Green Synthesis of Copper Nanoparticles, Characterization and their Catalytic Application in the Synthesis of Dibenzoxazepine

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Abstract

In this research a green method was employed to synthesize copper nanoparticles by the reduction and precipitation of copper nanoparticles from copper sulphate solution using leave extracts of spinach and peppermint as capping and reducing agents while ascorbic acid acted as the anti-oxidant. The synthesized copper nanoparticles were then applied as catalyst in the synthesis of dibenzoxazepine from salicylaldehyde and aniline with a mixture of potassium carbonate, sodium bicarbonate and sodium carbonate as base in the presence of methanol. The synthesized nanoparticles were characterized by Fourier Transform Infra-Red spectroscopy (FTIR), powder X-ray diffraction (p-XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The IR spectra obtained indicated that the extracts were adsorbed (capped) on the surface of the copper nanoparticles through the functional groups present thereby preventing agglomeration. The p-XRD pattern were matched with those of cubic copper and this is also supported by EDS analysis which confirmed the presence of copper. The SEM images showed mostly spherical copper nanoparticles with an average size of about 10 μm. Finally, the FTIR spectrum showed the formation of a dibenzoxazepine using the copper nanoparticles via one pot approach.

Keywords: green synthesis, copper nanoparticles, chemical reduction, room temperature

Introduction

In recent times, copper nanoparticles have found different applications due to their unique optical, catalytic, anti-microbial, mechanical and electrical properties. (Khodashenas and Ghorbani, 2014). Copper plays an important role in electronic circuits because of its excellent electrical conductivity. Copper nanoparticles have also been used as catalysts in organic reactions and is of high efficiency due to its high surface area. (Kaur et al., 2015) It is a good alternative for the noble metal catalysts such as silver and gold because of its high natural abundance, very conductive and more economical. Copper nanoparticles have been synthesized through different techniques including chemical reduction (Chandra and Kumar, 2016) electrochemical synthesis (Zhang and Hua, 2014), reverse micelles (Malik et al., 2012) microwave assisted synthesis (Tanghatari et al., 2017) thermal decomposition method (Kim et al., 2008) and green synthesis (Kulkarni and Kulkarni, 2013). The chemical reduction method mostly involving reducing agents that provide electrons for the reduction of Cu salts (such as CuSO₄, copper (II) acetyleacetonate, CuCl₂ or Cu(NO₃)₂). Reducing agents used for this purpose often include cetlytrimethyl ammonium bromide (CTAB) (Wu and Chen, 2004), sodium borohydride (Dang et al, 2011), hydrazine (Saikova et al., 2010, Sierra-Ávila et al., 2014). Capping agents such as starch (Valodkar et al., 2011) chitosan (Usman et al., 2012)
and Poly vinyl pyrrolidone-PVP (Kulkarni and Kulkarni 2013) have also been used to stabilize the ensuing Cu NPs and to control the particle growth. Copper nanoparticles (CuNPs) in chitosan was synthesized via the chemical reduction method. The nanoparticles were synthesized in an aqueous solution in the presence of chitosan as stabilizer and copper sulphate as the precursor. The synthesis proceeded with addition of sodium hydroxide (NaOH) as pH moderator, ascorbic acid as antioxidant and hydrazine as the reducing agent. (Usman et al., 2012). The microwave assisted synthesis is a relatively new approach which uses microwaves as an alternate energy source for the reaction. In this process, the reaction mixture is irradiated with microwaves whose electromagnetic energy is converted into heat and accelerates the synthesis of Cu-based NPs. Tanghatari et al used a rapid microwave-based method for the preparation of metallic Cu NPs by reduction of copper nitrate with ascorbic acid and PVP as capping agent. This approach offers high reaction rates and yields a product with a narrow particle size distribution of about 15 nm. 

Amongst the various methods of synthesizing copper nanoparticles, the green method of using plant derived extracts as both capping and reducing agents is an emerging method that requires special mention. This is because it avoids the use of toxic chemicals thereby making it an eco-friendly way. The synthesis of copper nanoparticles using Hibiscus Rosasinensis plant leaf extract as capping agent was reported by Subbaiya and Masilamani Selvam in 2015. The synthesized CuNPs showed good antimicrobial activity against clinically important pathogens like Bacillus subtilis and E. coli. It is also illustrated that the synthesized Cu-NPs were acting as an effective drug to treat lung cancer. Terminalia Arjuna plant extract was used to reduce copper nitrate under the MW irradiation conditions by Yallappa et.al. in 2013 which resulted in the formation of stable copper nanoparticles. The importance of copper nanoparticles cannot be overemphasized; hence research is still on going about getting stable nanoparticles. In this research, copper nanoparticles were prepared using copper sulphate as precursor, peppermint and spinach leave extract as both capping and reducing agents and ascorbic acid as anti-oxidant. The synthesised copper nanoparticles were characterised with p-XRD, SEM, EDX and FTIR. The nanoparticles were then tested as catalyst for the synthesis of dibenzoxazepine.

Experimental

Preparation of Spinach and Peppermint Leaves Extract

Fresh African Spinach and peppermint leaves were bought from a local market in Lagos. The leaves were washed several times with distilled water and was air dried for a few days. Then the leaves were ground to a fine powder and kept separately in different air-tight containers. 5 g of spinach or peppermint powder was weighed and transferred to a beaker. 50 ml of distilled water was measured and transferred to the beaker. It was placed on a hot plate and allowed to boil for 15 minutes. After boiling, it was allowed to cool and filtered using a filter paper. It was kept in a bottle and kept refrigerated until needed.

Preparation of Precursor Solutions

Copper sulphate pentahydrate salt was weighed (0.50 g, 0.04 M) and dissolved in little distilled water in a beaker. The resulting mixture was transferred into a 50 ml standard flask and distilled water was added up to the mark. 5 g of ascorbic acid was dissolved in 50 ml distilled water. It was stirred until a clear solution was obtained.

Green Synthesis of Copper Nanoparticles with Peppermint and Spinach Extracts

50 ml of the copper sulphate pentahydrate solution was measured into a three-necked round bottom flask. Then 50 ml ascorbic acid was added to the copper sulphate solution followed by 25 ml of the extracts (peppermint and spinach). The resulting mixture was heated on a hot plate for 1 hour under rapid stirring at 60-80 °C using a magnetic stirrer under nitrogen atmosphere. On the addition of ascorbic acid, the colour changes from blue to light green. The green solution now turned reddish brown after adding the extracts indicating the formation of copper nanoparticles. The brown solution was then centrifuged, washed with distilled water and left to dry completely.

The Use of Copper Nanoparticles as Catalyst for the Synthesis of Dibenzoxazepine

The procedure used was according to the one in literature but with modifications (Chandra and Kumar, 2016) Methanolic solution of salicyladehyde (0.117 g, 0.001 mol) was put in a round bottomed flask and stirred. To this solution, aniline (0.102 g, 0.001 mol) was added followed by copper nanoparticles (25 mol %) and 0.001 mol of K₂CO₃ / KHCO₃/Na₂CO₃ as the base in methanol at room temperature. The whole reaction
mixture was refluxed for 2 h and monitored by TLC. After completion of the reaction and allowing it to cool, the mixture was diluted with distilled water and the product extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulphate and the solvent was removed in vacuo. The crude product was purified by column chromatography using ethyl acetate in petroleum ether (1: 4) as an eluent to give the desired product (yellow crystals). The reaction scheme was depicted in Figure 1 below:

**Figure 1** showing the reaction scheme for the synthesis of dibenzo oxazepine

**Results and Discussion**

**Copper Nanoparticles**

The synthesized copper nanoparticles were characterized using FTIR, EDX, SEM and p-XRD.

**Figure 2** shows the FTIR of extracts and copper nanoparticles capped with extracts

The peak at 3321 cm\(^{-1}\) is attributed to OH stretching. This peak became broadened and there is a shift in the IR spectrum of nanoparticles capped with extract indicating that there is adsorption of OH bond on the surface of the nanoparticles. The C=O stretching peak (1637) found in the extract disappeared in the synthesized nanoparticles capped with extract suggesting that oxidation must have taken place, hence confirming the use of the extracts as reducing agent.

**Figure 3** shows the p-XRD pattern obtained for the synthesised nanoparticles.

The p-XRD pattern was used in the identification of the synthesised nanoparticles and was found to match with face centred cubic copper (ICDD NO: 00-003-1005) with some traces of copper oxide.

The formation of copper nanoparticles was also confirmed by the EDS spectrum (Figure 4) which showed the presence of copper in about 55%.
Figure 4 is an EDS spectrum of the synthesised copper nanoparticles.

The SEM images of copper nanoparticles stabilized by spinach and peppermint leaves extract (Figure 5) revealed a nearly monodispersed distribution of particle sizes. The nanoparticles are spherical with average particle size of about 10 μm.

Figure 5 shows the SEM image of the copper nanoparticles.

Characterisation of Synthesised Dibenzoaxepine

FTIR was used to characterise the product formed. Figure 6 shows the IR spectra of the starting materials as well as the product.

Figure 6 shows the FTIR of salicylaldehyde, aniline (starting materials) as well as the product formed. In Figure 6, the third IR spectrum (red) showed disappearance of absorption bands of primary amine (3431 cm⁻¹ and 3353 cm⁻¹) and the carbonyl of salicylaldehyde (1661 cm⁻¹). The appearance of a strong stretching frequency at 1615 cm⁻¹ is attributed to the imine functional group (C=N) while carbon to oxygen bond (C-O) absorption bands of ether occurred at 1277 cm⁻¹ and 1184 cm⁻¹ respectively. From the above data, it can be deduced that a new dibenzoaxepine has been formed via one pot synthesis using copper nanoparticles.

Conclusion

Copper nanoparticles was successfully prepared using anhydrous copper sulphate as precursor, a mixture of spinach and pepper mint extracts as capping / reducing agents and ascorbic acid as antioxidant. The FTIR result shows the adsorption of the nanoparticles on the functional groups present in the extract. SEM, XRD and EDX were used in characterising the copper nanoparticles. The copper nanoparticles were then used as a catalyst in reaction between salicylaldehyde and aniline to form dibenzoaxepine which was confirmed by using FTIR.

References


