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ORIGINAL ARTICLE

Catalytic and recyclability properties of phytogenic copper oxide nanoparticles derived from *Aglaia elaeagnoidea* flower extract

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Abstract The phytogenic synthesis method to highly active, recoverable and recyclable heterogeneous copper oxide nanocatalyst and encapsulated within biomaterial that acts as a nontoxic and renewable source of reducing and stabilizing agent. The biosynthesized CuO NPs were characterized using UV–Vis absorption spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and thermo gravimetric analysis-differential scanning calorimetry (TGA–DSC), techniques. The formation of CuO NPs with the size 20–45 nm range is shown in TEM image. Significantly, in aqueous phase CuO NPs have high catalytic activity for the reduction of Congo red (CR), methylene blue (MB) and 4-nitrophenol (4-NP) in the presence of the sodium borohydride ($NaBH_4$) at room temperature. In addition, CuO NPs catalyst can be easily recovered by centrifugation and reused for 6 cycles with more than 90% conversion efficiency. CuO nanocatalyst, leaching after catalytic application was investigated by ICPAES (Inductively coupled plasma atomic emission spectroscopy). CuO NPs possess great prospects in reduction of pernicious dyes and nitro organic pollutants in water.

1. Introduction

Organic pollutants and dyes are toxic and most hazardous materials representing as an important source of environmental contamination. Particularly nitrophenol, methylene blue, methyl orange, methyl green, Congo red etc., are most common and versatile organic pollutants and dyes. These are broadly used in the insecticide, textile, drugs, fungicides and other manufacturing industries that are released into the water bodies causing daunting challenges to human health [1].

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Removal of these nitrophenols and dyes is very difficult by chemical, physical and biological methods such as precipitation, adsorption, UV irradiation, electro catalysis and microbial degradation because of their stability and these techniques possess inherent limitations such as high cost, formation of hazardous by products [2–7]. For the past few years degradation of these toxic organic pollutants and dyes in waste water has been intriguing to the chemist. Therefore, in the present scenario, it is very important to develop aqueous phase conversion of this organic pollutants and dyes under mild conditions by the catalytic reduction method [8]. Nanotechnology has emerged as a simple and viable alternative approach incorporated in the treatment of waste water by the nanocatalytic activity [9].

Nanocrystalline noble metal and metal oxides have significant, intriguing applications in recent years due to their unique properties. Among various noble metals, copper oxide (CuO) nanostructure have gained significant attention because it is a very reactive, simple p-type metal oxide semiconductor with monoclinic structure and their high surface volume exhibits remarkable applications in catalysis [10,11], high-temperature superconductors [12], solar cell [13], optical [14], sensors [15] and antimicrobial, anti-fouling, anti-biotic and anti-fungal [16]. In addition to this, CuO NPs have other unique super-hydrophobic properties [17]. Several physical, chemical methods used in the synthesis of CuO nanoparticles, raise several problems like high temperature and pressure, reducing agents and organic solvents and hazardous chemicals [18]. To meet this technological need and mitigate the drawbacks, use of plants as a sustainable route for synthesis is proposed in this study. Moreover, CuO is cheap, abundant, and the economic material with short reaction time under normal conditions is advantageous in green synthesis of nanoparticles [19]. Green chemistry method of an eco-friendly approach for the synthesis of copper oxide nanoparticles was developed, it highlights the use of biological entities for the synthesis of copper oxide nanoparticles [20].

Aglaia elaeagnoidea (syn. *A. roxburghiana*) is a tree widely distributed in the tropical forests of Asia [21]. It is the most widespread and one of the more morphologically diverse, complex species in the largest genus of the mahogany family [22]. *A. elaeagnoidea* as a medicinal plant has antipyretic, astringent, antidiarrhoeal, antidysenteric, anti-inflammatory, anticancerous properties and also used in treating skin diseases and tumors [23]. The bio-efficacy of plant compounds against Helicoverpa armigera and Spodopfera litura larvea [24]. Henceforth, in this perspective, this study focused on and demonstrated the factual principles of green chemistry applied in the synthesis of copper oxide nanoparticles, an eco-friendly approach using an aqueous flower extract of *A. elaeagnoidea* and evaluated their efficacy for the catalytic reduction of pernicious organic pollutants and dyes namely 4-nitrophenol (4-NP), methylene blue (MB) and Congo red (CR) from liquid phases by homogeneous and heterogeneous methods. A Specialty of aqueous flower extract of *A. elaeagnoidea* contains high levels of diverse phenolic compounds and other phytochemicals that can act as both reducing and capping agents for CuO NPs. To the best of our knowledge, this is the first report on *A. elaeagnoidea* flowers extract derived CuO NPs.

2. Materials and methods

2.1. Materials

Copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) and 4-nitrophenol (4-NP) were purchased from Himedia Laboratories Ltd. India. Methylene blue, Congo red and Sodium borohydride was purchased from Sigma–Aldrich.

2.2. Preparation of extract

The flowers of *A. elaeagnoidea* were collected locally and shade dried for three days and machine-ground into fine powder. About 10 g of flower material was soaked in 250 ml of conical flask with 125 ml of deionized water refluxed on a magnetic stirrer for 10 min. The extract was centrifuged at 5000 rpm for 10 min to separate plant debris and the extract was stored at in 4 °C for further experiment.

2.3. Phytosynthesis of copper oxide nanoparticles

In a typical preparation of copper oxide nanoparticles, Five milliliters of flower extracts of *A. elaeagnoidea* were mixed to 45 ml 1 mM copper nitrate solution and stirred continuously for 5 min at the room temperature. The color of the solution gradually changed from light brownish red to brick red with a number of intermediate stages, which indicates the formation of CuO NPs.

2.4. Characterization methods

The phytogenic reduction of $CuNO_3$ to CuO NPs formation was recorded using double beam UV–Vis spectrophotometer at regular intervals. Specifically, to evaluate the change in optical properties, the 200–600 nm range of wavelength was used. To assess morphology and particle dispersion of CuO NPs by transmission electron microscopy (TEM, JEOL; model 2010) field emission scanning electron microscopy (FESEM, Carl Zeiss) studies, the aqueous CuO NPs were sonicated and a drop was placed on carbon-coated Cu grids and allowed to dry overnight. FESEM along with energy dispersive X-ray spectroscopy (EDAX, S3700N) were performed to know the chemical composition of synthesized nanostructures. Moreover, to know the stabilization mechanism of nanostructures fourier transform infrared (FTIR) spectrophotometer was carried out in the transmittance mode of the range of 400–4000 cm^{-1}, on the KBr pellet with diluted CuO NPs. X-ray diffraction (XRD) measurements for CuO NPs, equipped with a graphite monochromator crystal (Philips PW 3710/3020) were performed. The wavelength of X-ray was 1.5405 Å and the diffraction patterns were recorded with scanning speed of 2/min. Thermogravimetric analysis and Differential Scanning Calorimetry (TGA-DSC instruments, Model: Q20 DSC) were used for the determination the CuO nanocatalyst, weight loss of after its catalytic application. These studies were conducted under a nitrogen flow. To measure the CuO NPs weight loss, the samples were placed and heated at a rate of 10°/min from 30 °C to 800 °C. Copper ions lixiviate was analyzed by ICPAES (Inductively coupled plasma atomic emission spectroscopy).