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Fe_3O_4-Cu Photocatalyst for Chemoselective Reduction of 5-Nitroisopthalic Acid

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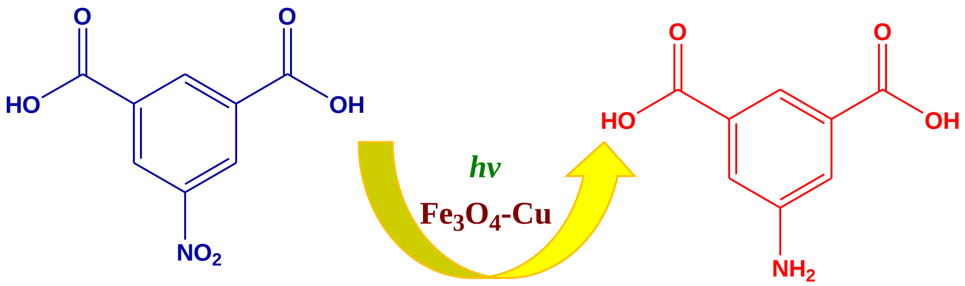
Graphical abstract



Abstract: The spherical shaped Fe_3O_4-Cu nanocomposite was synthesized by a simple chemical reduction method by using L-arginine as a linker. The resultant Fe_3O_4-Cu nanocomposite was characterised and used for chemoselective reduction of 5-nitroisopthallic acid in the presence of sodium borohydride by UV-Visible spectrophotometric method. Fe_3O_4-Cu photocatalyst is cost-effective, easily recyclable, and do not affect environmental conditions. Also, we compared the catalysis study of Fe_3O_4 nanoparticles and Fe_3O_4-Cu nanocomposite for reduction of 5-nitroisopthallic acid. Fe_3O_4-Cu nanocomposite showed better catalytic activity than Fe_3O_4 nanoparticles. The unique properties of Fe_3O_4-Cu nanocomposite make an ideal platform for catalysis, sensing applications and in green chemistry.

Keywords: Fe_3O_4-Cu, Photocatalyst, 5-Nitroisophthalic Acid, 5-Aminoisopthalic acid, Catalytic reduction.

1. INRODUCTION

One of the most pretending features of nanotechnology is its potential use in catalysis. The field of nanocatalysis has been rapidly growing in last few decades, both in the form of homogeneous and heterogeneous catalysis [1]. Owing to their high surface area, nanocatalysts have displayed high catalytic activity and selectivity, excellent stability, easy separation and excellent atom economy [2]. The magnetic nanoparticles have recently emerged as viable alternatives to conventional materials for catalyst supports [3,4]. Isolation and recovery of the catalyst can be done by use magnetic nanoparticle. They are the promising candidate for high accessibility with improved reusability [5-7]. Their insoluble and superparamagnetic nature enable trouble free separation of the nanocatalysts from the reaction mixture using an external magnet, which eliminates the necessity of catalyst filtration [8-11]. Several methods are known in the art for synthesis of Fe_3O_4 magnetic nanoparticles [12-14].

5-aminoisophthalic acid (5AIPA) is an important intermediate in producing an X-ray contrast agent [15], catalysis, environmental remediation [16,17] and synthesis of coordination compounds [18]. It is usually used as the intermediate or raw material in organic synthesis. After brief literature survey it was found that only few methods are available for the synthesis of 5AIPA [15]. However, these methods are time consuming and tedious. Therefore, we have decided to reduce 5-nitroisophthalic acid (5NIPA) to 5AIPA by using magnetic photocatalyst Fe_3O_4-Cu nanocomposite. Patra et. al have demonstrated method for reduction of 5NIPA to 5AIPA by Cu nanospheres using UV-visible absorption studies [19]. Herein, we have demonstrated a facile method for chemoselective reduction of 5NIPA using Fe_3O_4-Cu nanocomposite in the presence of sodium borohydride by UV-visible spectroscopic method.

2. EXPERIMENTAL

2.1 Chemicals

Anhydrous ferric chloride (98%) laboratory reagent ($FeCl_3$), Copper sulphate, pentahydrate ($CuSO_4.5H_2O$, 98%) laboratory reagent, and ammonia solution (NH_4OH, 30%) analytical reagent were obtained from Thomas baker pvt. ltd Mumbai. Potassium iodide extrapure (99%) and sodium borohydride ($NaBH_4$, 98%) obtained from S.D. fine chemicals pvt. ltd. Mumbai. L-Arginine (free base 99%) was purchased from Sisco research laboratory and 5-Nitroisophthalic acid (98%) (5NIPA) was supplied from sigma Aldrich. All chemicals were reagent grade and used without any purification. De-ionized water was used throughout the experiment.

2.2 Preparation of catalyst.

a) Preparation of iron oxide nanoparticles (Fe_3O_4 Nps). Synthesize of Fe_3O_4 Nps was carried out by chemical reduction method. In a typical procedure 4.86 gm (0.0299 M) of anhydrous ferric chloride was dissolved in 40 ml of distilled water to prepare aqueous solution A. Then 1.64 gm (0.0098 M) of potassium iodide was dissolved in another 10 ml distilled water to prepare a solution B. The solution B was poured in solution A and the mixture was stirred at room temperature for 1 h. Then mixture was sonicated for 30 minutes. Then mixture was filtered out to separate the precipitate of iodine. The filtrate was hydrolysed by drop wise addition of 30% ammonium hydroxide (pH = 10-13) with vigorous stirring until complete precipitation of black magnetite was achieved. The reaction mixture was washed with distilled water until the pH of solution become 7 and dried at 70 ^{0}C for 10 hours to get Fe_3O_4 Nps.

b) Preparation of Fe_3O_4-Cu nanocomposite.

25 mg synthesized Fe_3O_4 Nps were dispersed in 25 ml of distilled water and 0.25 gm (0.0014 M) of L-arginine was added into it. The mixture was sonicated for 30 minutes. 15 ml $CuSO_4$ solution (0.8 mM) was rapidly added into the above reaction mixture with vigorous stirring for 30 min. Then 0.6 gm (0.0158 M) of $NaBH_4$ was quickly added. The mixture was stirred for 1 hr. The product was separated magnetically, washed with distilled water to remove the impurity, dried to get Fe_3O_4-Cu nanocomposite.

2.3 Characterization

The crystallographic analysis of catalyst in diffraction patterns were recorded using a Bruker D2 phaser X ray diffractometer with Cu Kα (λ = 1.542 A˚). Surface morphology was characterized by JEOL JSM-6360 scanning electron microscope (SEM). Transmission electron microscopy (TEM) analysis was carried out by model JEM 2100F; JEOL, Japan. Agilent Technologies Cary 60 UV-Vis Spectrophotometer was used to monitor the progress of conversion of 5NIPA to 5AIPA.

2.4 Photocatalytic reduction of 5NIPA.

The reduction of 5NIPA to 5AIPA by Fe_3O_4-Cu was carried out in a standard quartz cuvette at room temperature. In a typical procedure, 1.5 ml of 1×10^{-4} M 5NIPA and 500µl $NaBH_4$ (5×10^{-2} M) was mixed in a standard quartz cuvette. 100 µl Fe_3O_4-Cu nanocomposite (2 mg/10ml) was added in above mixture. The reaction was monitored by using UV-Visible absorption spectra. Absorption study was carried out by observing absorption spectra of absorbance vs reaction time. The same procedure was carried out for Fe_3O_4 Nps.

3. RESULTS AND DISCUSSION

3.1 Characterization of Fe_3O_4 Nps, Fe_3O_4-Cu nanocomposites

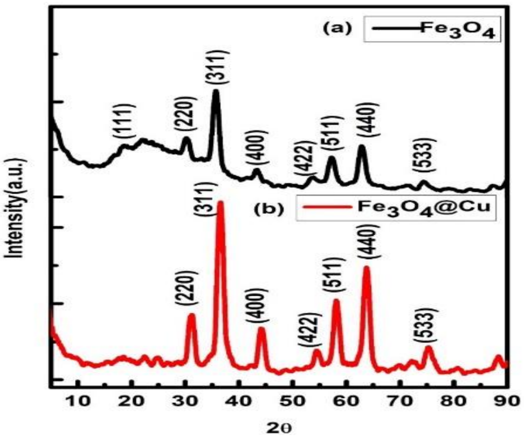


Figure 1. XRD pattern of a) Fe_3O_4 Nps, b) Fe_3O_4-Cu nanocomposite.

The X–ray diffraction patters of Fe_3O_4 and Fe_3O_4-Cu nanostructures are shown in Figure 1. For Fe_3O_4 Nps eight characteristic peaks were observed at 18.4°, 30.2°, 35.4°, 43.3°, 53.7°, 57.3°, 62.87° and 74.48° corresponds to (111), (220), (311), (400), (422), (511), (440) and (533) lattice planes respectively. All these XRD peaks were compared with standard JCPDS card 19-0629. The crystallite size of Fe_3O_4 Nps is 6.38 nm, calculated by Debye Scherrer formula. For Fe_3O_4-Cu nanocomposites, the peaks observed for Cu at 43.3° and 74.48° corresponds to (111) and (220) planes. These two peaks were overlapped with Fe_3O_4 peaks at 43.3 and 74.48 corresponds to (400) and (533) planes. The formation of Fe_3O_4-Cu nanocomposite was confirmed by comparing the data with standard JCPDS card 19-0629. The obtained crystallite size of nanocomposites is 8.36 nm, calculated by Debye Scherrer formula. The diffraction patterns indicate formation of Fe_3O_4-Cu nanocomposites with L-arginine as a linker.

Figure 2a and 2b show SEM images of Fe_3O_4 Nps and Fe_3O_4-Cu nanocomposite respectively. The results show the formation of highly ordered spherical shaped Fe_3O_4 Nps and Fe_3O_4-Cu nanocomposites. Fig. 2c and 2d show TEM images of Fe_3O_4 Nps and Fe_3O_4-Cu nanocomposites. TEM images predict the spherical morphology of Fe_3O_4 Nps and Fe_3O_4-Cu nanocomposites.

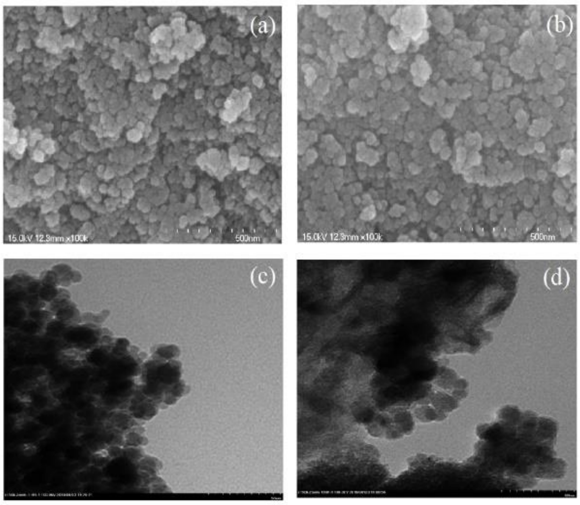


Figure 2. SEM images of a) Fe_3O_4 b) Fe_3O_4-Cu and TEM images of c) Fe_3O_4 d) Fe_3O_4-Cu nanostructures.

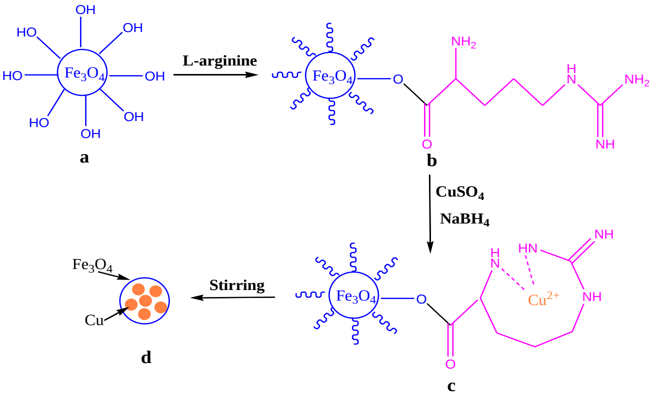


Figure 3. Synthesis route of Fe_3O_4-Cu nanocomposite from Fe_3O_4 nanoparticles a) Fe_3O_4 b) L-arginine linked to Fe_3O_4 c) F_3O_4 – L-arginine – Cu^{2+} coordinate complex d) Fe_3O_4-Cu nanocomposite.

The mechanism for the formation of Fe_3O_4-Cu nanocomposites from Fe_3O_4 Nps is illustrated in Figure 3. Fe_3O_4 nanoparticles with hydroxyl groups on their surfaces were modified with L-Arginine to introduce $-NH_2$ groups. These NH_2 groups bind to Cu^{2+} ions after addition of $CuSO_4$. Fe_3O_4–L-arginine–Cu^{2+} coordinate complex was formed as shown in 3c step. The bound Cu^{2+} ions were then reduced to Cu by addition of $NaBH_4$ to form the Fe_3O_4-Cu nanocomposite.

3.2 Mechanism of catalytic activity of Fe_3O_4-Cu nanocomposites-

Chemoselective reduction study of 5NIPA was carried out under UV-visible spectrophotometer. Catalytic study was done in the absence and presence of photocatalysts. We compared the catalysis study for Fe_3O_4 Nps and Fe_3O_4-Cu nanocomposite for reduction of 5NIPA.

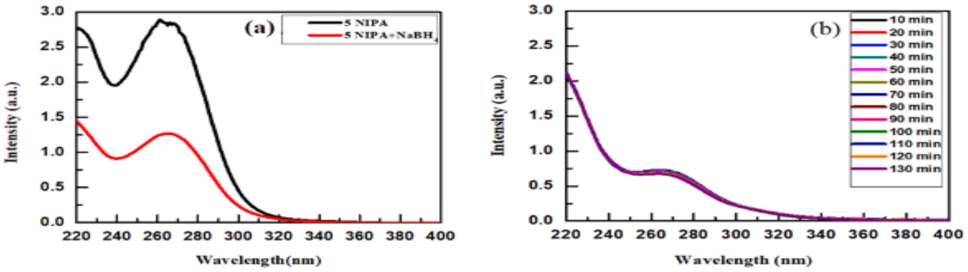


Figure 4. a) UV-Visible spectra of 5NIPA and 5NIPA with $NaBH_4$ b) Reduction of 5NIPA without catalyst.

Figure 4a showed reduction of 5-NIPA to 5-AIPA in the presence of $NaBH_4$. The reduction process was monitored by tracking the changes in absorption peaks after certain interval of time. The 5NIPA solution exhibits absorption peak at 262 nm whereas, it shifted to 266 nm after addition of $NaBH_4$. This peak indicates the formation of nitroisophthalate ions in basic condition. Figure 4b illustrates that no changes were observed in absorption peaks after standing for 130 minutes for above reaction mixture in the absence of catalyst. The same reaction was carried out in the presence of catalyst. The time for completion of the reaction was different for Fe_3O_4 Nps and Fe_3O_4-Cu nanocomposite. Complete reduction of 5NIPA to 5AIPA was not observed until 35 minutes in the presence of Fe_3O_4 Nps as shown Figure 5a. There is no sharp peak was observed at 309 to 312 nm. Therefore, the complete reduction of 5NIPA to 5AIPA not observed in the presence of Fe_3O_4 Nps as shown in Figure 5a. In the presence of Fe_3O_4-Cu nanocomposite reduction was completed within 16 min as shown in Figure 6a.

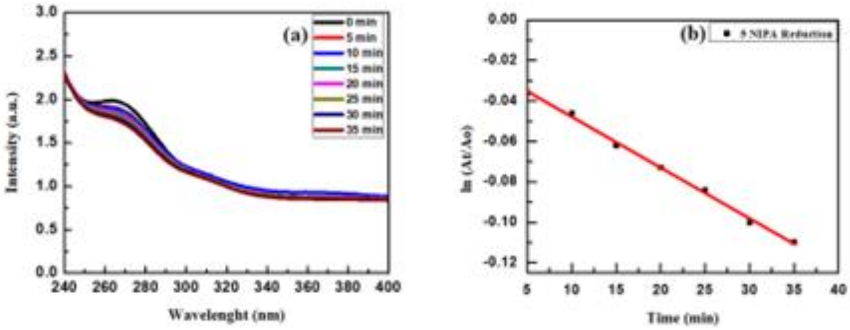


Figure 5. a) UV-visible spectra for conversion of 5NIPA to 5AIPA in the presence of Fe_3O_4 Nps and b) Kinetic Curve.

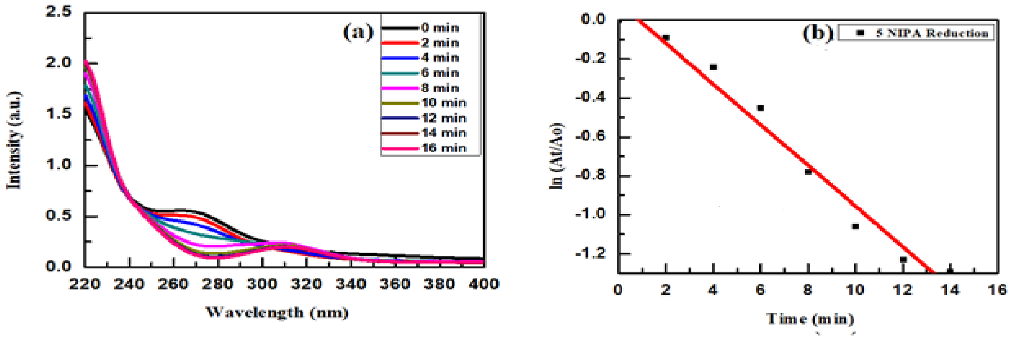


Figure 6. a) UV-visible spectra for conversion of 5NIPA to 5AIPA in the presence of Fe_3O_4-Cu Nanocomposite and b) Kinetic Curve.

After the addition of Fe_3O_4-Cu nanocatalyst the absorption peak of 5-nitroisophthalate ions at 266 nm was decreased with increase in time. After complete reduction absorption peak was shifted from 266 nm to 312 nm. Sharp peak was observed at 312 nm, predicts the complete reduction of 5NIPA to 5AIPA. The time required for reduction is much less in the presence of Fe_3O_4-Cu nanocatalyst than Fe_3O_4 Nps. Linear relation of ln (A_t/A_0) against reaction time indicating the reduction of 5NIPA in the presence of Fe_3O_4 Nps and Fe_3O_4-Cu nanocomposite follow the pseudo first-order kinetics. The rate constant (k) was calculated by linear plot of ln (A_t/A_0) verses time. According to the slope obtained from graph the rate constant for reduction reaction in the presence of Fe_3O_4 Nps (Figure 5b) and Fe_3O_4-Cu nanocomposite (Figure 6b) are 0.0025 min^{-1} and 0.10 min^{-1} respectively. From all these results we can conclude that Fe_3O_4-Cu nanocomposite photocatalyst is a superior catalyst than Fe_3O_4 Nps for chemoselective reduction of 5NIPA to 5AIPA.

The prepared Fe_3O_4-Cu nanocomposite showed catalytic as well as magnetic properties which can be easily recycled by external magnetic field after the reduction reaction. The catalyst can be easily recovered and reused for at least 5 successive cycles of reduction reactions.

4. CONCLUSION

We have demonstrated facile method for the synthesis of spherical shaped Fe_3O_4-Cu nanocomposite by chemical reduction method using L-arginine as a linker. The Fe_3O_4-Cu photocatalyst showed high catalytic activity for the reduction of 5NIPA to 5AIPA in the presence of $NaBH_4$. The reduction studies were carried out by UV-visible spectrophotometry. The Fe_3O_4-Cu exhibited enhanced performance compared Fe_3O_4 Nps for the reduction of 5NIPA to 5AIPA. The Fe_3O_4-Cu is magnetically separable and reused for successive reduction cycles. Fe_3O_4-Cu nanocomposite selectively reduce the nitro group into amine group; therefore, reaction is chemoselective. This study represents a promising new way for photocatalytic chemical transformations. The knowledge acquired in this study could be useful in the development of new heterogeneous photocatalysts to produce important chemicals, functionalized anilines and others, and in understanding photocatalytic systems for organic reactions.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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