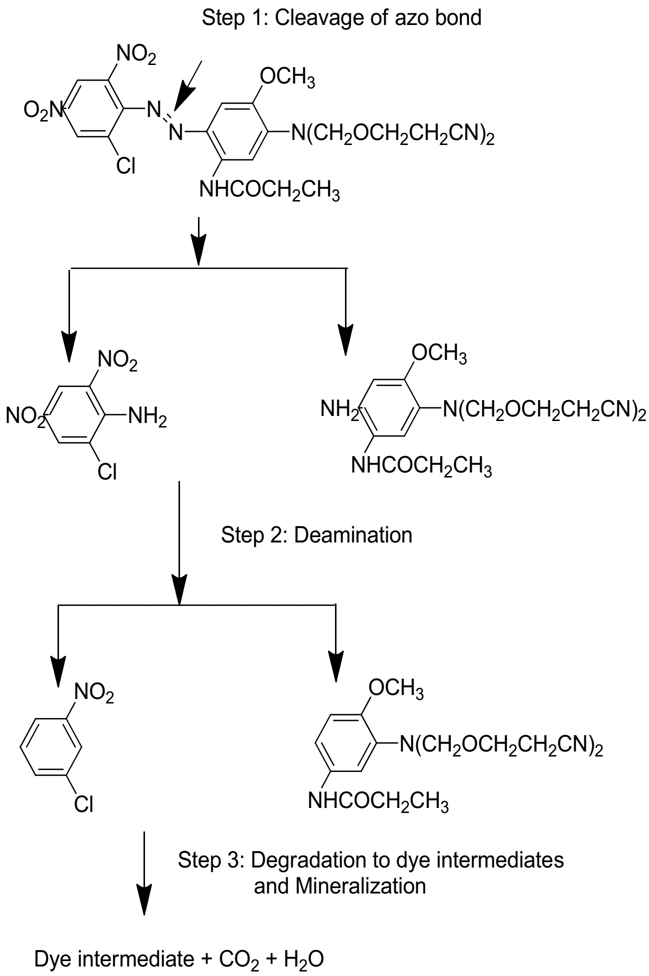

Fig. 6. Degradation pathway of disperse yellow 125 dye.

this dye took place via the breakage of an azo bond (N=N) as shown in Fig. 6. In the second step, deamination took place. Overall, it can be said that our dye molecules were broken down into different intermediates, which were finally converted into the simplest products such as carbon dioxide and water. The following possible mechanism may demonstrate the degradation of disperse yellow 125 dye by copper nanoparticles (Cu-NPs).

4. Conclusion

Agro-waste material comes under the category of agricultural waste, which could be a potential candidate for the synthesis of nanoparticles. Copper nanoparticles (Cu-NPs) were synthesized via a green route from *Citrus paradisi* (grapefruit) fruit peel aqueous extract. Grapefruit peel aqueous extract reduced the Cu^{2+} ions to Cu^0. Copper nanoparticles were synthesized using grapefruit peel aqueous extract and Cu-NPs were characterized by SEM and crystallinity was determined by XRD spectra. Cu-NPs were applied to decolorize disperse yellow 125 dye. The targeted dye was decolorized up to 77% at 0.01% dye concentration, pH 6, 0.005 g/L copper nanoparticles concentration at 50°C. COD and TOC values were found to be 75.56% and 77.23%, respectively. The degradation pathway confirmed the formation of the simplest products. So, it can be concluded that biosynthesized copper nanoparticles could be successively used for the remediation of other azo dyes.

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