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Immobilization of copper nanoparticles on perlite: Green synthesis, characterization and catalytic activity on aqueous reduction of 4-nitrophenol

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ABSTRACT

We report the facile synthesis of environmentally benign Cu NPs/perlite composites without employing any toxic reductants or capping agents. Renewable natural *Euphorbia esula L.* not only functioned as a reductant, but also served as a stabilizer for the formation of Cu NPs. Cu NPs synthesized using aqueous extract of the leaves of *E. esula L.* was immobilized on perlite by a very simple and inexpensive method. The structural investigation was performed using XRF, XRD, SEM, EDS, TEM, TG–DTA, BET and FT-IR. The Cu NPs/perlite shows favorable activity and separability on the catalytic reduction of 4-nitrophenol, and can be reused several times without a decrease in the catalytic activity. Their reaction rate constant was calculated according to the pseudo-first-order reaction equation.

1. Introduction

The homogeneous Cu catalyst is known as one of the most efficient catalytic systems for various organic reactions [1–4]. However, homogeneous catalysts suffer from certain disadvantages such as metal aggregation and precipitation which cause catalyst decomposition and a considerable loss of catalytic activity, and are difficult to purify and reuse after chemical reactions which leads to a loss of expensive metal and ligands and contamination to the products [1–4]. Catalyst separation is a critically important issue, and catalysts that are active but difficult to recycle/recover from the reaction mixture are generally not preferred in the chemical industry. Thus, the use of heterogeneous copper catalysts is often desirable from the perspective of process development due to their easy handling, simple recovery, and recycling.

Since catalysis takes place on metal surface, nanoparticles (NPs) are much more reactive than the particulate metal counterpart due to their small sizes and large surface areas [5]. So, heterogeneous catalysts are more and more used in the form of nanoparticles. Unfortunately, the agglomeration of metal NPs is inevitable due to their small size, resulting in a remarkable reduction in their catalytic activities [6]. To prevent the agglomeration of metal nanoparticles (MNPs) and the over-stoichiometric use of Cu reagents, the catalytically active metal NPs are usually immobilized on/into less expensive solid supports such as polymers, carbon, metal oxides, grapheme, gum and zeolite regarded as ideal supports for heterogeneous catalyst due to their excellent stability, high surface area, tunable pore size, and robust surface chemistry [2–4,7–11]. However, most of these supports suffer from inefficiency to achieve highly distributed and stable noble metal NPs. Therefore, it is desirable to develop an efficient and new support for the immobilization of metal NPs.

Perlite is a naturally occurring dense glassy volcanic rock and can be expanded up to 10–20 times its original volume when heated rapidly at 700–1200 °C [12]. Perlite is generally chemically inert and has a pH of approximately 7. It contains silica (greater than 70%), aluminum, potassium, sodium and 3–5% water and is used filler in various processes such as paint, enamels, glazes, plastics, and resins [13]. Since perlite granules are highly porous media, they can naturally act as an excellent support. So far of our knowledge, there is no report of using of perlite as a support for the preparation of new catalysts. This study considers perlite could be used

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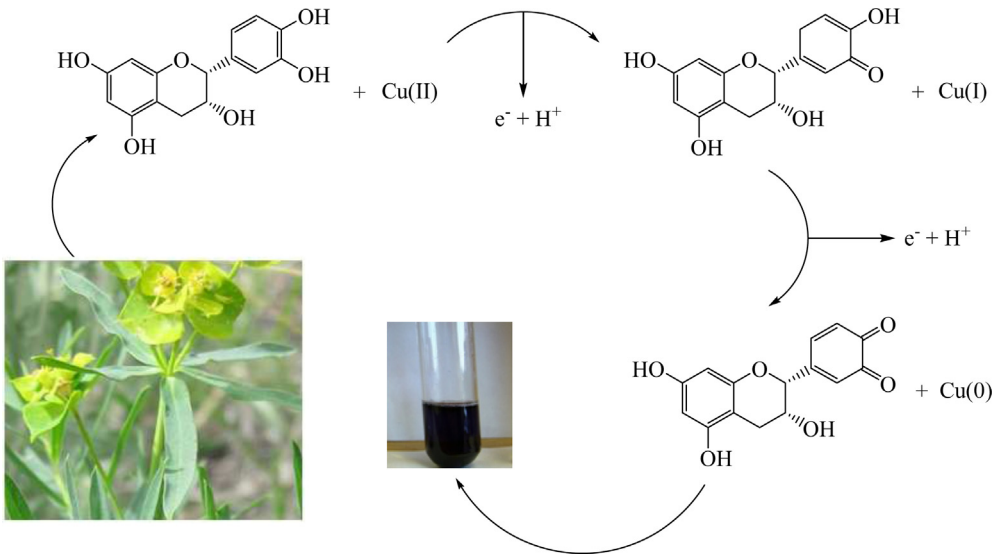

Fig. 1. Bioreduction of metallic ions using the flavonoids as potent antioxidants in aqueous extract of the leaves of *E. esula L.*

as a support for the immobilization of copper NPs. The purpose of this study was to evaluate the catalytic activity of Cu NPs/perlite composites for reduction of 4-nitrophenol in water. Copper (Cu) is relatively cheap compared to other noble metals such as gold (Au), palladium (Pd) and platinum (Pt).

2. Experimental

2.1. Instruments and reagents

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. Melting points were deter-mined in open capillaries using a BUCHI 510 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DRX spectrometer at 400 and 100 MHz, respectively. The element analyses (C, H, and N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on PerkinElmer 240c analyzer. X-ray diffraction (XRD) was performed at 25 °C (D/Max-2550 PC, RIGAKU, Japan) in reflection mode using Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet 5700 spectrometer (Thermo Nicolet Corporation, US) at the wavenumber range 4000–400 cm^{-1} at ambient conditions. Morphologies of catalyst were observed using a scanning electron microscope (JSM-5600LV, JEOL Ltd., Japan) with an operating voltage of 15 kV. The elemental composition of catalyst was analyzed using an X-ray energy dispersive spectroscopy (EDS) detector (IE 300X, Oxford, UK) attached to the SEM. Thermogravimetric–differential thermal analysis (TG–DTA) was performed using STA 1500 Rheometric Scientific (England). The flow rate of air was 120 mL/min, and the ramping rate of sample was 2 °C/min. The shape and size of Cu NPs crystals were identified by transmission electron microscope (TEM) using a Philips EM208 microscope operating at an accelerating voltage of 90 kV. The Brunauer–Emmett–Teller (BET) specific surface areas (SBET) and the porosity of the samples were evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a BELSORP-max nitrogen adsorption apparatus (Japan Inc.). Ultraviolet–visible (UV–vis) absorption spectra were recorded by a Shimadzu UV 2100 PC UV–vis spectrophotometer.

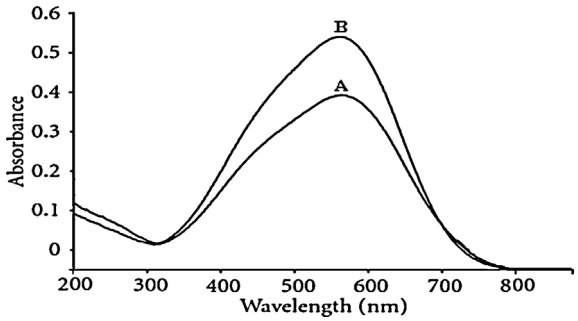

Fig. 2. UV–vis spectrum of Cu NPs synthesized using aqueous extract of the leaves of *E. esula L.* (A: 20 min and B: 30 min).

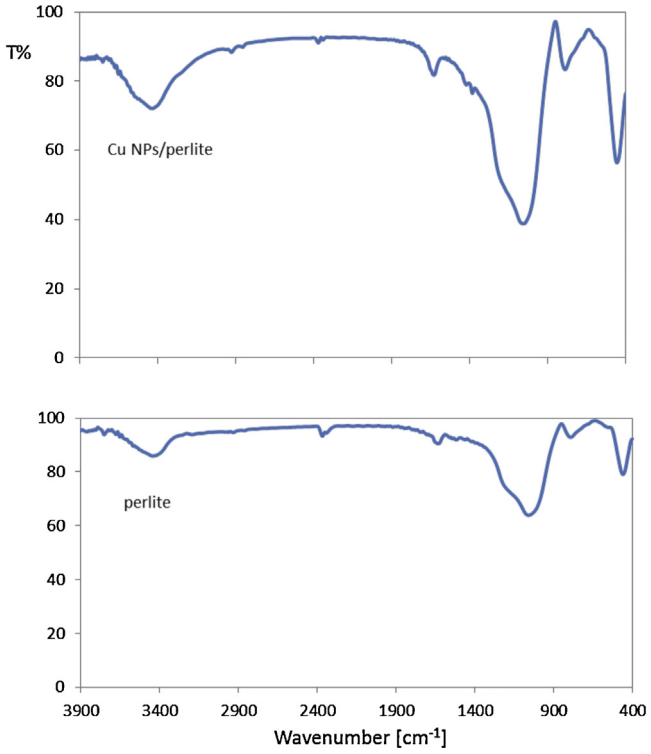

Fig. 3. FT-IR spectrum of Cu NPs/perlite and perlite.