Solanum Nigrum Leaf Extract Capped Copper Oxide Nanoparticles and its Tetrahedral $L_2Cu(\eta^2-BH_4)$ Complex for Effective Degradation of Congo Red

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Abstract

In this work, we reported the green synthesis of *Solanum nigrum* extract capped copper oxide nanoparticles (SN@CuO NPs) at room temperature, avoiding harsh, toxic, and environment unfriendly chemicals. The synthesized SN@CuO NPs, were analyzed with the help of spectroscopic techniques. UV-visible spectroscopy confirmed the synthesis of SN@CuO NPs in reaction mixture while fourier transform infrared spectroscopy (FTIR) results revealed capping of phytochemicals of *Solanum nigrum* over the surface of CuO NPs. Morphology and elemental composition of formed SN@CuO NPs were explored with the help of FE-SEM, TEM, and EDS, respectively. Crystalline nature, surface charge and specific surface area was characterized using XRD pattern, DLS and BET analyses, respectively. The data obtained from spectroscopic analyses specified the formation of mesoporous, positively charged and highly stabilized CuO nanoparticles due to adsorption of phytochemicals present in *Solanum nigrum* leaf extract on the CuO nanoparticle's surface. SN@CuO NPs have shown promising catalytic activity towards reduction of highly carcinogenic dye Congo red making use of sodium borohydride. Negatively charged reactants like anionic Congo red molecules and BH_4^- ions eagerly adsorbed on positively charged, small sizes (5–6 nm), mesoporous SN@CuO NPs surface having wide surface area. It is proposed that BH_4^- ions interacted with SN@CuO NPs to form Cu tetrahydroborates dihydrogen bonded (DHB) tetrahedral $\text{L}_2\text{Cu}(\text{H}_2\text{-BH}_4)$ complex, which is proved as an effective reducing agent. This complex acts as dihydrogen source for rapid reduction of azo bond. UV-visible, FTIR, ^1H NMR, ^{13}C NMR, and LC-MS studies of reaction mixture at different reaction stages have shown that the major degradation intermediates were benzidine and α -naphthol. The apparent rate constants for the products at intermediate and final degradation stages have been found to be 0.468 min^{-1} and 0.0189 min^{-1} , respectively. A plausible degradation mechanism for Congo red reduction has also been proposed in this study.

1. Introduction

In the comparison of natural colorants, synthetic dyes, mainly azo dyes containing $-\text{N}=\text{N}-$ group is an essential class of coloring materials due to the production of a vast range of colors, low cost, easy product coloration, and long lifetime of color stability, however, these are simultaneously responsible for environmental and health hazards (Sha et al. 2016). Despite high carcinogenic nature, Congo red has widely been used in printing, textile, cosmetic, leather, paper, and pulp manufacturing industries (Kalwar et al. 2013, Kamal et al. 2016, Nasrollahzadeh et al. 2016, Zhang et al. 2014). A significant quantity of Congo red is drained into the aquatic system as common waste, especially during the dyeing process (Ganapuram et al. 2015). Thus, excessive use of Congo red is responsible for environmental pollution, which needs an easy and cost-effective method for its degradation and complete removal (Rajesh et al. 2014).

In the past, several physical techniques like adsorption, (Ma et al. 2012, Meng et al. 2015) ultrafiltration, (Dos Santos et al. 2007) and ion exchange, (Labanda et al. 2009) have been applied for the removal of azo dyes; however, these methods have drawbacks such as high cost, problem of secondary wastes, slow

process, transfer of dye from one medium to other and production of toxic byproducts which are difficult to destroy. The biological methods using bacteria, fungi, and yeasts have also been reported; however, treatment methods have strong selectivity and require harsh degradation conditions (Banat et al. 1996, Martins et al. 1999, Wesenberg et al. 2003). In comparison of above methods, the chemical treatment of dye degradation is considered as efficient and fast method. The chemical treatment methods utilize decolorization, reduction, oxidation and degradation of hazardous dyes using suitable catalysts. In the catalytic reduction, azo bond of dye molecules are cleaved and converted into less toxic and environmentally benign products. In the past, zero valent metals such as iron, (Rodriguez et al. 2014) iron-nickel alloy, (Bokare et al. 2008) and cobalt (Sha et al. 2016) have been used as effective eco-friendly reductive catalysts for dye degradation. Large number of works have been published on catalytic degradation of Congo red in the last decades, in which most of the works were on borohydride reductive degradation using metal nanoparticles catalysts (Naseem et al. 2018). However the metals used in the above studies, like Ag, Au, Pt, Pd etc and the chemicals are either very costly or very hazardous to living organism. Therefore there is a challenge before researches to generate low cost and environmentally sustainable routes to produce catalysts, which can be applied efficiently in reduction of dye using sodium borohydride.

Among various transition metal oxides, CuO nanostructures have gained enormous attention due to their low cost, optical, catalytic, and antimicrobial properties (Kannan et al. 2020). Copper is a coinage metal having a wide range of applications in our day to day life, which belong to the 3d transition series of the periodic table with 29 protons in its nucleus. It is a highly malleable and soft metal abundantly available in nature, with sufficiently high thermal and electrical conductivities (Aazadfar et al. 2018). Among the different transition metals, copper and copper oxide nanostructures are more affordable than similar other transition metals, for example, platinum, silver, and gold (Reddy 2017). Copper oxide nanostructures have attained great interest in diverse research areas, such as catalysis, (Manjari et al. 2017, Ramachandran et al. 2019) solar cells, (Sharma et al. 2015) biodiesel, (Varghese et al. 2017) water treatment, (Paternela et al. 2018) and supercapacitors (Pendashteh et al. 2013). It also possesses different valuable and important properties, such as low cost, non-toxicity, rapid, and ease of preparation (Pendashteh et al. 2013). The physical and, chemical methods used to synthesize CuO nanostructures involve several problems like high temperature and pressure, reducing agents, organic solvents, and hazardous chemicals (Araújo et al. 2018).

The major limitation of nanoscale copper oxide particles is lack of sufficient stability because of large energy associated with their high surface area of their dispersions and therefore they have strong tendency to aggregate and form larger clusters (Hotze et al. 2010, Solioz 2018, Wozniak-Budych et al. 2017, Zhou et al. 2019). The cluster formation leads to rapid sedimentation which diminishes reactivity and activity of copper oxide, gained from nanomaterials size (Hotze et al. 2010). To overcome this problem surfactants like SDBS, CTAB, AOT etc. have been used as stabilizers and to generate nanoparticles with uniform size (Morsy 2014, Usman et al. 2013).

To meet out above limitation and to mitigate the drawbacks, the use of plants is a sustainable route for synthesis. Currently, green fabrication of metal oxide nanostructures plays a key role in the betterment of humanity and for the sustainment of nature. 'Green Chemistry' is supposed to be the best alternative for the synthesis of metal oxide nanomaterials in contrast to toxic and harsh chemical methods (Araújo et al. 2018, Kruk et al. 2015, Solairaj et al. 2017). Plant extract mediated synthetic approach is not only very fast and cost-effective for bulk production of highly stable nanostructures, but also act as stabilizer due to capping of phytochemicals over NPs surface (Iravani 2011). Recent researches have shown that biological materials mediated synthesis of CuO nanostructures is based on the ability of biomolecules such as, honey, egg white, bacteria, fungal and plant extracellular compounds, (Jain et al. 2011) to reduce copper salts and to stabilize nanostructures. Particularly extracts from various plant materials have demonstrated the use in the fabrication of CuO nanocrystalline materials due to bioactive components, which act as capping and reducing agents and thus help to evolve different morphologies and small sizes nanostructures (Buazar et al. 2019, Manjari et al. 2017, Muthuvel et al. 2020, Qasem et al. 2020, Venkata et al. 2019). *Solanum nigrum* is a most common plant which is medicinally important, easily available and widely employed plant in oriental medicine, wherein it is believed to be highly antioxidant, anti-tumorigenic, anti-inflammatory, diuretic, hepatoprotective, and antipyretic (Jain et al. 2011). In this work, a new approach has been developed to synthesize SN@CuO NPs, mediated by *Solanum nigrum* leaf extract without utilization of any toxic and harsh chemicals or reagents. The catalytic activity of as produced SN@CuO NPs has been examined for degradation of Congo red as a model reaction in the presence of sodium borohydride.

Congo red molecules are not reduced readily in aqueous media by addition of reducing agent NaBH₄ as such, because reaction is not kinetically feasible. For reduction of congo red, electrons need some support and pathway to move rapidly from borohydride ions to congo red molecules (Naseem et al. 2018). Because of high surface area, large surface-to-volume ratio having surface active sites, mesoporous nanostructured metal oxides have been extensively used catalysts for waste water treatment. Adsorption of dyes onto the adsorbents depend upon surface charge, hydrogen bonding, pH of medium, coordination effect, surface properties and porosity, functional groups of adsorbed molecules and morphological diversity of adsorbents (Labanda et al. 2009). Moreover, the borohydride ions in suitable reaction environment interact with copper to form Cu tetrahydroborate dihydrogen bonded (DHB) tetrahedral L₂Cu(η²-BH₄) complexes. The DHB complexes involving both bridging and terminal hydride hydrogens are proved to be effective reducing agents (Belkova et al. 2017).

In view of above facts, the present investigation is focused on generation SN@CuO NPs via a novel sustainable method using *Solanum nigrum* leaf extract as reducing and outshining agent, and to understand role of size, surface properties, porosity, surface charge and metal-borohydride coordination of SN@CuO NPs on catalytic activity for degradation of dye Congo red.

2. Experimental

2.1 Materials

Analytical grade copper sulfate pentahydrate (Sigma-Aldrich Pvt.Ltd.), Congo red and NaBH_4 (Loba Chemie Pvt. Ltd.), ethanol, diethyl ether, acetone, acetonitrile and HCL were purchased from fischer scientific Pvt. Ltd. and used in the experiments without further distillation. The *Solanum nigrum* leaves were collected from Babasaheb Bhimrao Ambedkar University campus.

2.2 Preparation of *Solanum nigrum* leaf extract

Fresh and good quality leaves of *Solanum nigrum* were plucked from the university campus and washed gently, three or four times with distilled water, followed by milli-Q water in a glass bowl to remove any kind of unwanted dust particles and other impurities present along with the leaf sample. These washed up leaves were then sun-dried for two days and grounded in the form fine powder. 10g of grounded leaf powder was refluxed with 250 mL of milli-Q water for 90 minutes in a 500 mL round bottom flask. Therefore, refluxed solution was allowed to cool and then solution was filtered using filter paper (Whatman no. 1). The supernatant, a wine red colored *Solanum nigrum* leaf extract, was kept in a flask, was wrapped and stored at 4°C for further use.

2.3 Synthesis of SN@CuO NPs using *Solanum nigrum* leaf extract

In this method, 100 mL of *Solanum nigrum* leaf extract was poured in 500 mL of 15 mM $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ aqueous solution. This reaction mixture was agitated vigorously (1000 rpm) using a magnetic stirrer at room temperature. The gradual change in color of reaction mixture from green to blackish-green designated the formation of stable SN@CuO NPs at room temperature. The centrifugation was done at 7000 rpm for half an hour to segregate the fabricated SN@CuO NPs, and the obtained solid material residue was washed repeatedly with milli-Q water, ethanol and acetone, to take out impurities and unwanted phytochemicals. The thoroughly washed SN@CuO NPs were then dried for 4 hr and stored in a sample vial for characterization and further use.

2.4 Characterization:

The UV–Visible spectra of SN@CuO NPs and degradation product were recorded in absorption mode with a Carry 100 dual-beam spectrophotometer between the 200–800 nm regions. FTIR spectra of leaf extract of *solanum nigrum* and synthesized SN@CuO NPs have been recorded on Perkin Elmer Spectrum II equipment. The X-ray diffraction pattern of synthesized SN@CuO NPs was recorded on PANalytical's X'Pert Pro X-ray diffractometer in the 2θ range 20–90°. FE-SEM and energy dispersive X-ray (EDS) analyses of the SN@CuO NPs were carried out on Zeiss (Merlin Compact) equipment. Transmission electron microscopy images of the SN@CuO NPs were recorded using JEOL-2100 equipment. Nitrogen adsorption-desorption and pore-size diameter have been estimated by Belsorp mini-II instrument. Zeta potential of SN@CuO NPs has been measured using Zetasizer ZS90 (Nano series Malvern Instrument) at room temperature. NMR Studies of degradation product of Congo red were performed on 400 MHz solution state (Bruker) instrument, and LC-MS was performed on Agilent 6520 Q-TOF mass spectrometer.

2.5 Catalytic reduction of carcinogenic water pollutant Congo red

The catalytic performance of as-synthesized SN@CuO NPs was examined for degradation of anionic dye; Congo red as a model reaction. In the experimental work, 10 mL of freshly prepared aqueous NaBH₄ (0.30 M) solution was added to 10 mL aqueous solution of Congo red (1.0 mM), and UV-Visible spectra was studied for detection of any change in color or reaction mixture i.e. reaction progress but no visible change in either color or intensity was detected even after 8 hours without SN@CuO NPs. However, in the presence of 5 mg of SN@CuO NPs, the rapid disappearance of red color of Congo red detected within 432 seconds. An aliquot of reaction mixture was separated, extracted using diethyl ether and analyzed using FTIR, ¹H NMR, ¹³C NMR, and LC-MS, to identify the intermediate formed, while the rest part of reaction mixture was monitored again for further degradation. Moreover, The rate of Congo Red degradation was also investigated.

3 Results And Discussion:

The UV-visible spectrum of SN@CuO NPs formed using *Solanum nigrum* leaf extract has been depicted in Fig. 1. It contains specific absorbance band at 320 nm belonging to cinnamoyl rings of phenolic compounds present in the *Solanum nigrum* leaf extract and nearly at 225 nm related to benzoyl system of phytochemicals (Nasrollahzadeh et al. 2019). This spectrum consists of a sharp band at 368 nm suggesting the formation of SN@CuO NPs at room temperature. The surface plasmon resonance shown by SN@CuO NPs is due to the spherical shape and small size of these nanostructures (Naika et al. 2015).

The FTIR investigation was done to recognize the nature and class of phytochemicals present in *Solanum nigrum* leaf extract in charge of fabrication of SN@CuO NPs and adsorbed on the surface of nanospheres as outshining or stabilizing agents. The FTIR spectrum of *Solanum nigrum* leaf extract (Fig. 2a) involved three leading peaks nearly at 3309 cm⁻¹, 2125 cm⁻¹, and 1634 cm⁻¹. The broad and strongest peak at 3309 cm⁻¹ commonly correlates to N-H stretching, and the second peak in spectra at 1634 cm⁻¹ indicates the stretching frequency of the carbonyl (C = O) group of secondary amides. It also consists of minor peaks between 1240–1260 cm⁻¹, which indicates an amide band of random coils of protein molecules (Ramesh et al. 2015). The broad and intense peak between 3250–3450 cm⁻¹ is due to O-H and N-H stretching of phenols, (Larsson 2014) amines, and amide linkages of enzymes or proteins (Shankar et al. 2003). In the FTIR spectrum of *Solanum nigrum* leaf extract outshined CuO nanoparticles (Fig. 2b) peak at 3309 cm⁻¹ due to N-H stretching remains unvaried; however, C = O stretching frequency of secondary amides has been somewhat conveyed to the lower frequency at 1626 cm⁻¹. This designates that the interplay of secondary amides of *Solanum nigrum* leaf extract with Cu^{II} ions occurs through C = O (Cu-C = O). The FTIR results demonstrated that *Solanum nigrum* leaf extract participated in two main purpose, i.e., in the formation of SN@CuO NPs and their stabilization by adsorbing or outshining on nanoparticle surface.

The synthesized CuO nanoparticles capped by *Solanum nigrum* leaf extract were dried in oven @80°C, and an XRD pattern was recorded to detect the phase and crystallinity of SN@CuO NPs. In the XRD pattern (Fig. 3) appearance of sharp, intense, and broadened peaks specified the preparation of well crystalline, mesoporous nanospheres. The significant peaks were brought to light at 2θ values 32.1, 35.4, 38.2, 46.4, 48.3, 53.9, 57.6, 61.8, 65.7, 67.6, 72.6, 74.7 and 80.8° representing the reflection planes (Miller indices; (hkl)) of (110), (002), (111), (112), (-202), (020), (202), (-113), (-311), (-220), (311) and (-222)), respectively, which indicated the formation of CuO (JCPDS card no: 45–0937), as reported earlier. The mean size of *Solanum nigrum* leaf extract mediated CuO nanoparticles was calculated using the Debye Scherrer formula, Eq. (1).

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

1

Where D is the mean crystallite size, λ signifies wavelength of X-ray (0.1546 nm) used, β stands for FWHM (full width at half the maximum) in radians, while θ for the Bragg's angle. The calculated mean size of the SN@CuO NPs was found to be 9.5 nm using (111) XRD peak.

The morphology, size and elemental composition of fabricated SN@CuO NPs were examined by FE-SEM, TEM and Energy-dispersive X-ray spectroscopy (EDS) analyses as shown in Fig. 4. In the FE-SEM images, 80–120 nm diameter spherical particles are clearly visible (Fig. 4a,b). FE-SEM images further revealed that most of the SN@CuO NPs have indistinguishable shapes and sizes, stipulating uniformity throughout the SN@CuO NPs sample. The EDS spectrum and elemental mapping of *Solanum nigrum* leaf extract outshined CuO nanoparticles revealed that apart from Cu and O, the presence of P, S and Cl due to presence of phytochemicals on the surface of CuO nanoparticles (Fig. 4c). In order to examine clear morphological view of *Solanum nigrum* leaf extract outshined CuO nanoparticles, TEM micrographs have been recorded (Fig. 4d-h). TEM images revealed that spherical shapes, observed in the FESEM images, are composed of small sized (5–6 nm) SN@CuO NPs. These small size SN@CuO NPs are regularly arranged and uniformly distributed in bigger size spherical aggregate (80–120 nm diameter) of SN@CuO NPs. The selected area electron diffraction pattern (Fig. 4i) specifies the polycrystalline nature while the ring pattern of the same confirms the formation of monoclinic CuO nanoparticles. The size distribution of CuO nanoparticles has been determined using ImageJ software, which signifies that more than 70% *Solanum nigrum* capped nanospheres belong to the size range of 4–7 nm (Fig. S1 supporting informations) (Rueden et al. 2017).

Nitrogen adsorption/desorption isotherm plots were analyzed to calculate the fundamental surface properties of synthesized SN@CuO NPs such as pore-size distribution and specific surface area. A type-IV isotherm plot and H1-type hysteresis loop were supported the mesoporosity for synthesized SN@CuO NPs (Fig. 5) (Al Bataineh et al. 2020). The specific surface area, calculated using the standard multi-point Brunauer-Emmett-Teller (BET) method, was $128 \text{ m}^2\text{g}^{-1}$. Barrett-Joyner-Halenda (BJH) method was applied to estimate the average pore diameter and was found to be 12 nm (Fig. 5 inset). The higher

surface area of SN@CuO NPs indicates the presence of large number of catalytic sites and is thus expected to show high catalytic properties (Abbas et al. 2019).

The surface charge of synthesized SN@CuO NPs was evaluated using Dynamic light scattering (DLS) analysis. The Zeta potential curve of SN@CuO NPs was determined in the range of -150 to +150 mV. *Solanum nigrum* leaf extract outshined copper oxide nanoparticles possess positive and high zeta potential value of 56 ± 05 mV (Fig. S2). The high absolute zeta potential value designates a strong force of repulsion among the SN@CuO NPs and prevents the aggregation of particles. Zeta potential analysis result has suggested the highly stable nature of synthesized SN@CuO NPs.

The catalytic activity of SN@CuO NPs has been examined in the reduction of dye Congo red using reductant sodium borohydride as a model reaction. In this experiment, 10 mL of freshly prepared aqueous NaBH_4 (0.30 M) solution was poured immediately into 10 mL (1.0 mM) aqueous solution of Congo red dye, thus the pH of resulting solution increased instantaneously from 7 to 10. In the UV-Visible absorption spectrum of pure Congo red solution, the observed peak at 495 nm is associated with azo chromophore ($-\text{N}=\text{N}-$). The reduction of Congo red was also investigated in the presence and in absence of SN@CuO NPs catalyst using UV-visible spectrophotometer (Fig. 6a). In the absence of SN@CuO NPs catalyst, no significant change in the absorption maximum at 495 nm (due to the azo group $-\text{N}=\text{N}-$) has been observed even after eight hour time, while in the presence of 5 mg of SN@CuO NPs, the decolorization of Congo red solution taken place rapidly. Time-dependent absorption spectra of reaction solution (Fig. 6b), shows that intensity of absorption band at 495 nm is continuously lowering down and red colour of solution continuously fading with increasing treatment time. This band completely diminished and reaction mixture became colorless within 432 seconds of time. The disappearance of the absorption maximum at 495 nm confirmed the complete catalytic reduction of the $-\text{N}=\text{N}-$ group of Congo red. Concurrently a new peak appeared at wavelength 285 nm in the UV-visible absorption spectrum of reaction mixture, which can be explained as a result of cleavage of the azo bond ($-\text{N}=\text{N}-$) and formation of a new reduction product. The appearance of the absorption peaks at 285 nm is correspond to benzidine on 432 seconds of reaction time (Khan et al. 2017).

In order to further confirm the reduction products after disappearance of azo group (Stage-1), a fraction of reaction mixture was centrifuged at 6000 rpm for 10 minutes, and the SN@CuO NPs catalyst was separated. The supernatant of reaction mixture was extracted thrice using diethyl ether, dried with the help of anhydrous sodium sulfate, and evaporated under reduced pressure. The obtained solid degradation product was examined using FTIR, ^1H -NMR, ^{13}C -NMR, and LC-MS. The FTIR spectrum of pure Congo red has shown peaks at 3468 and 1586 cm^{-1} , which are correspond to $-\text{N}-\text{H}$ and $-\text{N}=\text{N}-$ stretching respectively of Congo red (Fig S3). The peak at 1448 cm^{-1} is for aromatic $\text{C}=\text{C}$ stretching vibration, 1357 cm^{-1} for $\text{C}-\text{N}$ bending vibrations, and 1225 , 1178 , and 1063 cm^{-1} are attributed to $\text{S}=\text{O}$ stretching vibrations of $-\text{SO}_3$ group of Congo red (Telke et al. 2010). FTIR spectrum of the reduction products exhibited a peak around 3378 cm^{-1} for $\text{N}-\text{H}$ stretching, 2923 cm^{-1} and 2851 cm^{-1} for $\text{C}-\text{H}$ stretching vibration, 1609 cm^{-1} for $\text{N}-\text{H}$ bending, and 1497 cm^{-1} for $\text{C}-\text{H}$ bending. The intensity of peaks

corresponds to 1178 cm^{-1} is decreased while the peak at 1238 cm^{-1} is blue shifted. The peak of -N=N- at 1586 cm^{-1} is completely disappeared in the FTIR spectrum of the products indicating the complete reduction azo group (-N=N-) of Congo Red. ^1H NMR (400 MHz, DMSO) results of obtained solid product have shown δ at 7.22 (4H, d), 6.61 (4H, d), 6.56 (4H, s), 5.20 (3H, s), 3.47 (6H, s), 2.50 (1H, s) (Fig. S 4). The ^{13}C NMR (100MHz, DMSO) has shown δ values at 146.62 (s), 129.51 (s), 126.53 (s), 115.18 (s) (Fig. S 5). From LC-MS (ESI-TOF) (Fig. 7), the major peaks have m/z values at 185.4 (ppm error – 2.04) which has corresponding molecular formula $\text{C}_{12}\text{H}_{12}\text{N}_2$. Based on the above data, the major reduced product is found as benzidine; (M + H) + on 432 second of reaction time. In the HRMS result, some minor reduction products also found at m/z values 168, 152, 134, and 113 which are correspond to aminobiphenyl, biphenyl, 4-carboxybutanoate and hydroxy hexadienolate, respectively. The apparent rate of catalytic reduction of Congo red using SN@CuO NPs (Stage-1) has been deduced. The absorbance versus time graph was plotted and the kinetic Eq. (2) has been used to calculate the magnitude of apparent rate constant.

$$\ln \frac{A_t}{A_0} = \ln \frac{C_t}{C_0} = -kt$$

2

where k signifies the pseudo-first-order reaction rate constant. Based on data fitting ($R^2 = 0.9720$) the rate of reduction of azo group (absorption peak at 495 nm) of Congo red is found to be 0.468 min^{-1} .

After complete disappearance of UV-visible peak at 495 nm, the reaction continued for elongated time for complete disappearance of remaining peaks of UV-visible spectrum of Congo red at 350, 285 and 247 nm and degradation has been monitored by recording UV-visible absorbance of reaction mixture as function of time. Figure 8a shows that all remaining peaks; at 247, 285 and 350 nm have completely disappeared after additional 300 minutes of reaction time (Stage-2). The rate of degradation of 285, 247 and 350 nm UV-visible peaks (Stage-2) has been determined using Eq. (2). The data fitting coefficient R^2 value found as 0.9931 and the apparent rate constant for the degradation of above peaks has been determined as 0.0189 min^{-1} (Fig. 8b).

In the TLC measurement of resulting reaction mixture, no spot has been detected. The SN@CuO NPs has been separated from reaction mixture by centrifugation. The adsorbed degradation products at the SN@CuO NPs surface have been extracted in acetonitrile and LC-MS of extract has been recorded. In the LC-MS spectrum (Fig. 9) the major peaks observed at m/z value of 145, along with few minor peaks at m/z values 116, 127, 156, and 223 which are correspond to α -naphthol, succinic acid, biphenyl, naphthylidiazene, and naphthionic acid, respectively.

From above results it is found that the as produced *Solanum nigrum* mediated CuO nanoparticles are efficient catalyst for degradation of Congo red. In the first stage, only 5 mg of nanocatalyst enabled to reduce azo group, present in 10 mL of 1.0 mM dye solution using of 10 mL of 0.30 M NaBH_4 solution (Fig. 6) within 7.2 minutes. In the second stage, reaction mixture (reduced products of Congo red) has

completely been free from Congo red dye content within 300 minutes. Thus the reaction mixture become completely free from dye content within total 307.2 minutes of time (Fig. 6,8). Catalytic efficacy of SN@CuO NPs in this study has been compared with that of some latest reported nanocatalysts (Chen et al. 2014, Indana et al. 2016, Jayapriya & Arulmozhi 2021, Narasaiah & Mandal 2020, Singh et al. 2017, Subair et al. 2016, Umamaheswari et al. 2018). From Table 1 it is obvious that SN@CuO NPs is better catalyst for degradation of Congo red. In these reports costly materials and hazardous chemicals have been used to prepare catalysts while in present study, less expensive SN@CuO NPs synthesized via sustainable route to degrade Congo red rapidly than above catalysts.

Table 1

S.No.	Catalyst	Reducing Agent	Time (minutes)	Rate constant (min^{-1})	Reference
1	Cubic Gold Nanorattles	NaBH_4	15 min	0.362	Chen et al., 2014
2	Au NPs-Dp-p(EI) membrane	NaBH_4	29	0.209	Indana et al., 2016
3	$\text{Fe}_3\text{O}_4@\text{PANI}@Au$	NaBH_4	20	—	Jayapriya and Arulmozhi, 2021
4	Ag NPs	NaBH_4	15 min	0.148	Narasaiah and Mandal, 2020
5	Ag/TiO ₂	NaBH_4	20 min	—	Singh et al., 2017
6	Au NPs	NaBH_4	10 min	0.27	Subair et al., 2016
7	Pd Nps	NaBH_4	14 min	0.2387	Umamaheswari et al., 2018
8	SN@CuO NPs	NaBH_4	7.2min	0.526	Present work

It is well established that for catalytic reduction of congo red, both reactants, Congo red and BH_4^- ion, must be adsorbed onto the surface of the particles, which in turn can react, and the products dissociate from the surface of the catalyst. Without SN@CuO NPs, bare NaBH_4 could not reduce Congo red even after eight hour of reaction time while in presence of only 5 mg SN@CuO NPs, Congo red solution completely mineralized within 307.2 minutes. The LC-MS results have shown that degraded products are adsorbed on the surface of CuO nanoparticles which indicates that reaction has taken place at the surface of SN@CuO NPs. Several factors, such as porosity/surface area, pH of reaction mixture and electrostatic attraction between adsorbate dye and adsorbent SN@CuO NPs are responsible for adsorption of Congo red at the surface of SN@CuO NPs (Labanda et al. 2009). Congo red is a dipolar

molecule which exists in anionic form in alkaline medium having deep red color, while in acidic medium protonation of azo group takes place, resulting appearance of deep blue color of dye solution. In presence NaBH_4 solution the pH of reaction mixture become 10, thus Congo red exists in anionic form. TEM and BET results revealed that SN@CuO NPs have very small size, large surface area and mesoporous structure while zeta potential value has shown high positive charge at the surface of SN@CuO NPs. Due to positive charge on SN@CuO NPs surface, the reactants; negatively charged Congo red and BH_4^- attracted to positively charged SN@CuO NPs and adsorbed on free catalytic sites, which are present in large number. Rajesh *et al.* reported that borohydride ions (BH_4^-) generated from the dissociation of NaBH_4 and molecules of congo red readily diffused from an aqueous reaction solution to the surface of nanoparticles occupying active sites (Rajesh et al. 2014). During reduction of Congo red, nanoparticles work as a relay center for transfer of an electron between borohydride ions (BH_4^-) ions and congo red molecules in which borohydride ions (BH_4^-) act as electron donor whereas congo red molecules act as electron acceptors. It is supposed that BH_4^- interacted with SN@CuO NPs to form Cu tetrahydroborates dihydrogen bonded (DHB) tetrahedral $\text{L}_2\text{Cu}(\eta^2\text{-BH}_4)$ complexes. The DHB complexes involving both bridging and terminal hydride hydrogens are proved to be effective reducing agents (Belkova et al. 2017). Further, FTIR spectrum of leaf extract mediated CuO nanoparticles (Fig. 2b) has shown that interaction of secondary amides of *Solanum nigrum* leaf extract with Cu ions take place through $\text{C}=\text{O}$ ($\text{Cu}-\text{C}=\text{O}$), leaving $-\text{NHR}$ of secondary amide free for interaction with sulphonate group ($\text{CR}-\text{SO}_3^-$) of Congo red. Now congo red molecules transfer electrons to nanoparticles, which activate azo bonds of congo red molecules, whereas borohydride ions, in the form of $\text{L}_2\text{Cu}(\eta^2\text{-BH}_4)$ complexes, act as dihydrogen sources. Hydrogen released from $\text{L}_2\text{Cu}(\eta^2\text{-BH}_4)$ complexes attack on activated azo bonds. Due to conversion of $(-\text{N}=\text{N}-)$ to $(-\text{HN}-\text{NH}-)$ and finally breakage of $(-\text{HN}-\text{NH}-)$ bond due to uptake of dihydrogen through nano-catalyst ($\text{L}_2\text{Cu}(\eta^2\text{-BH}_4)$ complexes), congo red starts fading rapidly and becomes colorless after completion of reduction reaction within 432 seconds (Jia et al. 2014). The plausible mechanism for the degradation of Congo red has been presented in Scheme I.

After reduction of $-\text{N}=\text{N}-$ group within 432 seconds of reaction time, benzidine is the main degradation product in this experiment, however, some other degradation products have also been detected in LC-MS result (Fig. 7, Scheme-I). When reaction further proceeded for an elongated time 300 minutes, then the reaction mixture become completely free from Congo red and its degradation products, like benzidine and other small fractions, and the UV-visible peaks at 285, 247 and 350 nm completely disappeared. However, degraded products, which are mainly α -naphthol and some other molecules in small fraction, are still found to be adsorbed on the surface of SN@CuO NPs. This indicates that SN@CuO NPs act as support and provide suitable medium and works as relay center for movement of electrons between reactants. Due to this interplay of electrons, degradation products (after disappearance of azo group), like benzidine (major) and other molecules (minor), degraded to final products α -naphthol (major) and some other molecules (minor) in small fraction, present at the surface of SN@CuO NPs in adsorbed form (Scheme-II).

4. Conclusion

In summary, it has been established that low cost SN@CuO NPs prepared via a green sustainable route using *Solanum nigrum* leaf extract as a stabilizing or outshining agent, is a better nanocatalyst than many earlier reported catalysts for degradation of Congo red dye. By suitable reaction engineering very small sizes, spherical (5–6 nm) SN@CuO NPs having mesoporous structure, capped with phytochemicals, positively charged and stable nanoparticles surface could be generated. This resulted fast and effective adsorption of reactants like anionic dye molecules and BH_4^- ions on positively charged SN@CuO NPs surface, exhibiting excellent catalytic activity in the reduction of carcinogenic water pollutant, Congo red using sodium borohydride as the reductant in aqueous solution at room temperature. From various spectroscopic analyses, it is clear that the obtained intermediate of degradation product of Congo red is benzidine (as major product) after 432 seconds of reaction time, which finally degraded to α -naphthol (as major product) within 300 minutes of reaction time. Dihydrogen bonded (DHB) tetrahedral $\text{L}_2\text{Cu}(\text{H}^2\text{-BH}_4)$ complex acts as a dihydrogen source for reduction of the azo group and thus degradation of Congo red. The Congo red has completely been removed from reaction mixture within 307.2 minutes, however degradation products (mainly α -naphthol and some other molecules in traces), adsorbed on the surface of SN@CuO NPs are comparatively harmless. The best part of this study is that the green synthesized SN@CuO NPs is very efficient nanocatalyst for degradation of Congo red, which can easily be separated by centrifugation and repeatedly used with negligible loss in activity for multiple times.

5. Declarations

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Contribution:

Kijay Bahadur Singh was the incharge of this experiment and analyzed the experimental data along with Neelam Gautam and Deen Dayal Upadhyay. Gulam Abbas and Gajanan Pandey were major contributors in writing the manuscript. All authors read and approved the final manuscript. All authors of this manuscript have directly participated in the planning, execution, and analyses of this study.

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Ethics approval

Ethical approval was not required for this research.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

UV-visible spectrum of CuO NPs formed using *Solanum nigrum* leaf extract

Figure 2

FTIR spectrum of *Solanum nigrum* leaf extract (a) and *Solanum nigrum* leaf extract mediated produced CuO NPs (b)

Figure 3

XRD pattern *Solanum nigrum* leaf extract mediated produced CuO NPs

Figure 4

FE-SEM (a,b), EDX (c), TEM (d-h) and SAED (i) images of CuO NPs

Figure 5

Nitrogen adsorption/desorption isotherm plot by CuO NPs Brunauer-Emmett-Teller (BET) method and inset Barrett-Joyner-Halenda (BJH) method

Figure 6

UV-visible absorption spectra of pure Congo red, Congo red in presence NaBH₄ only and Congo red in presence of NaBH₄ and catalyst CuO NPs (a), UV-visible absorbance spectra of reaction mixture as a function of reaction time up-to disappearance of azo group (b) and pseudo first order kinetics plot for catalytic reduction of Congo red using CuO nanocatalyst (c)

Figure 7
HR-MS spectrum of degradation product when azo group disappeared (Stage-1)

Figure 8

UV-visible absorbance spectra of reaction mixture as a function of reaction time up-to disappearance of peaks at 350, 285 and 247 nm (a) and pseudo first order kinetics plot for catalytic reduction peaks at 350, 285 and 247 nm (b)

Figure 9

HR-MS spectrum of degradation product when peaks at 350, 285 and 247 nm disappeared (Stage-2)

Supplementary Files

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