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Aqueous extract from seeds of *Silybum marianum* L. as a green material for preparation of the Cu/Fe_3O_4 nanoparticles: A magnetically recoverable and reusable catalyst for the reduction of nitroarenes

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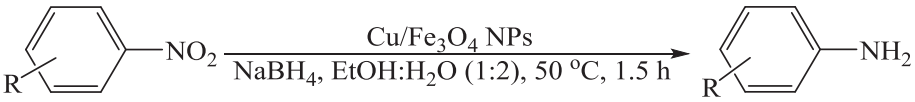
HIGHLIGHTS

- Green synthesis of Cu/Fe_3O_4 nanoparticles by *Silybum marianum* L. seeds extract.
- Catalyst was characterized using XRD, TEM, EDS and UV–vis.
- Reduction of nitroarenes in EtOH/H_2O.
- The catalyst can be recovered by a magnet and reused several times without significant loss of catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we report the green synthesis of the Cu/Fe_3O_4 nanoparticles using *Silybum marianum* L. seeds extract and their application as magnetically separable nanocatalyst for the reduction of nitroarenes. Our method is clean, nontoxic and environment friendly. The synthesized nanocatalyst is characterized by XRD, TEM, EDS and UV–visible techniques. UV–visible spectroscopy is used to monitor the kinetics of the Cu/Fe_3O_4 nanoparticles formation. The results from Fourier transform infrared spectroscopy showed that the C=O and C—O groups in the plant seeds extract played a critical role in capping the nanoparticles. The expected reaction mechanism in the formation of nanoparticles is also reported. The catalyst is recoverable by magnetic decantation and could be reused several times without significant loss in catalytic activity.

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1. Introduction

Aromatic amino compounds are important organic industrial raw materials which are widely used as key intermediates in dye, pharmaceutical, herbicide, agrochemical and pesticide industry [1]. Classical methods for the synthesis of amines have involved amination of aryl halides using palladium catalysts in the presence of toxic phosphine ligands [2], amination of various groups (H, F, Cl, Br, I, OH, etc.) via the corresponding diazonium salts [3] and catalytic or non-catalytic reduction of nitroarenes [4–13]. However, the selective reduction of aromatic nitro compounds is the best route to obtain industrially important aryl amines.

There are several reports in the literature for the reduction of the nitro aryl compounds, these include metal/acid reduction [4,5], catalytic hydrogenation [6–8], electrolytic reduction [9], homogeneous catalytic transfer hydrogenation [10], heterogeneous

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catalytic transfer hydrogenation [11–13], etc. However, each of these methods suffers from different drawbacks [14]: metal/acid system are readily inactivated and less selectivity and acid brings severe corrosion to the equipment; catalytic hydrogenation employs a higher reaction pressure which may bring great danger; homogeneous or heterogeneous catalytic transfer hydrogenation could perform well only in the existence of expensive metals such as palladium, platinum, and ruthenium, and separation of the target product is difficult. Base-metal Cu has a low price, low toxicity, and it can reduce the consumption of noble metals and remove the kinetic barrier of the reaction to support electron relay for the reduction [15]. Thus, copper is an excellent choice to alter catalyst activity and selectivity [16,17].

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. In addition, NPs can be recovered through a centrifugation or filtration process and be reused for the next reaction. However, the agglomeration of the Cu NPs is inevitable. To prevent the agglomeration of the metal NPs and the over-stoichiometric use of the metal reagents, several inorganic materials such as CuO [18], zeolites [19,20], magnetic-materials [21], graphene [22–25] and gums [26] have been used as a support for metal NPs. Compared with other supports, iron oxide magnetic nanoparticles (Fe_3O_4-MNPs) could be a more desirable support substrate for growing and anchoring metal NPs due to its large specific surface area, chemical stability, unique magnetic properties and ease of recovery with an external magnet [21,27]. These supported catalysts proved to be effective and easily separated from the reaction media by applying an external magnetic field without using any filtration or centrifugation.

Till date, several chemical synthetic procedures and physical methods have been reported for the preparation of the metal/Fe_3O_4 nanoparticles, but these methodologies suffer from numerous limitations such as the use of toxic, expensive chemicals and flammable organic solvents, and formation of toxic by-product make it very difficult to meet the requirements of environmentally friendly chemical processes [21,27]. Also, there are problems in case of physical synthetic methods due to the enormous consumption of energy required to maintain the high temperature and pressure conditions needed for these methods. In contrast, biosynthetic routes employing either biological microorganisms or plant extracts provide a simple and viable alternative, environmental-friendly means of obtaining metal nanoparticles [28–32]. Green synthesis of metal NPs using plant extracts as the biogenic agents has several advantages easy availability, simplicity, very mild reaction conditions, and use of non-toxic solvents such as water, elimination of toxic and dangerous materials and cost effectiveness as well as compatibility for biomedical and pharmaceutical applications [28–31]. In addition, this synthetic procedure is applicable at room temperature and pressure, thus saving huge amount of energy.

Silybum marianum L. belonging to *Compositae* is mainly used as a medical plant due to the presence of active phytochemical compounds. The seeds of the plant are a major source of silymarin flavonoids which is a mixture of three flavonolignans, including silybin (silibinin), silidianin, and silichrystin (Fig. 1). Other flavonolignans identified in *S. marianum* L. include dehydrosilybin, deoxysilycistin, deoxysilydianin, silandrin, silybinome, silyhermin, and neosilyhermin. In addition, the plant contains potential antioxidant phytochemicals such as apigenin, taxifolin, silybonol, myristic, oleic, palmitin, and stearin acids therefore; it can be used as an important source for bioreduction of metallic ions and producing the nanoparticles [33–35].

In continuation of our previous efforts for the development of greener catalytic protocols for various synthetic transformations [28–31], and herein, we report a new and rapid protocol for the preparation of the Cu/Fe_3O_4 NPs by using *S. marianum* L. seeds extract as a reducing and stabilizing agent and their application as magnetically separable nanocatalyst for reduction of nitroarenes. The heterogeneous catalyst could be recovered easily by an external magnet and reused many times without significant loss of its catalytic activity. The present protocol is highly potent to address the industrial pre-requisites and environmental concerns.

Fig. 1. Image of *Silybum marianum* L. leafs and seeds.

2. Experimental

2.1. Instruments and reagents

All reagents were purchased from the Merck and Aldrich Chemical Companies and used without further purification. Products were characterized by comparison of their physical and spectral data with those of authentic samples. ^{1}H NMR spectra were recorded on a Bruker Avance DRX 400 MHz instrument. The chemical shifts (δ) are reported in ppm relative to TMS as the internal standard and J values are given in Hz. ^{13}C NMR spectra were recorded at 100 Hz. FT-IR (KBr) spectra were recorded on a Perkin–Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. TLC was performed on silica gel polygram SIL G/UV 254 plates. X-ray diffraction (XRD) measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. It was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded in the 2θ range (10–80) with scanning speed of 2°/min. The shape and size of Cu/Fe_3O_4 NPs crystals were identified by transmission electron microscope (TEM) using a Philips EM208 microscope operating at an accelerating voltage of 90 kV. The chemical compositions of the synthesized nanostructures were measured by EDS. UV–visible spectral analysis was recorded on a double-beam spectrophotometer (Hitachi, U-2900) to ensure the formation of nanoparticles.

2.2. Preparation of S. marianum L. seeds extract

100 g of dried seeds powdered of *S. marianum* L. was added to 500 mL double distillated water in 1000 mL flask and well mixed. The preparation of extract was done by using magnetic heating stirrer at 60 °C for 1 h. The colorless extract obtained was centrifuged in 7000 rpm then filtered and filtrate was kept at refrigerator to use further.

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