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Electrochemical synthesized copper oxide nanoparticles for enhanced photocatalytic and antimicrobial activity

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ABSTRACT

The electrochemical method has been investigated for the synthesis of copper oxide nanoparticles (CuO NPs) under different reaction conditions. The CuO NPs were used as excellent photocatalyst for the degradation of different organic dyes under the illumination of sunlight irradiation. The highest degradation was 93% for methylene blue. The rate constant for MB, MR, and CR was found to be first-order with values 0.02059, 0.02046, and 0.01749 min^{-1}, respectively. The antimicrobial efficiency of CuO NPs was investigated against bacterial strains (*Escherichia coli* and *Staphylococcus aureus*) and fungal strains (*Aspergillus nigres* and *Candida albicans*).

Introduction

Nowadays nanomaterials are of immense interest due to wide range of applications in chemical, biological, and environmental sciences [1–3]. The size and shape of the nanomaterials are key factors for shaping their properties such as, electrical, optical, magnetic, catalytic, and antimicrobial. Metal and metal oxide nanoparticles have found wide variety of uses, including heterogeneous catalysts, colloid science, environmental remediation, electronic, optoelectronics, chemical sensing devices, medicinal applications, separations, thin films, inks, disinfection, and antimicrobial activity [4–6]. The different applications of metal and metal oxide nanoparticles varied with morphology and size [7,8]. Among the metal oxide nanoparticles, copper oxide nanoparticles have been potentially used for the PN junction diodes, humidity sensing, lithium ion battery, organic synthesis, antimicrobial activity and biomedical field [9–11]. Copper(II) oxide with a narrow bandgap (E_g) of 1.0–2.08 eV behaves as a *p*-type semiconductor. The semiconducting nature of metal oxides makes them important for solar energy conversion, photocatalysis, antimicrobial, and antifouling applications [12,13]. In the past few years, different methods such as wet chemistry route, sonochemical preparation, alkoxide-based preparation, hydrothermal process, sol–gel, microemulsions, spray pyrolysis etc., have been reported for the preparation of the nanomaterials [14,15]. The toxicity and relatively high material cost of these methods restricted their use in a better way. So a simple, direct, and green route has been needed for the preparation of metal oxide nanoparticles. The electrochemical method, a cost effective and resourceful process has been reported for the synthesis of metal oxide in nanodomains [16]. This process is suitable for the synthesis of high surface area and highly efficient for noble metal oxide. Environmental pollution has been caused some unfavorable effects on the living organisms and breaks the balance of the ecological unit. The presence of organic waste and microbial contamination created a serious problem to human being. The removal of organic pollutants and microbes from wastewater has been the matter of increasing attention in the recent years. According to United States Environmental Protection Agency, water-related diseases kill a child every eight seconds, and are responsible for 80 percent of all illnesses and deaths in the developing world. Photocatalysis has been attracting much attention recently due to the wide range of applications in renewable energy self-sterilizing surfaces, photocatalytic lithography, microchemical systems, green synthesis of organic compounds, and the generation of hydrogen and

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environmental remediation [17,18]. Photocatalytic degradation of organic dye such as methylene blue, congo red, and methyl red is being paid much attention due to environmental effect of various industrial and agriculture pollutants. Copper oxide nanoparticles have been selected as photocatalyst and antimicrobial agent because of its low cost, high catalytic efficiency, and narrow bandgap. They possess optical, catalytic, mechanical, and electrical properties [19,20]. Copper oxide has been used for photoelectron chemical hydrogen production, printing electrodes, possess antimicrobial activity, and catalytic activity. The platelet-like CuO nanostructures have been demonstrated efficiently as catalyst for the degradation of methylene blue dye from the aqueous solution [21]. Hong et al. has reported that urchin-like CuO microspheres for the degradation of pyronin [22]. Flower like Cu_2O has been also reported as photocatalyst for the brilliant red X-3B dye degradation in solar light [23]. Furthermore, it is essential to improve the photocatalytic activities of copper oxide nanoparticles for the degradation of organic impurities. It has been revealed from the literature survey that only limited applications are available on photocatalysis in the presence of sunlight irradiations for the degradation of organic impurities. In the photocatalytic reactions, the semiconducting materials absorb energy more than or equal to energy gap and generates the hole and electrons, which further contributes to rise efficient oxidizers of organic dyes. The antibacterial activities of CuO NPs were reported against *E. coli, P. aeruginosa, B. subtilis* and *S. aureus* [24]. Copper nanoparticles were tested for antifungal activity performed against *Cryptococcus and Candida albicans* [25]. A mild inhibitory zone effect of *Candida albicans* has been observed. Copper nanoparticles showed antimicrobial activity against *Klebsiella pneumonia*, *Enterococcus faecalis*, *Salmonellatyphimurium*, *Proteus vulgaris, Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. In addition, *E. coli* and *E. faecalis* exhibited the highest activity to CuO nanoparticles compared to *K .pneumonia* [26].

In the present research work, the influence of reaction parameters was explored on the shape and size of CuO NPs, which were prepared using electrochemical method. The effectiveness of CuO NPs was studied for the photocatalytic degradation of methylene blue, congo red, and methyl red dyes from water system. Moreover, antimicrobial activity of copper oxide nanoparticles against Escherichia *coli, Staphylococcus aureus, Aspergillum nigres*, and *Candida albicans* was investigated.

Experimental

Chemicals and reagents

The main reagents used were sodium hydroxide(SH), sodium nitrate (SN), sodium carbonate (SC), acetonitrile (ACN), methanol, methylene blue (MB), congo red (CR), methyl red (MR). Deionized water was used throughout the experiments. The main instrument used in this study was electrophoresis (Instruments & Chemicals Pvt. Ltd.), Fourier transform infrared (Model RZX; Perkin Elmer), X-ray diffractometer (XRD; PAN alytical X'Pert), transmission electron microscopy coupled with energy-dispersive X-ray (FEI Tecnai F 20), scanning electron microscopy (Quanta 250, FEI Make Mode No. D9393).

Synthesis of copper oxide nanoparticles (CuO NPs)

Electrochemical deposition method was used for the synthesis of copper oxide nanoparticles (CuO NPs) under different reaction conditions. In typical procedure, 200 ml of supporting electrolyte was dissolved in 1.25 mM of sodium hydroxide, sodium carbonate, and sodium nitrate in water, water: acetonitrile (12:1), and water: methanol (12:1) solvents. The copper plate (3×2 cm^2) and inert platinum (1×1 cm^2) were used as a sacrificial anode and cathode, respectively. Before electrochemical deposition, both electrodes were cleaned with hydrochloric acid and distilled water. The distance between both electrodes was fixed at 1 cm for all the experiments. The electrolysis reaction was carried out in an undivided electrochemical cell at 50–100 V potential for 2 h with vigorous stirring at room temperature. The electrolysis was performed at currents of 20, 50, and 100 mA. After the electrolysis, the dark brown precipitates were centrifuged, washed with ethanol, and finally with distilled water. The products were then dried at 60 °C in a hot air oven for 2 h. The materials obtained in different conditions were calcined at 300, 600, and 900 °C for 1 h to study the effect of temperature on particle size.

The electrolytic cell can be represented as follow:

$$Cu_{(+)}|\text{Solvent} + \text{SE}|Pt_{(-)},$$

where SE represents the supporting electrolyte.

Characterization

Fourier transform infrared spectra of CuO NPs were recorded using KBr disk method. Crystal structure of the copper oxide nanoparticles were determined by powder X-ray diffractometer employing Cu–K_α radiation (λ = 1.5418 Å) at 50 kV and 200 mA. Transmission electron microscopy coupled with energy-dispersive X-ray studies were performed by dropping diluted solution of nanoparticles on copper grids covered with a thin amorphous carbon film at 200 kV. Scanning electron microscopy studies of CuO NPs were recorded at different magnifications.

Photocatalytic activity

Photocatalytic activities of CuO NPs were investigated for the degradation of methylene blue (MB), congo red (CR), and methyl red (MR) dyes under sunlight irradiation. Photocatalytic activities of CuO NPs obtained in water–ACN solvent, NaOH electrolyte, and sample which was sintered at 600 °C were studied. For the reaction, 0.1 g of CuO NPs was dispersed in 2×10^{-5}mol/L dye solutions in pyrex beaker, which was continuously stirred to establish the adsorption/desorption equilibrium. The dyes and CuO NPs suspension was then irradiated under sunlight with constant stirring for 120 min. Then, 5 ml of solution was withdrawn at specific interval of time. The absorbance maxima for MB, CR, and MR were determined at 664, 497, and 410 nm, respectively using UV–visible spectrophotometer. The % degradation of dyes was calculated using following formula [27]:

$$\%\,degradation = \frac{C_o - C_t}{C_o} \times 100.$$

The photodegradation kinetics of dyes was fitted in pseudo first-order kinetic model [28]:

$$\ln C_o - \ln C_t = k_{\text{appt}},$$

where C_0 is the concentrations of dye before illumination and C_t is the concentration of dye at time t, and k_{appt} is the apparent rate constant.

Antibacterial activity

Antimicrobial activity of CuO NPs was carried out by growth curve method against bacterial strains (*Escherichia coli* and *Staphylococcus aureus*) and fungal strains (*Aspergillus nigres* and *Candida albicans*) [29]. The bacteria were cultured overnight in nutrient broth and fungus was cultured in potato dextrose broth (PDB) solution at 37 °C incubator shaker. The microbial culture was exposed to CuO NPs with different concentration (25 μg/ml and