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Cuscuta reflexa leaf extract mediated green synthesis of the Cu nanoparticles on graphene oxide/manganese dioxide nanocomposite and its catalytic activity toward reduction of nitroarenes and organic dyes

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ABSTRACT

The present study reports an efficient, surfactant-free, novel and facile green method for the immobilization of Cu NPs on the surface of the graphene oxide/manganese dioxide (GO/MnO_2) nanocomposite using *Cuscuta reflexa* leaf extract. In fact the phytochemical content of the plant extract are responsible to biosynthesis of Cu nanoparticles (NPs) and their stabilization by functionalizing the surface of graphene. The Cu NPs were characterized by Fourier transformed infrared spectroscopy (FT-IR) and UV–visible spectroscopy. MnO_2 NPs and GO/MnO_2 nanocomposite were prepared by using a simple one-step hydrothermal method without using any toxic solvent. The synthesized GO/MnO_2 and Cu/GO/MnO_2 nanocomposites were characterized using X-ray diffraction analysis (XRD), field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM) images, Brunauer–Emmett–Teller (BET), Thermogravimetric analysis (TGA), vibrating sample magnetometer (VSM), energy-dispersive X-ray spectroscopy (EDS), elemental mapping and FT-IR spectroscopy. The synthesized Cu/GO/MnO_2 nanocomposite was then successfully used as a reusable catalyst for the reduction of 2,4-dinitrophenilhydrazine (2,4-DNPH), 4-nitrophenol (4-NP), Rhodamine B (RhB), Congo red (CR), methyl orange (MO) and methylene blue (MB) using $NaBH_4$ in water at ambient temperature. This method is clean and environmentally friendly without using any toxic reducing agents.

1. Introduction

Over the last few years, organic dyes and pigments have potential applications in a broad range of industries such as textile, cosmetic, plastic, paper, food, printing, and pharmaceutical industries [1]. Because of the presence of toxic organic dyes and nitroarene compounds in wastewaters and their visibility in surface waters, reduction of organic dyes and nitro compounds has become an essential topic of considerable interest [2,3]. Furthermore, these colored effluents are often extremely toxic for humans, animals and plants [4]. Thus, the development of novel technologies for the degradation of organic dyes and nitroarenes present in wastewater to nondangerous products is very important.

Degradation of azo dyes to nonhazardous products [5–7] and also nitroarenes to useful compounds [8–10] are difficult due to their complex structure, synthetic nature, their high biologically and chemically stability and low solubility in water. Variety of effluents treatment methods such as chemical, physical and combination of these methods are available [11,12]. Nevertheless, these methods suffer from some disadvantages such as harsh reaction conditions, high temperature, long reaction times, generation of waste sludge, formation of hazardous by-products and heavy operational costs [12]. Therefore, it is necessary to develop newer methods for the degradation of dyes and nitroarenes.

Recently, there are great interests in the application of metal nanoparticles (MNPs) such as Pd, Au, Ag and especially Cu NPs for the degradation of organic dyes and nitro compounds because of

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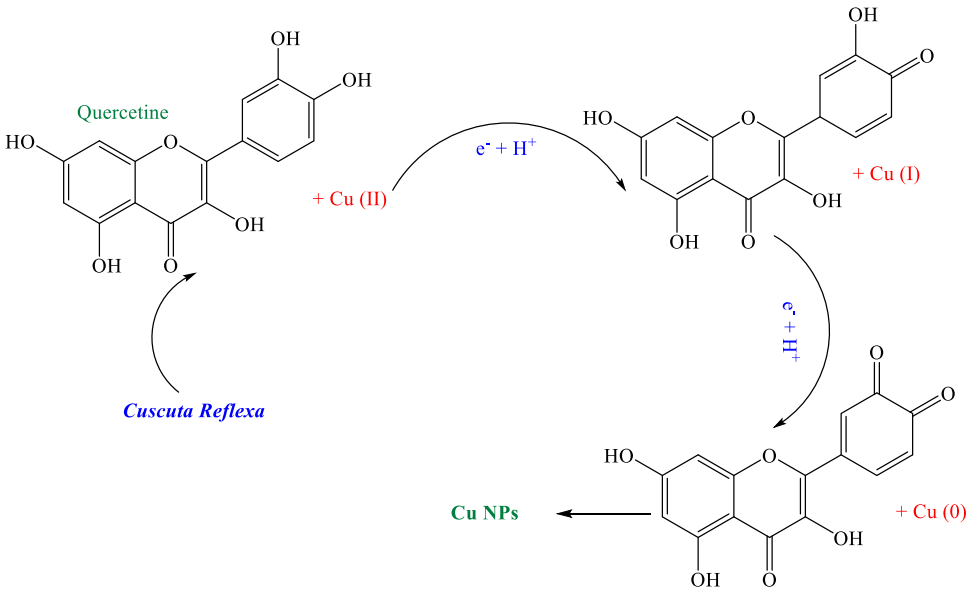
Fig. 1. Images of *Cuscuta reflexa* plant. Reproduced with permission from reference [46].



Scheme 1. Mechanism for biosynthesis of Cu NPs.

their unique properties such as their efficiency, high catalytic activity, high physical, chemical and thermal stabilities, great specific surface area and strong electron transfer abilities [13–16]. However, the physical and chemical methods for the synthesis of MNPs such as Cu NPs suffer from several disadvantages such as environmentally unpleasant use of toxic capping agents or stabilizers, harsh reaction conditions and use of organic solvents or dangerous materials [17–24]. Therefore, it is interesting to investigate highly efficient, environmentally benign and biological methods for the biosynthesis of different MNPs under mild conditions using various plant extracts or gums without use of toxic, corrosive and hazardous materials, high temperature or pressure and organic solvents [25–29].

Recently, we showed that 4-aminophenol (4-AP) can be obtained by reduction of 4-NP using sodium borohydride as the source of hydrogen in the presence of green synthesized Cu NPs in water at room temperature [30]. However, the agglomeration of MNPs without any support is usually inevitable [31–33]. Therefore, the development of heterogeneous catalytic systems via the immobilization of MNPs on a suitable solid support for decrease agglomeration problem has been a major challenge in organic transformations [31–33].

Among the most noted metal oxides, manganese dioxide (MnO_2) as an easily handled reagent was applied rapidly in energy storage [34], sensors and catalysis fields [35,36], due to its low cost, chemical stability, low toxic and high energy density [37]. Nevertheless, MnO_2 commonly provides a low surface area and limited catalytic activity. Graphene and graphene oxide (GO) can be defined as new class of two-dimensional (2D) lattice, extensively used as heterogeneous catalysts and also as ideal supports for the immobilization of MNPs, because of its great surface-to-volume ratio, high thermal stability, high adsorption capacity and good mechanical properties [38–43]. In this work, by combining the advantages of MnO_2 as an active catalyst and GO with large surface area and outstanding dispersion in water medium, a GO/MnO_2 nanocomposite has been produced by using a simple one-step hydrothermal method. Then, Cu/GO/MnO_2 nanocomposite was prepared using *Cuscuta reflexa* leaf extract via the reduction of Cu^{2+} ions to Cu NPs and immobilization of Cu NPs on the GO/MnO_2 nanocomposite surface.

The *Cuscuta reflexa* from the family of *Cuscutaceae* is an extensive climber parasite which mostly distributed in India, China, and East Asia especially in Afghanistan (Fig. 1). The *Cuscuta reflexa* has no chlorophyll and cannot make its own food by photosynthesis. Of course, some reported researches indicated that the plant has very low levels of chlorophyll and can slightly photosynthesis but other species of *Cuscuta* are entirely dependent on the host plants for nutrition [44,45].

For presence of numerous phytochemicals in the plant extract, it has many applications in Chinese herbal medicine which recommended for treatment of kidney and prostate disorders and different types of cancers. Many research studies about the plant confirmed the presence of various antioxidant phytochemicals such as Kaempferol, Kaempferol-3-O-glucoside (Astragalin), Myricetin, Myricetin glucoside, Quercetin, Quercetin-3-O-glucoside, Kaempferol-3-O-galactoside, Quercetin-

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