

Artificial Cells, Nanomedicine, and Biotechnology

An International Journal

ISSN: 2169-1401 (Print) 2169-141X (Online) Journal homepage: <https://www.tandfonline.com/loi/ianb20>

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To cite this article: Atena Naeimi, Sedighe Abbaspour & Seyedeh Atekeh Torabizadeh (2020) The first and low cost copper Schiff base/manganese oxide bio nanocomposite from unwanted plants as a robust industrial catalyst, *Artificial Cells, Nanomedicine, and Biotechnology*, 48:1, 560-571, DOI: [10.1080/21691401.2020.1725027](https://doi.org/10.1080/21691401.2020.1725027)

To link to this article: <https://doi.org/10.1080/21691401.2020.1725027>



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Published online: 11 Feb 2020.



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The first and low cost copper Schiff base/manganese oxide bio nanocomposite from unwanted plants as a robust industrial catalyst

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ABSTRACT

In this paper, the first bio-nano colloid including manganese oxide nanoparticles and copper nanocomplex in the presence of *Amaranthus spinosus* as one unwanted plant was prepared (Mn₃O₄/CuL bio-nanocolloid). As-prepared bio nanocolloid was analysed completely by different techniques such as FT-IR, ICP-AES, SEM, EDX, TEM and elemental analysis to have the size, structure, morphology and elements in this compound. This bio-nanocolloid showed high catalytic activity towards green oxidation reactions of alcohols using hydrogen peroxide under solvent free conditions. The longevity, easy and practical recoverability of the solid catalyst was also confirmed for six times. The natural starting material for a long-term stability catalyst preparation, using ideal oxidant (H₂O₂), solventless and easy work up show the great potential in scalability for actual industries applications.

ARTICLE HISTORY

Received 15 September 2019
Revised 27 December 2019
Accepted 28 December 2019

KEYWORDS

Amaranthus spinosus; green chemistry; oxidation of alcohols; bio nanocomposite

Introduction

Nanocomposites, having several outstanding properties as compared to conventional monolithic materials, are one of the most important classes of the engineered compounds [1]. Their possibilities in tuning the properties of nanocolloid composites gained much importance in different fields commercially and technologically [2–6]. In this regards, chemical synthesis of nanocomposite materials reduces their application in various field because chemical materials can impart toxicity to them. Toxicity related to these kinds of compounds has been directly linked to the use of chemicals as reducing and capping agent [7–12]. Recently, some studies have used less toxic chemical reducing agents, but these studies have used acidic/basic environment or surfactant for their synthesis, which can be toxic to environment and living organisms. Hence, the preparation of nanocolloid composites special metal matrix composites using natural substrates such as plants is becoming popular and attractive day by day to minimum or no use of harmful chemicals [13]. These methods are not only eco-friendly but also less time consuming, cost effective, stable operation, efficient and safer [14–19]. Among plants, weeds are plants that grow where they are not wanted and are therefore bad news to crop farmers. While, they can be very useful for many fields [20–24]. They find various potential applications such as catalysts, solar cells and treatment of water, pharmaceutical industry and Li-air batteries due to their low cost, earth abundance, environmental friendliness and variable oxidation states [25–29].

Oxidation reaction is one of the most important reactions in pharmaceutical industries [30]. The safety of oxidation systems in large scale can influence on the hesitation to employ. Fuel, energy and oxidant are three factors in reactors for performing oxidation reactions in industry [31]. Hence, green strategies attract so much attention as economical and environmental point of view. Oxidation of alcohols to aldehydes, esters and carboxylic acids, and ketones are one of the most essential chemical processes in both academic and industrial research, because alcohols can transfer to valuable products for pharmaceuticals, dyestuffs, agrochemicals and fragrances industries [31–34]. Many applied homogeneous catalysts for these reactions created many challenges from the environmental point of view. Hence, increasing efforts have been devoted in developing heterogeneous catalysts. Recently, metal matrix nanocomposites including metal oxides or/and nano transition metal oxide could replace instead of heterogeneous catalyst. Particularly and ideally in aqueous solution, H₂O₂ is greatly attractive for releasing active oxidative species and producing water as the only by-product. In this context, employing nano metal oxides along with nano-transition metal complex to fabricate efficient catalysts for alcohols oxidation with green oxidant is highly desirable [35].

To reach this goal and in continuing our works on synthesis of novel nanocatalysts for industrial application, we made copper nanocomplex (CuL) and fabricated nanocolloid including CuL nanocomplex based on Mn₃O₄ nanoparticles using ultrasonic irradiation in the presence of *Amaranthus spinosus* (AS). The catalytic activities of it were considered as a heterogeneous catalyst for selective oxidation of primary and

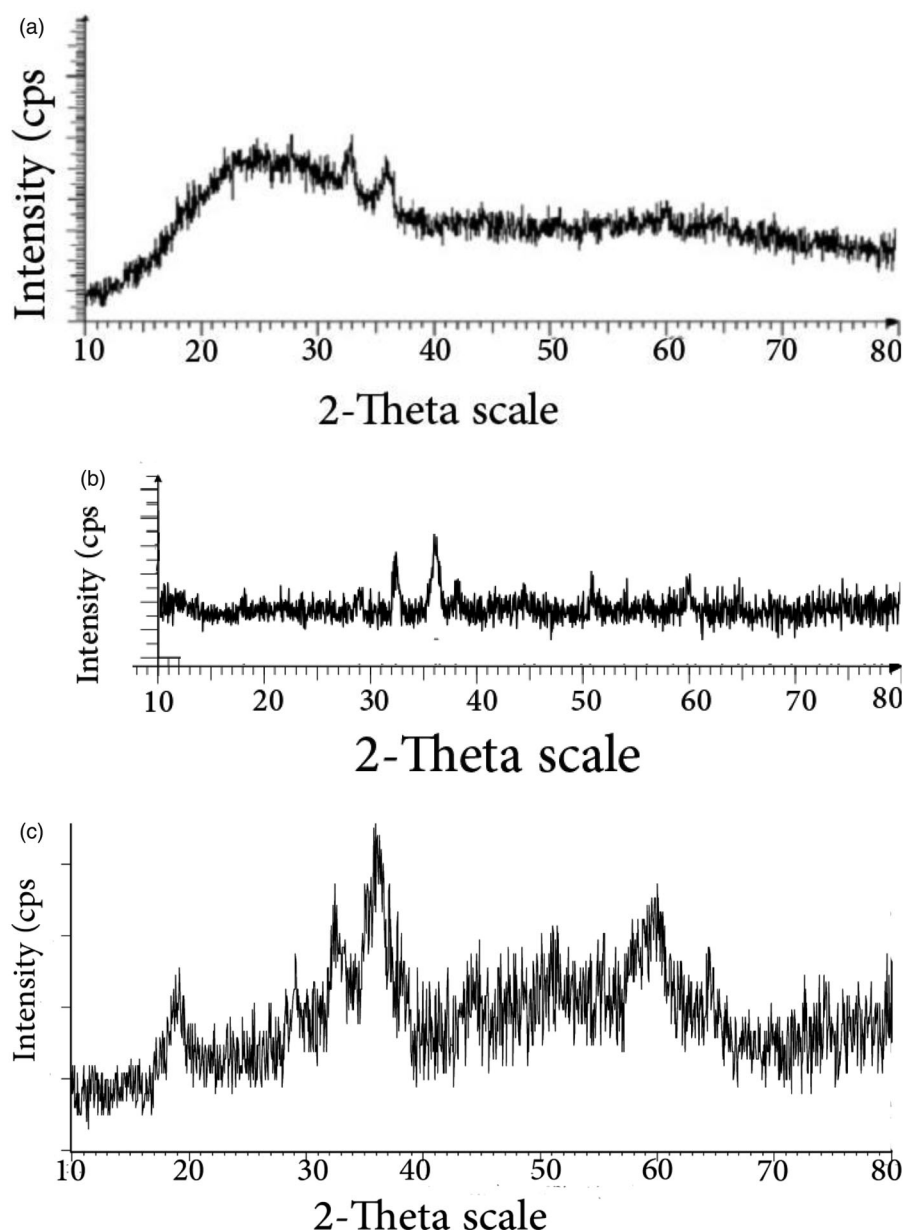


Figure 1. XRD of synthesized product from manganese salt in the presence of plant at pH = 7 (a), at pH = 9 (b) and XRD of $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid (c).

secondary alcohols to aldehydes and ketones products, respectively. As practical application point of view, H_2O_2 was used as ideal oxidant under solvent free conditions.

Materials and methods

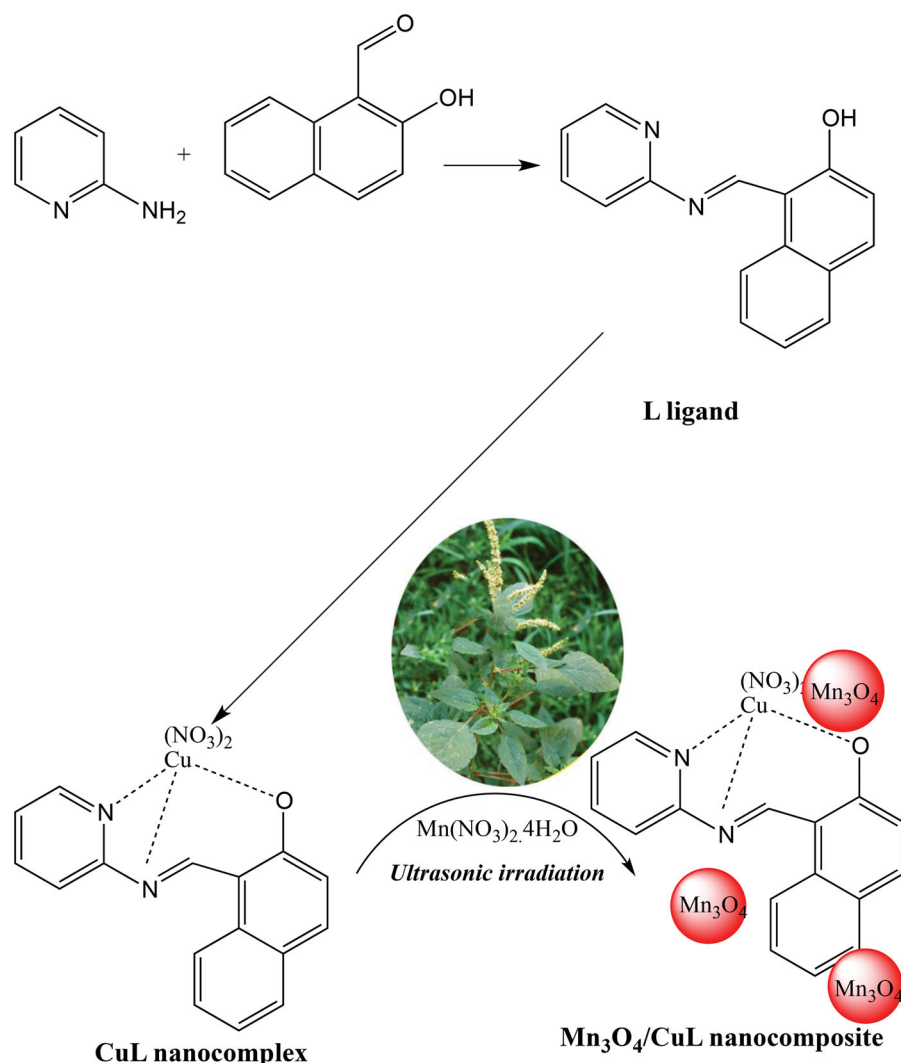
Amaranthus spinosus was collected from Mahmoodabad village, Jiroft, Iran. $\text{Cu}(\text{NO}_3)_2$, 2-hydroxynaphthalene-1-carbaldehyde and manganese nitrate tetrahydrate were purchased from Sigma-Aldrich (St. Louis, MO). 2-Amino pyridine and solvents were provided from Across and Merk Company, Iran, respectively. FT-IR spectra of L ligand, CuL nanocomplex and $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid were recorded by FT-IR spectrophotometer (NICOLET iS10). X-ray energy-dispersive spectroscopy (EDS) detector (IE 300X, Oxford Semiconductor Co., Ltd., Oxford, UK) attached to the SEM was used for analysis of morphology and percentage of elements in this novel nano-colloid. TEM microscope (Philips

CM30, Eindhoven, Netherlands) was employed for observing the shape of it. An ultrasonic bath was used for synthesis of CuL nanocomplex and $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid (Ultrasonic cleaner 5200iS3 model, SolTEC, Milan, Italy, frequency 40 kHz). XRD patterns of nanocomposite and nanoparticles were determined by Philips Netherland (Eindhoven, Netherlands), X'Pert Pro model. ^1H NMR and ^{13}C NMR spectra of ligand were recorded on Varian, UNITYInova 500 MHz. Elemental analysis of ligand was considered by CHSNO, ECS4010, Italy (University of Medical Science, Kerman, Iran).

Experimental

Synthesis of ligand (L)

Schiff base ligand was obtained by addition of a solution of 2-hydroxynaphthalene-1-carbaldehyde (1.7 g) in ethanol



Scheme 1. Synthesis of Mn₃O₄/CuL bio-nanocolloid under ultrasonic irradiation.

(40 ml) to a solution of 2-aminopyridine (5 mmol, 0.94 g) in ethanol (40 ml) and the reaction mixture was stirred for 24 h at room temperature. The obtained precipitate was filtered and dried in air. Finally, the product was characterized by IR, ¹H NMR and ¹³C NMR spectroscopy.

C₁₆H₁₂N₂O: anal. Found: C, 78.69; H, 4.43; N, 12.50; Calc.: C, 77.40; H, 4.87; N, 11.28, IR (KBr, cm⁻¹): ν_{O-H}, 3365; ν_{C=N}, 1472; ν_{CH=N}, 1608; ¹H NMR (301 MHz, DMSO-d₆) δ 15.18 (d, *J* = 7.8 Hz, 1H), 9.81 (d, *J* = 7.7 Hz, 1H), 8.51 (dd, *J* = 5.0, 1.9 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.04–7.82 (m, 2H), 7.71 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.37–7.25 (m, 2H), 6.84 (d, *J* = 9.4 Hz, 1H). ¹³C NMR (76 MHz, DMSO) δ 177.2, 152.8, 150.6, 148.9, 139.2, 139.2, 133.6, 129.3, 128.7, 126.4, 124.2, 123.9, 121.6, 119.61, 115.2 and 108.0.

Synthesis of copper nanocomplex (CuL)

A solution of L ligand (3 mmol or 0.74 g in 15 ml THF) was poured dropwise under ultrasonic irradiation into THF solution of Cu(NO₃)₂ (2 mmol or 0.56 g in 10 ml THF). After 12 h,

the obtained precipitate was filtered, washed by THF, and dried in the air.

Synthesis of Mn₃O₄/CuL bio-nanocolloid (Mn₃O₄/CuL)

Four grams of AS to 200 ml of Milli-Q water and heated at 80 °C. After settling for 1 h, the extract was vacuum filtered.

Two hundred millilitres of manganese (II) nitrate tetrahydrate (0.05 M) was added to the extract solution of AS (170 ml) and water (130 ml) at pH = 9 within 10 min at room temperature under ultrasonic irradiation and Mn₃O₄ nanoparticles was obtained. Then, 200 μl of aqueous solution of CuL (0.01 M) was injected in it and stirred. After 20 min, Mn₃O₄/CuL bio-nanocolloid was obtained.

Green oxidation of alcohols using Mn₃O₄/CuL bio-nanocolloid

To a mixture of alcohol (2 mmol) and Mn₃O₄/CuL bio-nanocolloid (0.014 g) under solvent free conditions, 0.8 mmol H₂O₂ (16 ml) was added and the reaction mixture was stirred at 80 °C for 5 h.

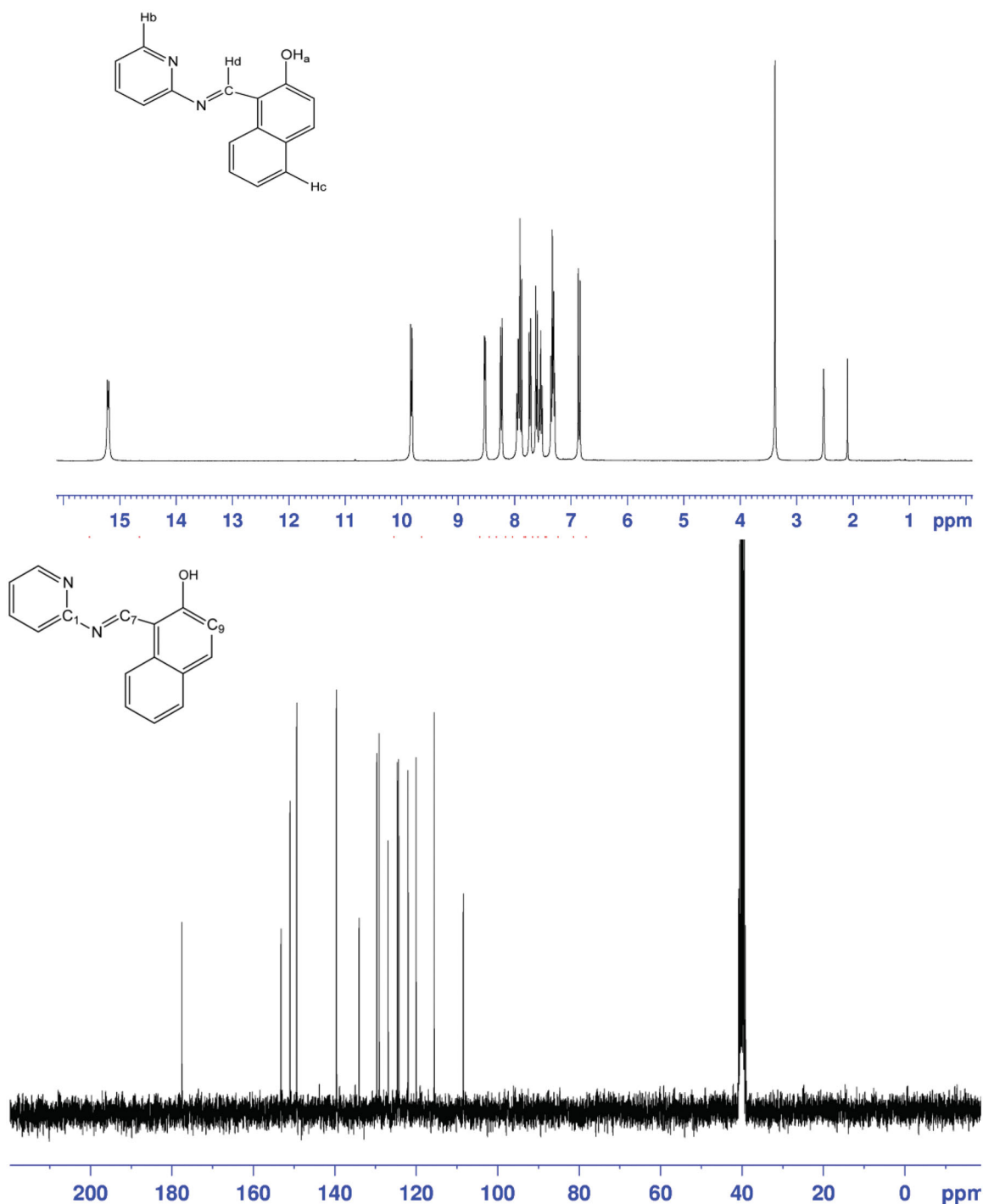


Figure 2. ^1H NMR (top) and ^{13}C (down) spectra of L ligand.

Recycling procedure of $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid on the oxidation of benzyl alcohol

To a mixture of benzyl alcohol (1 mmol, 0.1 ml) and $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid (0.007 g) under solvent free conditions, H_2O_2 was added (0.4 mmol, 8 ml) and the reaction mixture was stirred at 80°C for 5 h. After completion of the reaction, 1 ml ethyl acetate was added and catalyst was separated by centrifugation. $\text{Mn}_3\text{O}_4/\text{CuL}$ bionanocomposite as the isolated solid phase was dried under air and reused for next runs.

Results and discussion

Green Mn_3O_4 nanoparticles were performed by adding manganese salts to extraction solution of AS under ultrasonic irradiation. It should be noted that at $\text{pH} = 7$ of AS, the mixture of MnO_2 , Mn_3O_4 and Mn_2O_3 was obtained (Figure 1(a)) [36]. While, Mn_3O_4 nanoparticles were gained at $\text{pH} = 9$ as a sole product (Figure 1(b)). Figure 1(b) shows XRD of Mn_3O_4 exhibiting (211) predominant orientation at $2\theta = 36.1^\circ$ corresponding to tetragonal structure of Mn_3O_4 with I41/amd

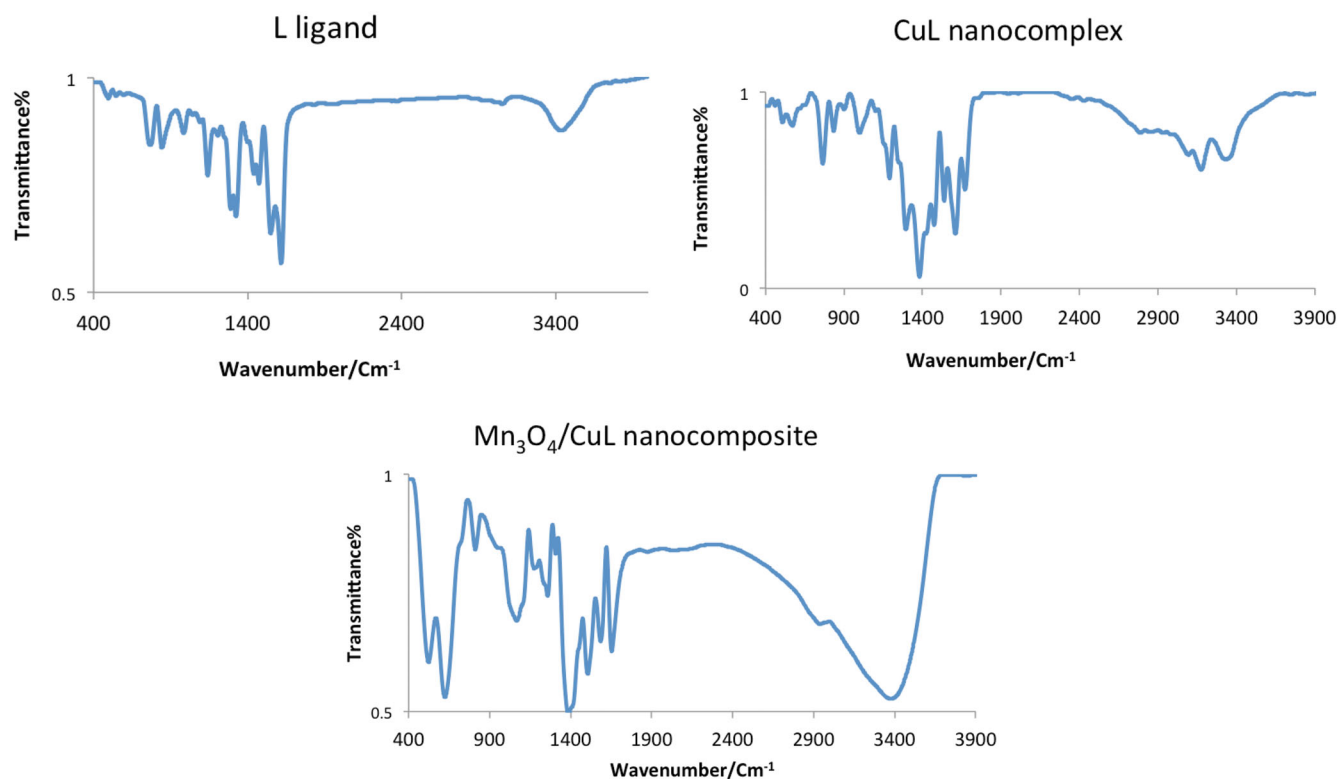


Figure 3. FT-IR of L ligand, CuL nanocomplex, and $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid.

(141) space group and an estimated crystallite size of 40 nm. Other different characterization peaks (112), (200), (103), (004), (220), (105), (321), (224) and (400) were at 28.9, 31, 32.3, 38.11, 44.54, 50.6, 58.78, 59.66 and 64.71°, respectively. The estimated lattice parameters are $a=b=5.7621$ Å and $c=9.4696$ Å which are good agreement with previous literature [37]. The same set of characteristic peaks was observed in the XRD pattern of $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid, which indicates the stability of the crystalline phase of nanoparticles during the synthesis of bio nanocomposite. The average crystallite size $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid (45 nm) was estimated using the Debye–Scherrer formula. Other peaks were related to CuL nanocomplex.

On the other hand, L ligand was obtained by condensation of 2-hydroxy 1-naphthaldehyde and 2-aminopyridine. By adding copper salt to L ligand under ultrasonic irradiation, water-soluble CuL nanocomplex was achieved. The mixture of CuL nanocomplex and Mn_3O_4 in the presence of AS, $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid was obtained (Scheme 1).

Proton NMR spectrum of the free ligand has been recorded in DMSO at room temperature (Figure 2, top). The ligand exhibits hydroxyl proton (Ha) appearing at δ 15.203 ppm, the aromatic pyridine proton (Hb) appearing at δ 9.832 ppm, Hc appearing at δ 8.30 ppm, Hd appearing at δ 6.857 ppm, and aromatic and heteroaromatic proton signals appearing at δ 7.25–8.539 ppm. The chemical shift of hydroxyl proton is very high (15.203 ppm) indicating intramolecular hydrogen bond. ^{13}C NMR spectrum (Figure 2, down) showed similar diagnostic features for the free ligand. Hydroxyl carbon (C-9) was found at 177.642 ppm, pyridine carbon (C-1) at 151.059 ppm and imine carbon (C-7) at

149.4526 ppm, and aromatic carbons were found at 108.474–149.426 ppm.

FT-IR spectra of L ligand, CuL nanocomplex and $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid are shown at Figure 3. In the free ligand (L), the band of 3365 cm^{-1} was observed and assigned to ν (O–H) absorption. The strong band at 1608 cm^{-1} was related to stretching vibrations of C=N functional group, which was confirmed by the presence of Schiff base. C=C was assigned at 1545 cm^{-1} [38]. Copper nanocomplex, ν C=N (1608 cm^{-1}) was shifted to 1596 cm^{-1} (lower frequencies), when complex was obtained [39]. The small bands at 495 and 522 cm^{-1} are related to Cu–N and Cu–O bonds in nanocomplex. FT-IR spectrum of $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid exhibits one strong band at 507 cm^{-1} , which can be attributed to the vibrations of metal-oxygen confirming the presence of Mn_3O_4 NPs [40].

The presences of all elements in $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid were confirmed at EDAX of it and elemental analysis of this compound (Figure 4). Copper, manganese, carbon and oxygen were observed as elements in this nanocolloid. 34.49% of C, 52.45% of O, 12.86% of Mn and 0.19% of Cu were in this material. The morphology, size, and shape of this bio-material were investigated by TEM and SEM (Figure 3). Aggregation of particles was observed as TEM image. SEM image shows nanocube morphology of prepared nanocolloid, with width of 80 nm in diameter and 3 mm in length.

Catalytic activities of $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid on the oxidation primary and secondary alcohols

The catalytic activity of $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid was investigated on the oxidation of alcohols (Scheme 2).

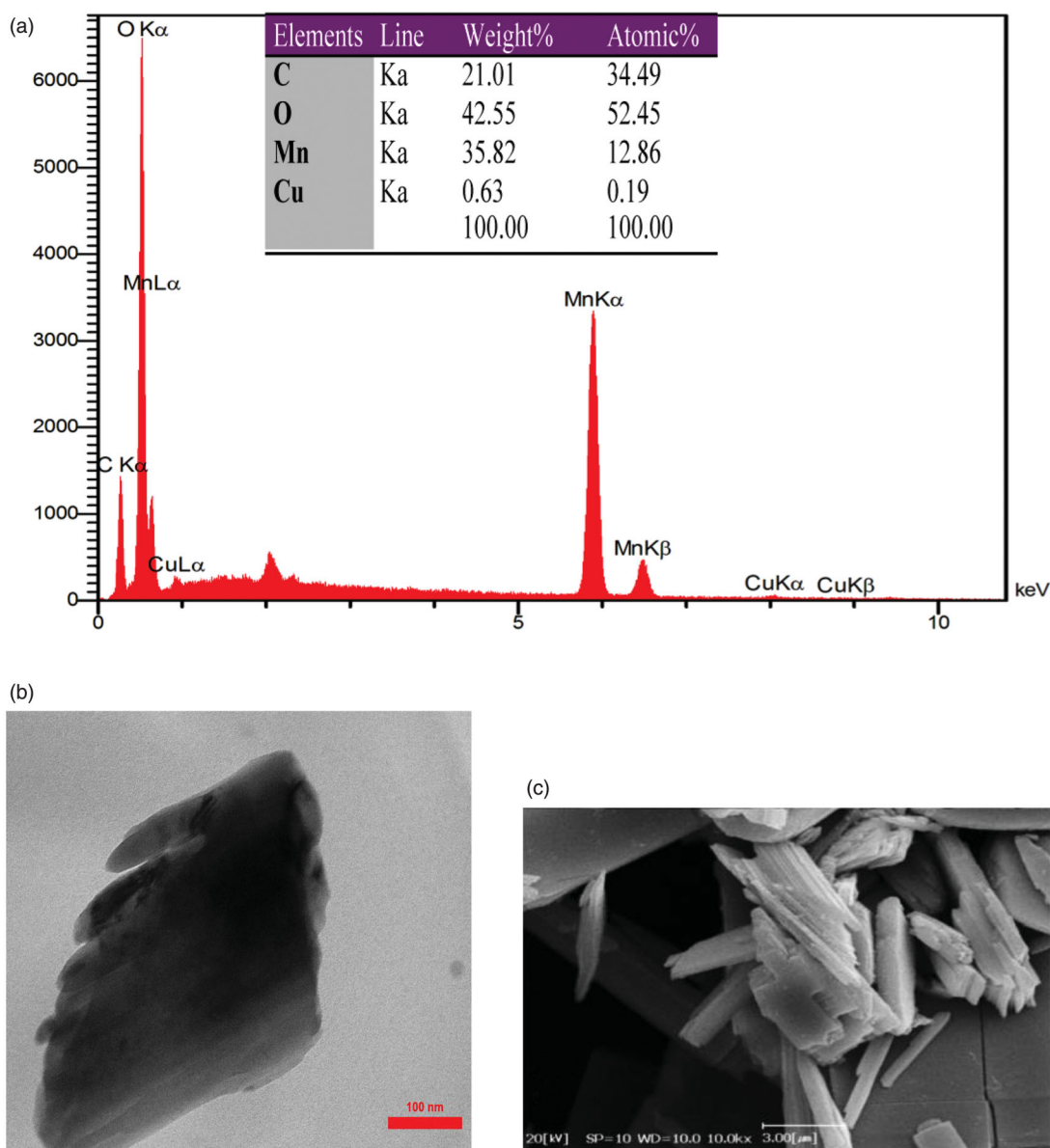
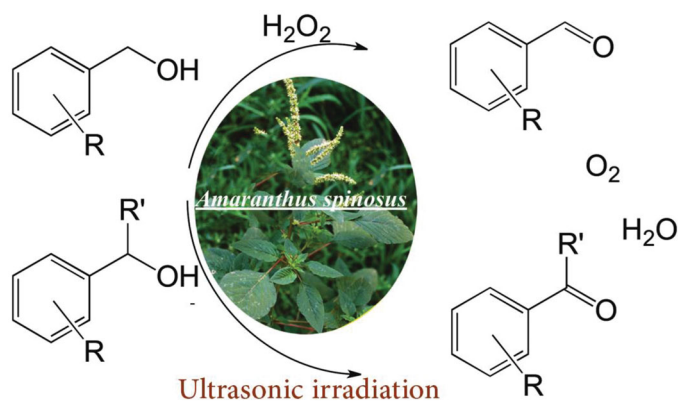


Figure 4. The EDAX (a), elemental analysis (a), SEM (b) and TEM (c) of Mn₃O₄/CuL bio-nanocolloid.

The catalyst-free condition does not have the ability to oxidize the benzyl alcohol under different conditions. In this regards, catalytic experiments were initiated with the oxidation of benzyl alcohol (1 mmol) under air in the presence of H₂O₂ to have the standard conditions of the reaction. In this hence, the nature of solvent and oxidant, temperature, reaction time and the quantity of catalyst were considered on the oxidation of benzyl alcohol as a blank reaction in this green system (Figure 5).

About 0.1 mmol concentration of alcohol and 80 °C are the best conditions for this oxidation reaction as the further evaluation demonstrated. The green oxidation of benzaldehyde was completed after 5 h (Figure 5(a–c)). Also, a survey of the results shown in Figure 5(e,d) revealed that a sufficient amount of catalyst loading of 0.007 g in the presence of 0.4 mmol oxidant led to higher conversion, but yield of product decreased with higher concentrations of catalyst. The effect of solvent on the catalytic performance is shown in Figure 5(f). The reaction did not proceed in aprotic and



Scheme 2. The oxidation of primary and secondary alcohols catalysed by Mn₃O₄/CuL bio-nanocolloid using H₂O₂ to have O₂ and water as byproducts under ultrasonic irradiation.

protic solvents such as ethanol (EtOH), methanol (MeOH), acetonitrile (CH₃CN), water and n-hexane. While, the solvent-free condition under air at 80 °C, benzyl alcohol was

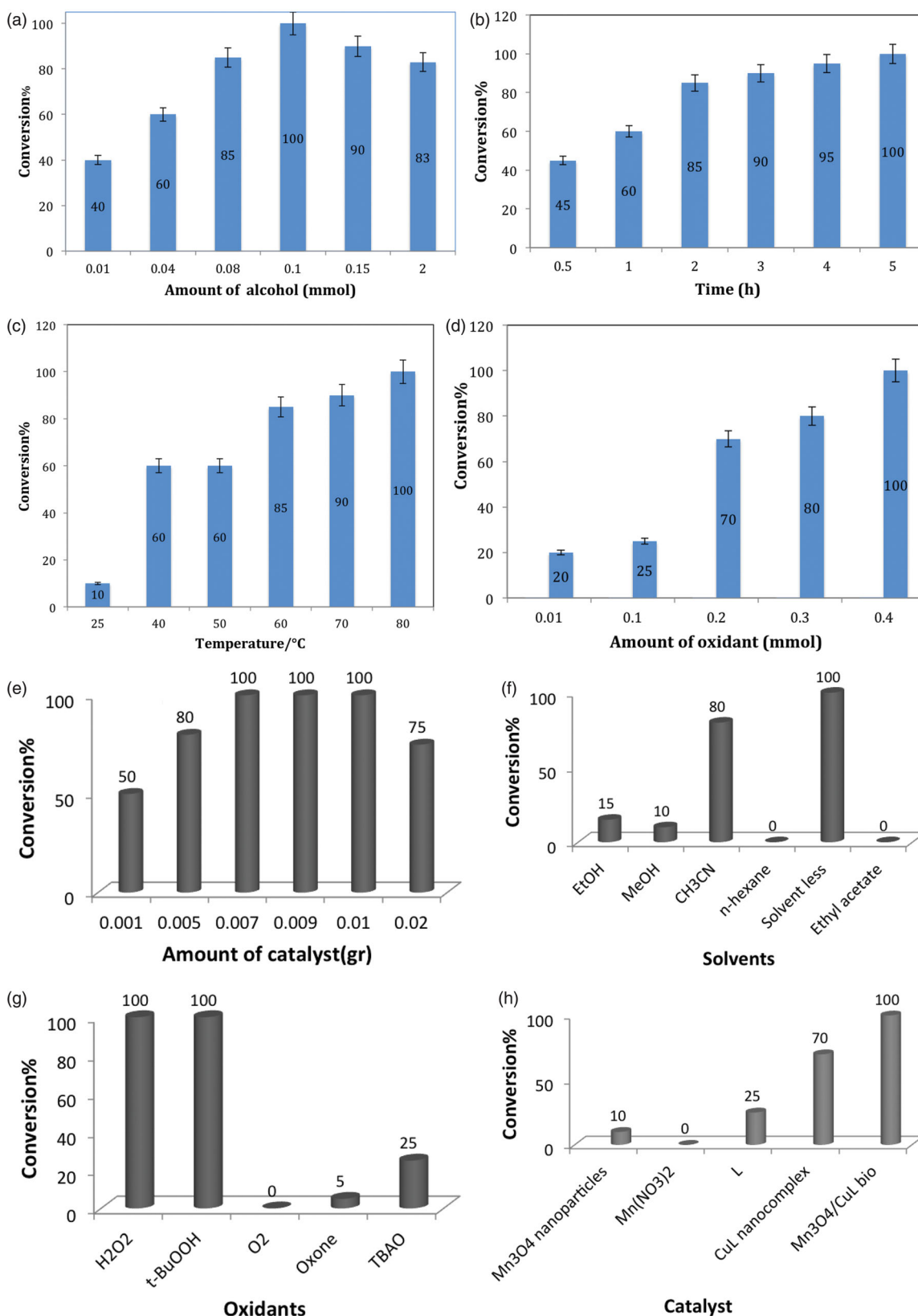


Figure 5. (a–h) Optimization of oxidation of benzyl alcohol.

converted to benzaldehyde completely. So, solventless was selected as a safe and green media for industrial applications. Based on the data in Figure 5(g), common oxidants such as O_2 , TBAO (tetrabutyl ammonium oxone) and Oxone[®]

were weaker oxidants than H_2O_2 and TBHP for this transformation. However, H_2O_2 was selected as an ideal oxidant for further investigation. The ability synthesized Mn_3O_4 , manganese salt, ligand (L) and CuL nanocomplex to promote the

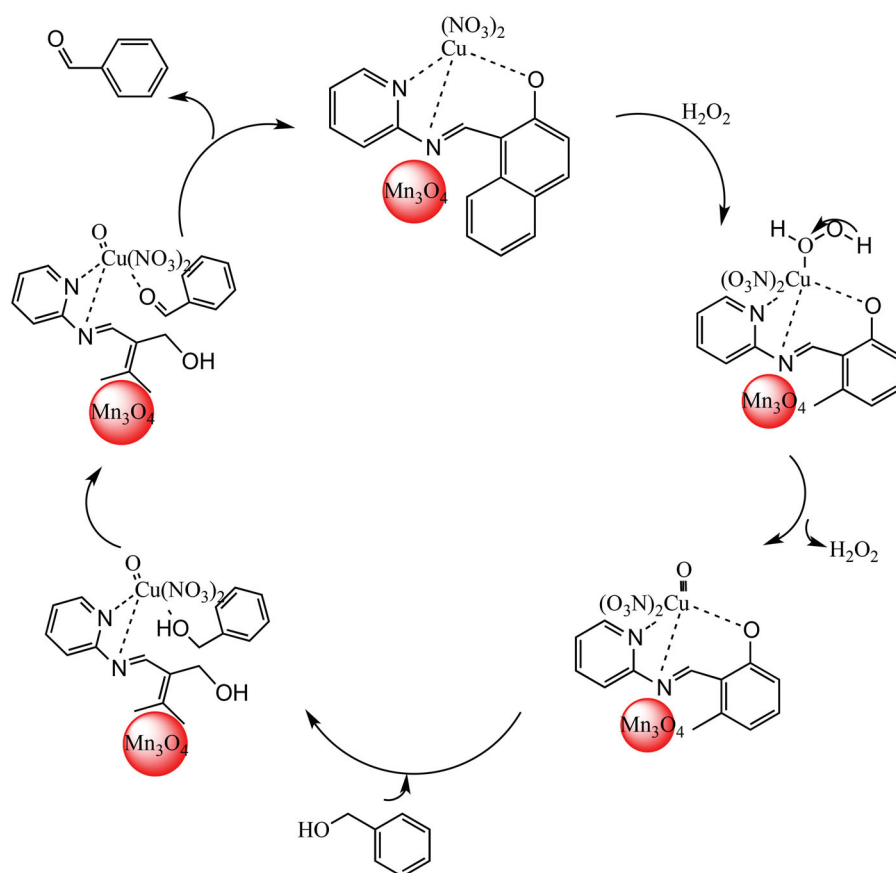


Figure 6. Proposed mechanism for the catalytic oxidation of benzyl alcohol by $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid.

oxidation of benzyl alcohol which was then probed under the obtained optimized condition (Figure 5(h)). These compounds exhibited poor activity under this condition and the preferable catalytic performance of $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid was confirmed.

As described in documents [41], Lewis acid sites were believed as the active sites in catalytic oxidation of benzyl alcohol with H_2O_2 [42]. In this case, aqueous phase of H_2O_2 (30%) and benzyl alcohol from alcohol phase may interact with the catalyst on the interphase to generate the product benzaldehyde. This species attacks benzyl alcohol to form peroxycarboximidic acid intermediate (Figure 6), which is then converted into benzyl alcohol with concomitant regeneration of the catalyst. In view of the proposed mechanistic pathways for the catalytic oxidation of benzyl alcohol, it can be concluded that both the phenyl ring and OH group of benzyl alcohol may interact with the metal centre of Cu, whereas the inner active sites remain intact. However, the interaction of the phenyl ring and OH group with the outer metal ions of Cu is also possible *via* adsorption of the phenyl ring on Cu, as reported in reference [43].

Thereafter, we focussed on the consideration of the substrate scope under stirring. In this regards, a set of structurally and electronically primary and secondary alcohols were selected for this safe and cost-efficient strategy (Table 1). As shown in Table 1, good to excellent yields were obtained for different primary and secondary benzyl alcohols, except for those with the aryl ring substituted with a nitro group.

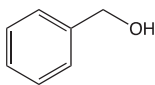
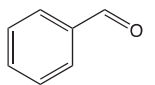
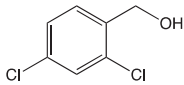
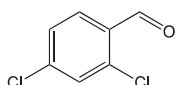
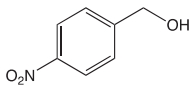
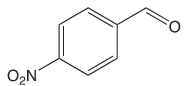
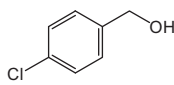
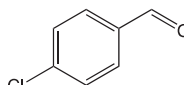
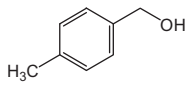
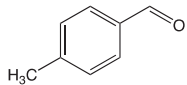
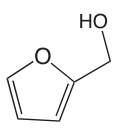
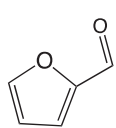
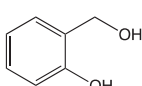
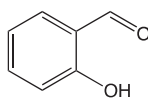
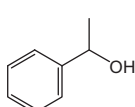
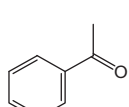
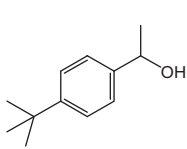
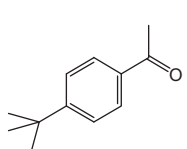
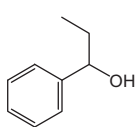
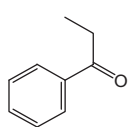
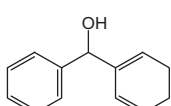
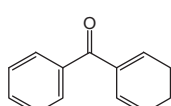
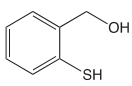
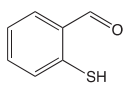
It should be noted that the corresponding carboxylic acids and ester were not observed in this green system and over-oxidation did not happen.

Finally, we compared the conditions of oxidation of benzyl alcohol in this clean and cheap system with the results of other reports using hydrogen peroxide in different conditions (Table 2). The results showed that this $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid bionanocomposite could be used as a robust, reusable and active heterogeneous catalyst in the oxidation of primary and secondary alcohols with H_2O_2 .

Reusability of catalyst

Recovery and the catalytic activity are imperative options for the industrial application of this biocatalyst. For this aim, the structure of catalyst must be unchanged. A comparison of the FT-IR spectra of the used $\text{Mn}_3\text{O}_4/\text{CuL}$ bio nanocolloid (six recovery cycles) with those of the fresh catalyst showed that the structure of the catalyst remained almost completely intact (Figure 7(a)). On the other hand, the reusability of the $\text{Mn}_3\text{O}_4/\text{CuL}$ bio nanocolloid was explored in the oxidation of benzyl alcohol. When the reactions were completed, the nanocolloid was separated by centrifugation after addition of the ethyl acetate. Recovered catalyst in dry state was used for the next runs. Stability as well as the activity of it was investigated and $\text{Mn}_3\text{O}_4/\text{CuL}$ bionanocolloid was recycled for six times. Remarkable results (100–90%) of benzaldehyde

Table 1. Oxidation of alcohols catalysed by $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid using hydrogen peroxide.

Entry	Alcohol	Product	Yield% ^a
1			100
2			80
3			90
4			95
5			95
6			80
7			100
8			100
9			100
10			90
11			100
12			100

^aThe reactions were run under air for 5 h at 80 °C under solvent free conditions using H_2O_2 (0.4 mmol) catalysed by $\text{Mn}_3\text{O}_4/\text{CuL}$ bio-nanocolloid (0.007 g) using stirring.

Table 2. Comparison of the result of this study with that of related references.

Entry	Catalyst	Time (h)	Con% (Selec%)
1	Mn ₃ O ₄ /CuL bio-nanocolloid	5	100 (100)
2	VHPW/MCM-41/NH ₂	8	97 (99)
3	Im-PW/GO	7	90 (99)
4	[₂ -PW12O ₄₀]3---IL-polymer support	12	99 (100)
5	Tungstate ions @periodic mesoporous organosilica-IL	12	75 (100)
6	Tetrakis(oxodiperoxotungsto) phosphate	0.7	77 (99)

(1) Tem: 80 °C; solvent: nonsolvent (this work); (2) Tem: 80 C; solvent: toluene [44]; (3) Tem: 90 C; solvent: nonsolvent [45]; (4) Tem: 80 C; solvent: CH₃CN [46]; (5) Tem: 90 C; solvent: CH₃CN/H₂O [47]; (6) Tem: 90 C; solvent: nonsolvent [48].

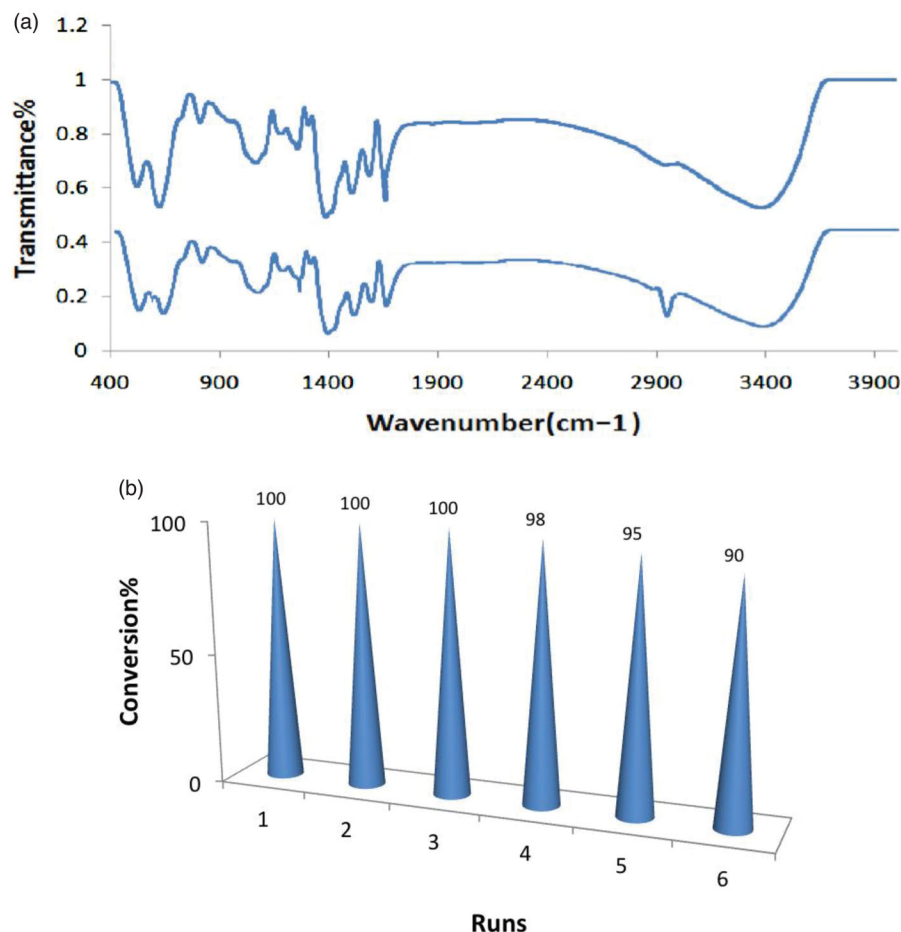


Figure 7. (a) The FT-IR of fresh catalyst (top) and reused catalyst after six times (down) and (b) recycling of catalyst.

were gained showing excellent catalytic activity of nanocolloid without noticeable loss (Figure 7(b)).

The features of our clean strategy on recycling of catalyst are the easy work up and convenient separation of product using green solvent (ethyl acetate or ethanol) from reactions. This method is not only eco-friendly but also less time consuming, cost effective, stable operation, efficient and safer. On the other hand, natural starting material for catalyst preparation, a long-term stability of catalyst, using ideal oxidant, and solventless show the great potential in scalability for actual industries applications. These features as concepts in economical and sustainable modern oxidation systems along with good reusability of the bio-catalyst render a practical strategy to address the environmental and industrial applications.

Conclusions

In summary, the first bio-nanocomposite based on weeds was synthesized. We prepared a novel of bionanocolloid successfully, by incorporating copper nanocomplex as a biocompatible molecule with Mn₃O₄ nanoparticles under ultrasonic agitation in the presence of *Amaranthus spinosus*. As a heterogeneous catalyst, the Mn₃O₄/CuL nanocatalyst efficiently oxidized a wide range of primary and secondary alcohols to the corresponding carbonyl compounds using H₂O₂ and under solvent free conditions as ideal oxidant and reaction media, respectively. Using cheap and natural starting materials, reusability, and recyclability of the catalyst are salient features of this green strategy from an economic and environmental point of view.

Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

We are thankful to University of Jiroft for their support on this work.

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