Copper Nanoparticles Encapsulated Alginate Composite for Reduction of Aromatic Nitro Compounds

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Abstract— Copper Oxide support sodium alginate polymer (CuO/SA) nanocomposite were prepared by green synthesis reduction method using leaf extract of Aglaia elaeagnoidea. The leaf extract of plant used as reducing, stabilizing and capping agent in the synthesis of nanocomposite. The reduction of copper nanoparticles and encapsulation in the polymer were confirmed by UV–Visible Spectra, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) techniques. The crystalline nature of copper nanoparticles was found to 18 nm with spherical shape on alginate, which has been obtained from characterization results. The produced copper oxide-sodium alginate nanocomposite was used as catalyst for the reduction of 4-Nitrophenol in the liquid phase. Nitrophenol conversion was confirmed using UV–Visible Spectra and the stability of nanocatalyst were tested by its recyclability and reuse.

Index Terms— Green synthesis; Aqueous leaf extract; Copper Oxide encapsulated alginate nanocomposites; 4-Nitrophenol reduction.

1 Introduction

The unique optical, chemical, physical, electrical, magnetic and mechanical properties of noble metal nanoparticles have gained significant attention [1]. Among a range of noble metal nanoparticles, copper (Cu) nanoparticles (NPs) has particular interest due to its distinctive properties and a wide range of remarkable application in sensors, biomedical, catalysis, environmental pollution remediation and batteries fields [2,3]. Several methods has been reported for the synthesis of copper and copper oxide nanoparticles such as laser ablation, vapour condensation, micro-emulsion, sonochemical and microwave [4-8]. Synthesis of CuO NPs by these methods have many drawbacks such as large energy inputs, labor-intensive, use of toxic and hazardous organic solvents and thereby leaving by-products into the environment [9]. Therefore, application of green chemistry in the synthesis of metal nanoparticles has been established as an alternative approach for safe and eco-friendly production [10].

Increase in industrialization and urbanization leads to increase in the discharge of organic pollutants such as hexachlorobenzenes, azo dyes, DDT, sulphonamides, toxaphene, aromatic nitro compounds, polychlorinated biphenyls, etc. into the environment [11]. Aromatic nitrophenol compound are one of the major notable stable water pollutant released from drug and agricultural products manufacturing industries [12]. Due to the importance in the conversion/reduction of nitrophenol to aminophenol, several methods has been established for the reduction nitrophenol compound to aminophenol such as metal/acid reduction, catalytic hydrogenation, electrolytic reduction and by hydrazine as reducing agent [13-16]. The reduction/removal of nitrophenol compound to aminophenol from water using these methods are very difficult and expensive due their stability [13]. In this circumstances, green synthesized metal nanoparticles offering hazardous free nanocatalyst for the reduction nitrophenol by a reducing agent as sodium borohydride ($NaBH_4$) has shown as promising method [17].

In continuance of our studies on the green synthesis of various metal and metal oxide nanoparticles on support material sodium alginate (SA) and its heterogeneous catalytic activity, we report a green procedure for the synthesis and encapsulation of CuO NPs on SA using leaf extract of Aglaia elaeagnoidea. The plant belongs to family Meliaceae, it was used as medicine in the treatment of tumors, skin diseases [18]. Hence, we demonstrated the synthesis of CuO NPs encapsulated in sodium alginate as a support material, an environmentally safe method for the heterogeneous catalytic reduction of nitrophenol (NP) from liquid phases. The plant phytochemicals acts as reducing, capping, stabilizing agent for the metal and metal oxide nanoparticles.

2 Experimental Section

2.1 Materials and Instruments

Aglaia elaeagnoidea leaves collected from Pondicherry University, are used as biomaterial for synthesis CuO/SA in this study. Copper (II) sulfate pentahydrate, Sodium alginate, Calcium chloride, Nitrophenol and Sodium borohydride were procured Merck and Aldrich. The optical properties of cryo grinded nanocomposite was measured by UV–Vis spectrophotometer (Hitachi, U-2900). FTIR spectra were recorded on a Thermo Nicolet Model: 6700 spectrophotometer. X-ray diffraction data were obtained using PAN XPERT diffractometer with Cu-K α radiation of λ = 1.5406, scanning speed of 2° min-1. Morphology of CuO/SA was obtained using high resolution transmission electron microscopy (HRTEM: Jeol/JEM 2100). The elemental composition of the green synthesized CuO/SA nanocomposite was investigated by Energy Dispersive X-ray Spectroscopy (EDXS).

2.2 Preparation of the extract

In a 250 ml conical flask, 10 g of Aglaia elaeagnoidea leaf powder was mixed to 125 ml double distillated water and heated on magnetic stirrer at 70°C for 15 min. The obtained extract were filtered using Whatman filter paper.

2.3 Preparation of CuO/SA nanocomposite using the leaf extract of the A. elaeagnoidea

In the preparation of CuO/SA nanocomposite, 10 ml of the leaf extract of the A. elaeagnoidea and Sodium alginate (1%, w/v) was added to 100 ml of 1 M $CuSO_4$ and stirred for 5 min and kept in dark for 48 h. This mixture was added dropwise to 200 ml of 0.1 M $CaCl_2$ on magnetic stirrer. Formation of brown color beads were observed in the $CaCl_2$ solution due to encapsulation of CuO in alginate.

2.4 General Procedure for Catalytic Activity of CuO/SA Nanocomposite

To assess the catalytic efficiency of the CuO/SA nanocomposite, 7.0 mg of the nanocatalyst was added to 5 ml of 10^{-4} M NP with 5 ml of 10^{-3} M freshly prepared sodium $NaBH_4$. The reaction of the mixture was examined by the UV–Vis spectra. The dark yellow color was slowly disappeared which indicates the aminophenol (AP) formation. The catalyst were recovered from the mixture after completion of reaction and then, washed with double distilled water for reuse.

3 Results and Discussion

3.1 Characterization of CuO/SA

The phytochemicals of leaf extract plays major role in the formation of CuO/SA nanocomposite. UV-Vis spectra of cryo grinded CuO/SA nanocomposite (Fig.1) illustrated the considerable changes in the absorbance and the excitation of metal nanoparticles due to of surface plasmon resonance (SPR). The red shift in SPR band with a maximum wavelength at 250-300 nm indicates CuO nanoparticles reduction, SPR is generally depend on the dielectric and morphology properties of the metal/metal oxide nanoparticles [17,19,20]. There is no UV-Vis spectrum absorbance were observed for the alginate alone [21].

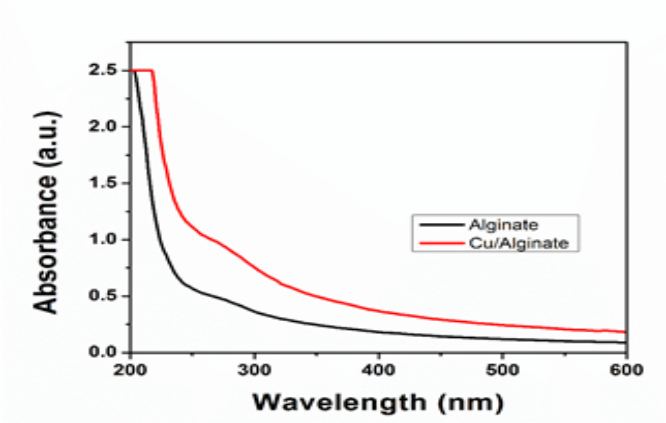

Fig.1. UV – Visible absorption spectrum of CuO/SA nanocomposite.

The phytochemicals of leaf extract of A. elaeagnoidea involvement in the formation of encapsulation of CuO in alginate were confirmed by FTIR spectrometer. The compared IR peaks of extract and CuO/SA was shown in the Fig. 2. The decrease and shift in the intensity of extract peaks corresponding O-H group related to phenolic compounds, which is completely utilized as reducing agent in the synthesis of CuO/SA [22]. The carbonyl stretching peaks of the extract, linkages of proteins are acts as capping agent in the encapsulation of copper oxide in alginate [23]. IR spectra results reveals the association of phenolic compounds and proteins in the synthesis of CuO/SA nanocomposite.

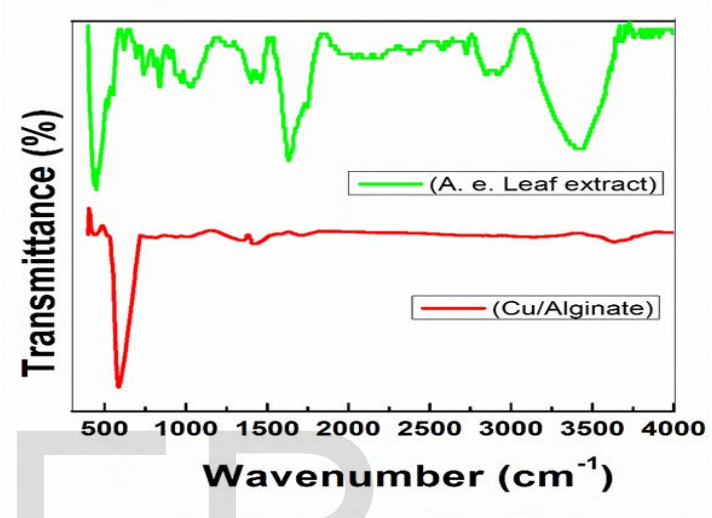

Fig.2. FTIR of A. elaeagnoidea leaf extract and of CuO/SA nanocomposite.

The XRD analysis of the CuO/SA nanocomposite and pure alginate is shown in Fig. 3. Bragg diffractions at 2θ is 32.37°, 38.07°, 53.87°, 58.72° and 68.32° corresponding to the (110), (111), (020), (202), and (220) of CuO in face centered cubic crystalline nature (JCPDS#01-089-2531) [18].

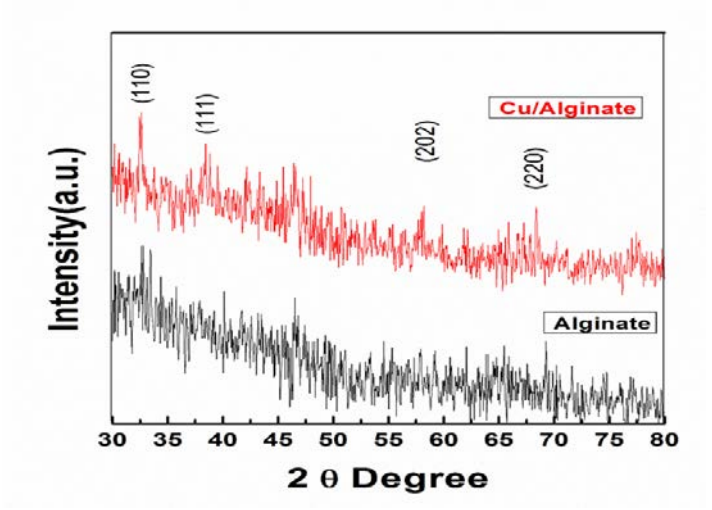

Fig.3. XRD pattern of pure alginate and CuO/SA nanocomposite.

The morphology and encapsulation of CuO inside the alginate were characterized using TEM image analysis. TEM image of

CuO/SA nanocomposite (Fig.4a) reveals the crystalline nature of spherical shaped CuO nanoparticles in alginate with an average size of 18 nm. The elemental composition of CuO/SA nanocomposite was investigated by EDXS analysis. This reveals the presence of copper, oxide, calcium and chloride, oxygen presence might be due to the oxidation during the synthesis of copper nanoparticles and calcium and chloride are related to alginate (Fig.4b). Because IJSER staff will do the final formatting of your paper, some figures may have to be moved from where they appeared in the original submission. Figures and tables should be sized as they are to appear in print. Figures or tables not correctly sized will be returned to the author for reformatting.

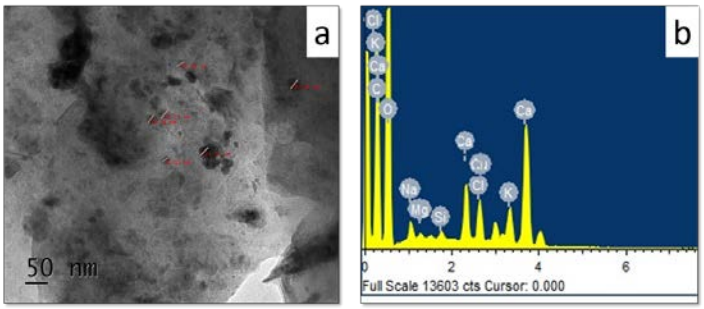

Fig.4. (a). TEM image (b). EDAX of CuO/SA nanocomposite.

3.2. Catalytic activity of CuO/SA nanocomposite

Metal oxide nanoparticles support on different materials reduce or degrade the organic pollutants from the environment via electron transfer mechanism. The surface area of CuO acts a substrate in the electron rely among reducing agent and organic pollutant [23,24]. The catalytic efficacy of CuO nanoparticles encapsulated in natural polymer alginate was assessed for the reduction of hazardous organic pollutant, NP in presence of $NaBH_4$. The nitrophenol shows the maximum absorption peak around 318 nm with pale yellow color while addition $NaBH_4$, a new peak around 400 were appear corresponding to the nitrophenolate ions with dark yellow in color. The absorption peak of nitrophenolate ions were constant for 24 h without CuO/SA nanocomposite. Therefore, a new absorption peak appears at 290 nm corresponding to aminophenol by addition of 7 mg of CuO/SA to the mixture (Fig.5a) [25]. The dark yellow color of nitrophenolate ions reduces and become decolorized within 30 min on the incorporation of CuO/SA nanocomposite. In the catalytic reaction, the reducing agent concentration is higher than nitrophenol compounds, it could be constant and to investigate the constant for nitrophenol kinetics pseudo-first-order were applied using below equation [17,26] :

$$\ln (C_t/C_0) = \ln(A_t/A_0) = kt \quad \text{..... (1)}$$

Where, (C_t/C_0) = NP concentration at time t and 0. (A_t/A_0) is Absorption at any time t and 0,

Fig. 5b shows the rate constant for NP and it could be calculated as 0.079 min^{-1} [27]. For the industrial application, reuse and recyclability was important. The stability of green synthesized CuO/SA nanocomposite were evaluated by its recyclability for the reduction/conversion of nitrophenol to aminophenol in the presence of reducing agent over six cycles with more than 70% of conversion efficiency (Fig.6).

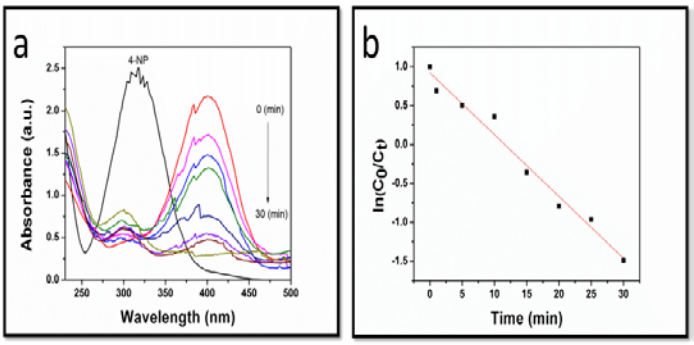

Fig.5. (a). NP reduction and (b). Rate constant

4 Conclusion

In this study summary, we have showed an eco-friendly and cost effective method for the synthesis of the CuO/SA nanocomposite using aqueous leaf extract of A. elaeagnoidea without any stabilizers or capping agents. The characterization of green synthesized nanocomposite using UV-Vis spectra and FTIR confirms the utilization of phytochemicals of extract in the reduction of metal ions and TEM along with EDAX confirms the encapsulation of CuO in alginate support material. In the reduction of NP in liquid phase were taken as model reaction to test the catalytic efficacy of CuO/SA nanocomposite. The results of the work might be used remove organic pollutants, particularly in the conversion NP and other applications in commercial level in natural method.

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