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Degradation of Organic Pollutants using Green Synthesized Bimetallic Nanoparticles: A Kinetic Study

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Abstract: *Nanotechnology is an interdisciplinary field that encompasses various disciplines of engineering, biology, physics and chemistry, which deals with nanoscale materials. It is a multiple areas field which covers diverse domains from the synthesis of nanoparticles (NPs) from plants is a green chemical approach that combines nanotechnology and plant biotechnology. Plant metabolites such as sugars, terpenoids, polyphenols and others play an important role in reducing metal ions to nanoparticles. So to complete the goal; a biological approach to filling in the gaps is imminent; For example, green synthesis uses extracts from biological sources from plant sources, which are superior to chemical and biological methods. Water pollution is defined as the existence of toxic bio- logical agents and chemicals that exceed the normal level of water and may pose a detrimental effect to human health and the environment. In the current report, here we synthesized silver, copper bimetallic nanoparticles (BMNPs) via a novel, robust, and inexpensive method using leaf extract of Azadirachta Indica as reducing as well as capping agent. The synthesized Ag-CuNPs was tested for degradation and degradation kinetics using Methyl Orange dye (MO) through an advanced oxidation process (AOP). The obtained kinetic result indicates the rate of degradation of MO induces significantly in presence of small concentration of BMNPs (1×10^{-8} s^{-1}) and UV-Visible spectrum changes are used to analyze the structure of intermediate and end products during the degraded process. This work promises good environmental safetyagainst dye contamination in water based systems.*

Keywords: Nanotechnology, Green Synthesis, Bimetallic Nanoparticles, Degradation.

I. Introduction

The issue of emissions of harmful organic pollutants being released into the aquatic environment has received a lot of attention in recent years and is now considered one of the most important problems facing scientists. Even Industries that handle pollutants rigorously dealing with harmful materials such as dyes, smelters, tanneries and paper mills release highly waste water into ecosystem, causing pollution. Intense colour that the dyes impart to the aquatic ecosystem is an aesthetic and serious ecological concern [1].Because most dyes are resistant to light, water and oxidizing chemicals, making them difficult to degrade if once they are discharged into the environment. Azo dyes that include one or more azo linkages (-N=N-) are known to be extremely hazardous and carcinogenic [2]. Advanced oxidation techniques have garnered a lot of attention in recent decades as a cutting-edge wastewater treatment technology for removing organic contaminants into less dangerous compounds[3, 4, 5,6].Several reactive oxidative species such as $^{\bullet}OH$,$O_2^{\bullet}$/$HO_2^{\bullet}$ can be made in AOP and are usually very effective for bleaching colour and even mineralization. Recently, AOPs based on sulphate radicals ($SO_4^{\bullet -}$) have attracted great scientific and technological interest in their environmental applications [7].By activating sulfate-based oxidants (PMS, PDS) with thermal, ultraviolet, microwave, and ultrasonic radiation and/or transition metal ions, sulphate radicals (SR) with a reduction potential of +2.6 V relative to NHE can be generated. As a result, it is envisaged that $SO_4^{\bullet -}$will be an excellent oxidising agent in contaminated water for decomposition of refractory organic molecules [8]. Plant extracts have been established in a number of recent studies to be safe precursors for the production of nanomaterials. Both technologically and scientifically, bimetallic nanoparticles (BMNPs) have gained more interest than monometallic nanoparticles, as BMNPs have better properties in many applications, especially in dye degradation, due to their synergistic effect[9,10].Green synthesis of Ag-Cu NPs using Kigeliaafricana fruit extract [11], Ginger rhizome powder [12], Opuntiaficus-indica[13], Date palm tree (Phoenix dactylifera) leaves [14], R. emodi roots extract [15], and Toddy palm [16]has been previously reported. The source of the plant extract affects the properties of the nanoparticles, as each plant extract contains a unique concentration and combination of organic reducing agents. [17].Methyl orange (MO), a type of azo dye, is widely used in industries such as dyeing, printing, textile, paper, and cosmetics. Moreover, MO is considered a hazardous substance which cannot be broken down effectively using conventional degradation processes [18].To date, very few attempts have been made to oxidize MO degradation in the presence of BMNPs [19, 20, 21]. Here we have developed a fast, environmentally friendly and convenient green route for the synthesis of Ag-CuNPs from copper sulphate and silver nitrate using aextract prepare from the leaves of the Indian medicinal plant, namely A. indica (Neem).This study investigates the catalytic activity of green-synthesized Ag-CuNPs in the oxidative degradation of MO by PDS in aqueous media. This study also includes the catalytic activity of Ag-CuNPs in dye-containing wastewater collected from a local industrial canal in Kota, Rajasthan, India. The current work is based on the excellent economics of the process in terms of cheaper chemicals, green methods that are fast and convenient.

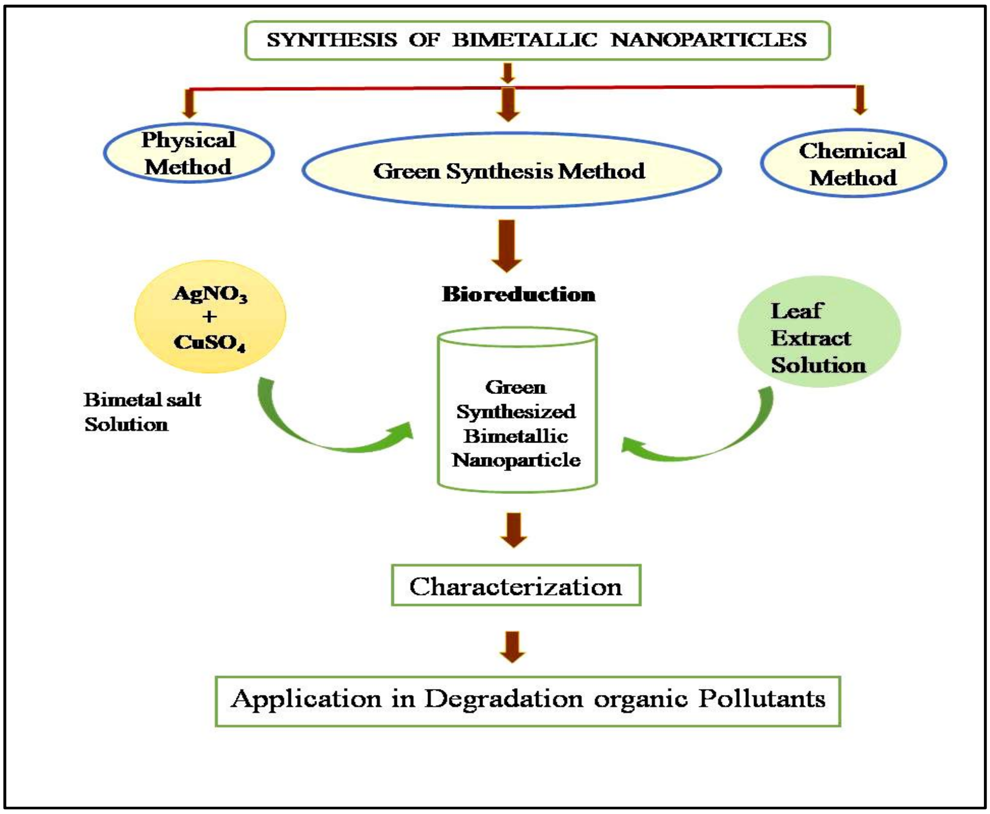

Figure 1: Green Synthesis of Ag-Cu BMNPs

II. EXPERIMENTAL

2.1 Chemicals and materials

Analytical grade copper sulphate dihydrate ($CuSO_42H_2O$), silver nitrate ($AgNO_3$), MO Dye, and other chemicals were used. Leaves of the Neem tree (Azadirachtaindica) were collected from Kota, Rajasthan, India. Fresh Neem leaves were used to make the extract, which was made by boiling them in deionized water.

2.2 Synthesis of Nanoparticles

For the synthesis of bimetallic nanoparticles, Leaves extract was added dropwise to required concentration of $AgNO_3$ and$CuSO_4 \cdot 2H_2O$solutionin round bottom flask under magnetic stirring at 80^0C. During this time, colour change from

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greenish to dark brown suspension with a yellow supernatant was observed (Figure-1). The products were centrifuged for 15 minand stored in refrigerator for further analysis.

2.3. Kinetic Measurements

Oxidative degradation of methyl orange (MO) was carried out with the desired reagent concentration in a closed Erlenmeyer flask at 30°C. The reaction is started by adding a known volume of PDS solution. The kinetics was monitored by the MO absorbance, which was measured spectrophotometrically at regular intervals at max 465 nm. It was observed that the absorption (A) of the dye solution decreased with increasing time, indicating the progress of dye degradation. Beer's law is observed at 465 nm in the concentration range (2.0 x 10^{-5} to 2.0 x 10^{-4}mol dm^{-3}); It was found that the molar absorption index of MO 24565 is ± 50 mol^{-1} dm^{3} cm^{-1} [4]. The degradation of the original dye samples with dyes was also carried out in the presence of Ag-CuNPs. A linear graph of 2 þ log (A) versus time was found, which shows pseudo first-order kinetics. The course of the reaction is followed by at least 80% of the reaction.

III. Results and Discussion

3.1 Characterization of Ag-Cu Nanoparticles

The colour of the dispersion transformed from green to dark brown, and UV–vis spectroscopy confirmed that the Ag-CuNPs were generated in a single process. The UV–vis spectra of dispersion were obtained after different time intervals from the start of the reaction, and the prominence of the SPR peak increased with time. The development of bimetallic NPs was confirmed by the detection of an SPR band characteristic of Ag-CuNPs about 490 nm (figure 2), owing to the continuous reduction of copper ions and silver ions into Ag-CuNPs[22].

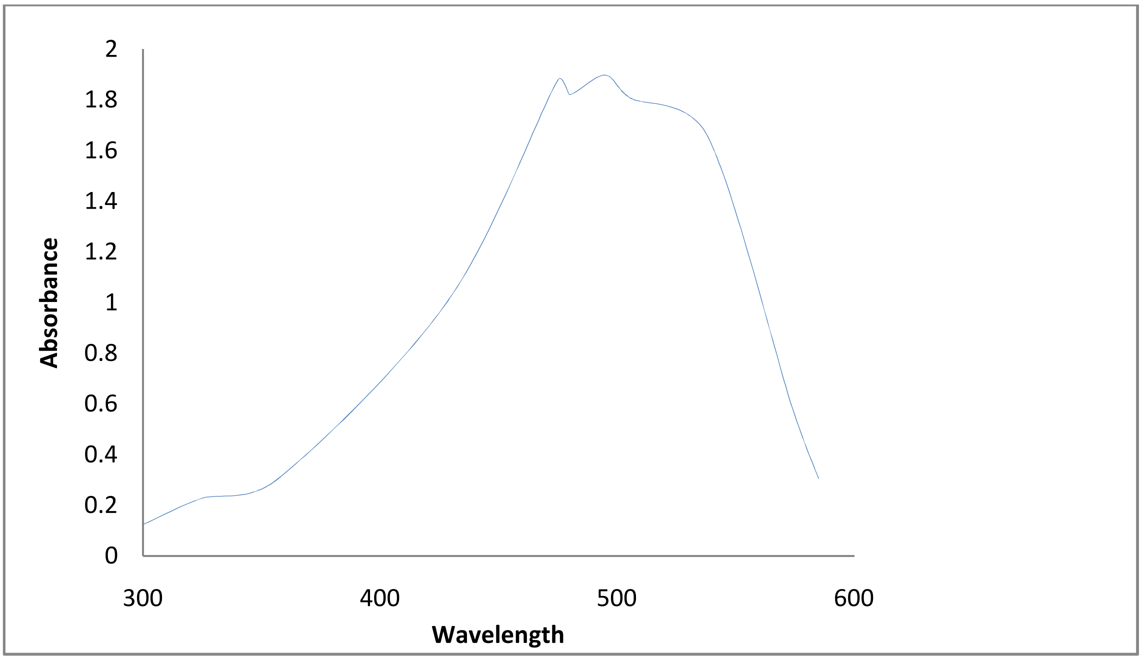

Figure 2: UV-Visible Spectra of Ag-Cu BMNPs

3.2. Peroxodisulfate Dependence

Ag-CuNPs-catalyzed oxidative degradation of MO was investigated at various PDS concentrations from1 x 10^{-4} to 1 x 10^{-3}mol dm^{-3} at 30 ^{0}C temperature, fixed concentration of [Dye] =5 x 10 $^{-5}$mol dm^{-3}, [Ag-CuNPs] = 1 x 10^{-8}mol dm^{-3} and pH = 6.5. The rate of dye degradation increased with increasing the initial PDS concentration .This may be due to the fact that $SO_4^{\bullet}$ radical ion is generated at the same time, which in turn increases the oxidation rate of the bimetal ion. The oxidative colour change of the MO occurs sequentially. In addition, the PDS concentration increases above 5 x 10^{-4}mol dm^{-3}, the MO degradation rate slowed down slightly. This may be because the higher concentration of PDS, the side reaction between persulfate anion ($S_2O_8^{2-}$) and $SO_4^{\bullet -}$become more significant, which will use more PDS, so the percentage of remaining PDS decreases with increasing PDS concentration.

3.3. Dye Dependence

The Reaction was carried out at a constant concentration of other reactants and by changing the initial concentration of MO from 1 x $10^{-5}$to 1x 10^{-4}mol dm^{-3} at 30 ^{0}C temperature. The results showed that the degradation rate increased with an increase in dye concentration up to 5 x 10^{-5}mol dm^{-3}, after that rate decreased with an increase in dye concentration. At constant PDS concentrations, the presence of $SO_4^{\bullet -}$ radicals may not be sufficient to cleave the dye molecules at higher concentrations. [23].

3.4. Product Analysis

The degradation products of MO in presence of BMNPs confirmed by UV-visible spectra of reaction mixture. The UV-visible spectra of pure MO arises at around 465 nm because of the extended aromatic ring and chromophore group of MO and the additional band obtained at 270 nm are due to the presence of the aromatic ring in MO molecule [24].As the degradation proceeded, polyaromatic ring present in MO convert into monosubstituted aromatic ring and end products, it is confirmed by thepresence of two new peaks at 222 nm and 319 nm in UV-visible spectra(Figure 3)[25].

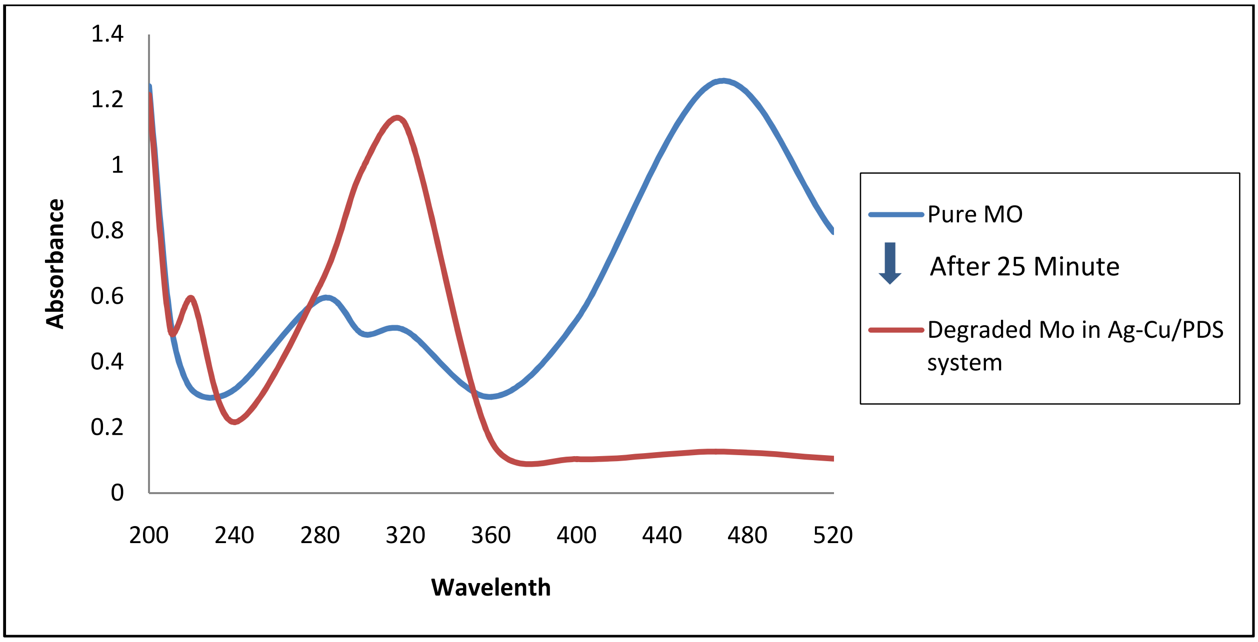

Figure 3: UV-visible spectra of Pure MO and degradation products of MO

VI. Conclusion

Ag-CuNPs synthesis with Neem leaf extract is cost-effective, easy to scale up, and environmentally benign. Biomolecules included in plant extracts act as a reducing and stabilising agent. As a result, without the usage of a protective gas, biosynthesized Ag-Cu NPs were found to remain stable for two months at 4°C in this investigation. The synthesised BMNPs exhibited a high catalytic activity for dye degradation in the presence of PDS. Increased PDS and catalyst concentrations accelerated MO degradation in the Ag-CuNPs/PDS mixture. Therefore, the study will be great significant in environmental remediation.

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