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Journal Name

ARTICLE

Biogenic $CuFe_2O_4$ Magnetic Nanoparticles as a green, reusable and excellent nanocatalyst for the acetylation reaction under solvent free conditions

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A convenient green method has been developed for the synthesis of biogenic $CuFe_2O_4$ magnetic nanoparticles using tea extracts within a very short reaction of time. The prepared nanoparticles with average size of 8.78 nm has been used as an effective catalyst for the acetylation of various alcohols, phenols and amines in good to excellent yields under solvent free conditions. The catalyst was characterized by XRD, XPS, VSM, SEM and TEM study. The magnetic study of the fresh and recycled catalyst after fourth cycle was observed by VSM measurements. The main advantages of this protocol are simple biogenic synthesis of the catalyst, reusable and heterogeneous catalytic system, and short reaction time with excellent yields.

1. INTRODUCTION

The main objective of Green Chemistry[1] is to develop atom economy[2] and synthetic methods that minimizes the waste by using solvent free and recyclable catalyst. The acetylation of alcohols, phenols, and amines has been widely used as protecting groups in multistep pharmaceutical synthesis and in agricultural industries. Acetylation reactions are normally performed by using acetyl chloride in the presence of a base[3-5] or acid catalyst[6-10] such as pyridine, tributylphosphine,[11] 4-(dimethylamino)pyridine (DMAP),[12]triethylamine, pyrrolidinopyridine etc. Various Lewis acid catalyst such as $ZnCl_2$,[13] $FeCl_3$,[14] $BF_3–Et_2O$,[15] $Cu(OTf)_2$,[16]$Sc(OTf)_3$,[17] $In(OTf)_3$,[18]$Ce(OTf)_3$,[19] $LiClO_4$,[20] etc has been cited in literature for the acetylation reaction. Although the use of triflates nowadays had emerged as an effective catalyst in acetylation reactions because of its strong acidic character by avoiding the use of a large excess of acetylation agents, metal triflates had become a growing concern for industrial applications owing to the high cost and susceptibility of the catalyst to the aqueous medium. Moreover acetylation reactions has also been carried out using ethyl acetate as an acetyl donor,[21] Poly-(N,N'-dibromo-N-ethyl-benzene-1,3-disulfonamide) and N,N,N',N'- Tetrabromobenzene-1,3-disulfonamide,[22] RHA/TiO_2,[23] Fe/SBA-15.[24] The above methods have some limitations such as use of harsh reaction conditions, halogenated volatile organic solvents, monotonous preparation of the catalyst, and poor yield ofthe products, and difficult work-up procedures.[25] These problems can be overcome by using eco-friendly solvent free conditions or by using a reusable catalyst. The nanomaterials provide versatility as a heterogeneous catalyst in a wide range of processes. Literature cited acetylation reactions using various nanocatalyst some of which includes SSA@MNPs[26] where eco-friendly, commercially available, chemically stable and cheap reagents are used; CuO-ZnO,[27] in which chemoselective acetylation of alcohols is being done at room temperature etc.

For heterogeneous catalysis the use of nanoparticles is evenly enhancing over the traditional catalyst systems as they are synthesized at the nanoscale level. The catalyst designed at the nanoscale level has enhanced stability, selectivity, chemical inertness etc. The activity of the nanocatalyst might be because of their excellent surface area to the volume ratio.[28,29] The larger surface area of the nanocatalyst provides better contact between the reactant molecules and the catalyst, which enhances the interaction of the heterogeneous catalytic system to achieve a higher reaction rate. Besides having all these advantages over the traditional catalyst system, the isolation and recovery of the nanocatalyst from the reaction mixture has been one of the promising drawbacks due to their nano size. To overcome these disadvantages the use of Magnetic Nanoparticles (MNPs)[30] have attracted a great deal of interest in present day catalysis reactions because of their easy isolation from the reaction mixture with the help of an external magnet and easy recyclability. Moreover the MNPs show high reactivity with a high degree of chemical and thermal stability. Thus the use of MNPs as catalyst are evenly enhancing over the other catalyst systems. Review articles have been published by Basset[31] and co-workers and Varma et al.[32] cited the use of magnetic nanomaterials as catalysts. Moreover, Verma et al.[33] and Varma et al[34] have developed an efficient method for the cynation of amines by using Fe_3O_4 mangnetic nanocatalyst and $Fe@g\text{-}C_3N_4$ respectively.

$CuFe_2O_4$ MNPs have been used as a catalyst in many reactions but they have certain limitations in the synthesis such as the use of toxic chemicals, harsh reaction conditions and supporting media. Herein we have synthesized biogenic $CuFe_2O_4$ MNPS for the first

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time using aqueous extracts of *Camellia sinensis* var. Assamica (Tea) within a very short reaction time. To the best of our knowledge, this is the most efficient method for the synthesis of $CuFe_2O_4$ MNPs. Leaves of *Camellia sinensis* var. Assamica (Tea) contains mostly diverse polyphenols, including flavonoids, epigallocatechingallate (commonly noted as EGCG) and other catechins.[35] It also contains small amounts of theobromine and theophylline, which are stimulants, and xanthines similar to caffeine. The presence of high amount of polyphenol[36] compounds in *Camellia sinensis* var. Assamica (Tea) might be mainly responsible for the biosynthesis of $CuFe_2O_4$ MNPs. The synthesized MNPs have been utilized for carrying out the acetylation reactions of alcohols, phenols, and amines. The mild reaction conditions, short reaction time, high to excellent yield and easy recyclability of the catalyst are the advantages of the protocol. Moreover, the reaction has been carried out in solvent free conditions without the use of any hazardous solvents and neither the use of any acid or base.

2. Experimental

2.1 Biogenic synthesis of $CuFe_2O_4$:

Camellia sinensis var. Assamica (Tea) were collected from Dibrugarh University campus, Assam, India and washed thoroughly with distilled water. They were cut into small pieces and approximately 20 gm was placed into 100 ml of distilled sterile water and heated for about 30 mins. The plant extract was then filtered through whatmann No.1 filter paper. A solution of $FeCl_3$ in copper acetate solution was added to the plant extract of *Camellia sinensis* var. assamica (Tea). 5 ml of 0.1 M NaOH solution was added to the solution and stirred for 1 hour at room temperature .The resulting solution was centrifuged and washed with ethanol. It was then subjected to annealing at 200°C for 2 hrs, which led to the formation of $CuFe_2O_4$ MNPs. The synthesized nanoparticles were characterized by powder-XRD, SEM-EDX, TEM and VSM. This method has several advantages in comparison to other reported methods (Table 1).

Table 1: Comparison of methodologies to synthesis $CuFe_2O_4$MNPs:

Type	Temp (°C)	Time (h)	Size (nm)	Ref.
Co-precipitation	90	2	35	37
Co-precipitation	90	5	30	38
Sol-Gel method	90	3	40	39
Biogenic Synthesis	Room temp	1	8.78	This Work

2.2 General Procedure for the acetylation reaction at room temperature:

The prepared $CuFe_2O_4$ MNPs were used in the acetylation reactions of alcohols, phenols and amines. In a reaction of 1 mmol of amines, alcohols and phenols, 2.56 mg (0.0107 mmol) of the magnetic nanocatalyst and acetic anhydride (2 mmol) were added to a round bottom flask under magnetic stirring at room temperature (Scheme 1). After completion of the reaction, the product was diluted with 20 mL of distilled water and extracted with chloroform, the combined organic layer was treated with saturated bicarbonate solution, washed with brine and dried over by using anhydrous Na_2SO_4 and evaporated in a rotary evaporator under reduced pressure. The confirmation of the products was done by ^{1}H-NMR and ^{13}C-NMR.

$$R\text{-}NH_2/R\text{-}OH + Ac_2O \xrightarrow[\text{Solvent free rt}]{\text{MNPs}} R\text{-}NHAc/R\text{-}OAc$$

R= Aliphatic/ Aromatic

Scheme 1: Synthesis of acetylated derivatives using $CuFe_2O_4$MNPs.

3. Results and Discussion

3.1 Characterisation of the Catalyst:

The biogenic $CuFe_2O_4$ MNPs were characterized by powder XRD-diffraction method as shown in figure 1. The sharp diffraction peaks show clearly the presence of highly pure crystalline $CuFe_2O_4$ nanoparticles. The diffraction peaks appeared at 2Θ = 36.4°, 38.84°, 42.28°, 61.36°, 73.70° corresponds to planes (111), (111), (200), (220) and (311) respectively.

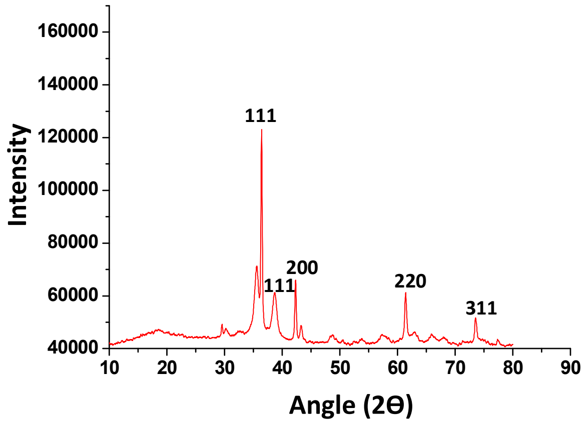

Fig. 1: Powder XRD pattern of the synthesized $CuFe_2O_4$ MNPs.

The structure and morphology of the synthesized nanoparticles are shown in SEM image (figure 2(a)). From these images the structure of the nanoparticles was found to be pure spherical and also the monodispersity of the nanoparticles was clearly observed from the SEM images.

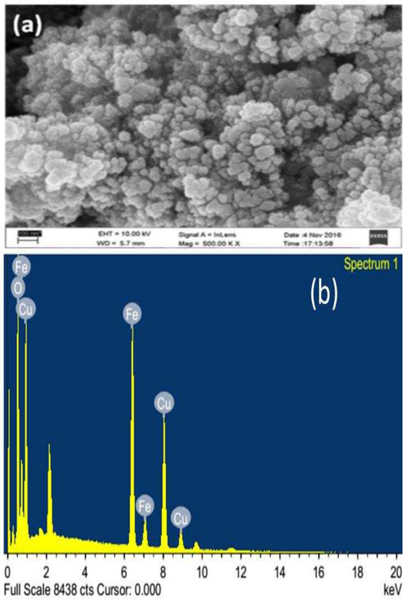

Fig. 2: (a) SEM images of the pure spherical $CuFe_2O_4$ MNPs, (b) EDX image of the Nano spherical $CuFe_2O_4$ MNPS.

The purity of the nanoparticles was observed from the Energy Dispersive X-ray (EDX) spectrum (figure 2b) which shows clearly the presence of copper, iron and oxygen element. The elemental mapping of the synthesized nanoparticles is shown in figure 3.

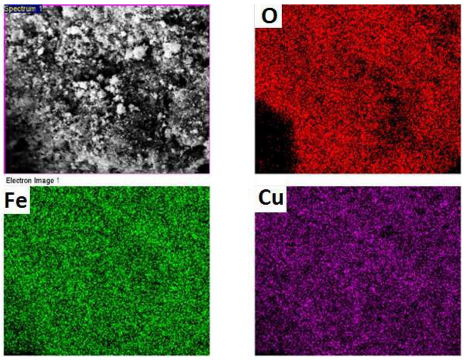

Fig. 3: Elemental mapping of $CuFe_2O_4$ showing O, Fe, Cu.

The size and morphology of $CuFe_2O_4$nanocrystals were determined from TEM and HR-TEM images (Figure 4). The figure 4(b) shows the selected area electron diffraction (SAED) pattern of $CuFe_2O_4$MNPS which contain the concentric diffraction of rings due to the (111), (220) and (311) reflection of the spherical Cu. The presence of bright spots in the SAED pattern confirmed the crystalline nature of the nanoparticles. From the HR-TEM image (figure 4c) the fringes separation was found to be 2.40A° which is in good agreement with (111) plane and the other fringe of 2.77A° was found to be in agreement with (200) plane of $CuFe_2O_4$ MNPs. The average diameters of the nanoparticles were found to be 8.78 nm from the size distribution (Figure 5).

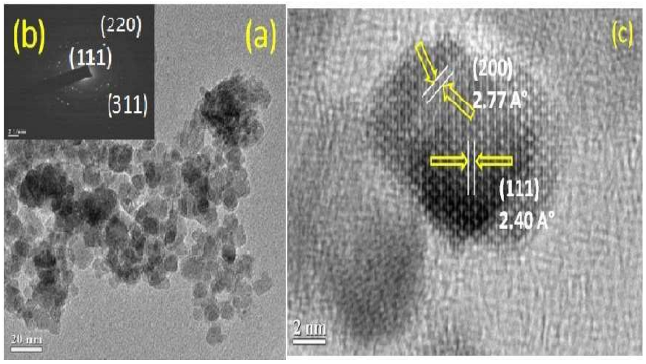

Fig. 4: (a) TEM images and (b) corresponding SAED pattern of the nanoparticles and (c) HR-TEM image of a selected region of $CuFe_2O_4$ MNPs

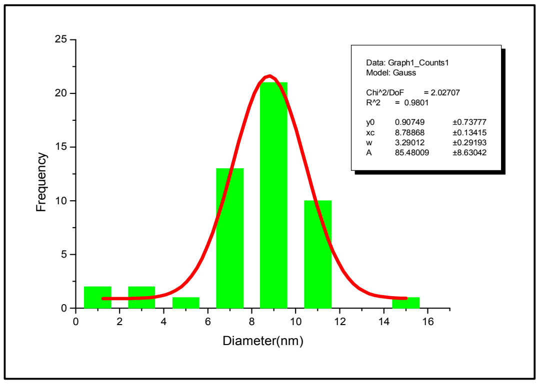

Fig.5 Size distribution of the $CuFe_2O_4$MNPs

By using VSM at room temperature the magnetic measurements were carried out (figure 6). The sensitivity of the prepared catalyst is strong enough to provide an easy and effective way to separate the catalyst from the reaction system.

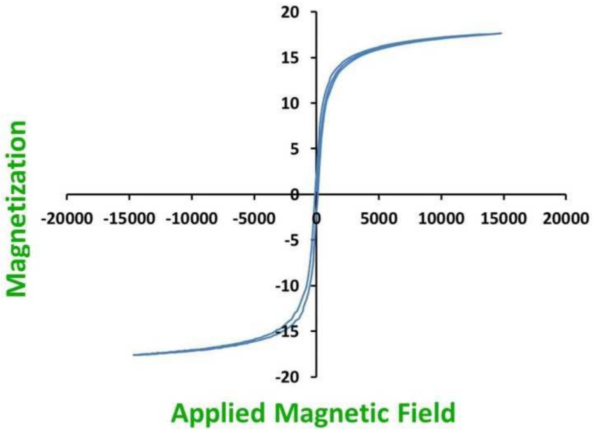

Fig. 6 VSM spectra of $CuFe_2O_4$ MNPs

From the X-ray Photoelectron Spectroscopy the oxidation state of the metal atoms were investigated. The XPS spectrum of Cu[40,41] (Figure 7) contains Cu $2p_{3/2}$ and Cu $2p_{1/2}$lines with binding energy of 932.8 (M_1) and 952.8 (M_2) eV, respectively. The S_1 and S_2correspond

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to the satellite peaks, which showed the presence of Cu^{2+} oxidation state in the compound.The peak for Fe $2p_{3/2}$ and Fe $2p_{1/2}$ at 709.5 and 722.7 eV with a small satellite (S) at 717.6 eV confirmed the presence of Fe^{3+}oxidation state in the compound. All of the above results confirmed the formation of $CuFe_2O_4$ MNPs.[42]

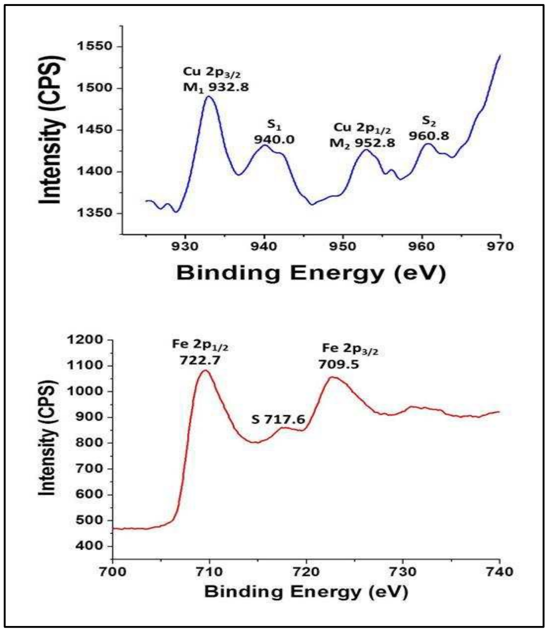


Fig. 7 (a) XPS of Cu, (b) XPS of Fe in $CuFe_2O_4$ MNPs

3.2 Acetylation of different substrates with the prepared $CuFe_2O_4$MNPs:

We optimized the reaction condition by using aniline and acetic anhydride as the model substrate. The results obtained from optimization are summarized in table 2. In the absence of the catalyst and solvent no product was obtained after 240 min (table 2, entry 7). But with the use of 2 mol% biogenic $CuFe_2O_4$ MNPs in-spite of the absence of the solvent maximum product yield of 98% was obtained (table 2, entry 6).

Table 2: Optimization of the reaction parameters for acetylation reaction[a]:

Entry	Solvent	$CuFe_2O_4$ MNPs (mol %)	Time (min)	Yield[b](%)
1	Toluene	5	240	55
2	Water	10	300	Trace
3	MeOH	10	240	50
4	CH_2Cl_2	10	240	70
5	CH_3CN	10	60	75
6	-	2	5	98
7	-	0	240	No product

[a] Reaction conditions: Aniline (1 mmol), Acetic anhydride (2 mmol), room temperature , Solvent (5 ml)
[b] Isolated Yields.

With the optimized conditions, the scope of the reaction was explored to a variety of amines, phenols, and alcohols. 20 different types of acetylation products were obtained with high yield using the above-mentioned reaction conditions (Table 3).

Out of the various substituents, the amines tested were converted to the corresponding acetates in excellent yields under optimized conditions compared to the phenols (Table 3, entry 1-3). The anilines containing both electron-donating and electron withdrawing groups gave excellent yields of 95-98% in 5-30 min at room temperature. The secondary aromatic amines such as diphenyl amine (Table 3, entry 9) also gave excellent results. Moreover a variety of other functional groups such as -OMe, -COMe, $-NO_2$ also survived under the reaction conditions.

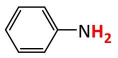
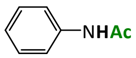
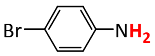
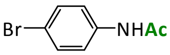
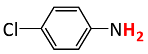
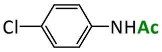
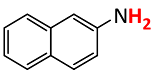
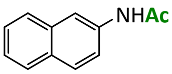
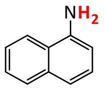
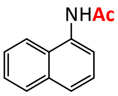
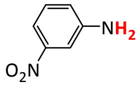
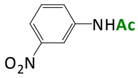
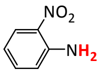
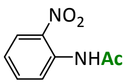
The primary benzylic alcohols were selectively converted to the corresponding acetates without any side products (Table 3, entries 15-17). Moreover, the benzylic alcohols proceeded at a higher rate in comparison to aliphatic alcohols.

For allylic systems also this protocol was efficient. Cinnamyl alcohol was selectively converted to the corresponding acetate and the double bond remained intact under these reaction conditions (Table 3, entry 20). Primary alcohols such as cyclohexanol and octanol also gave efficient products in 90-95% yield (Table 3, entry 18-19).

The benzylic alcohols with electron donating group (Table 3, entry 15) took less reaction time compared to the electron withdrawing group (Table 3, entry 17).

The chemoselectivity was however not observed for the compounds with two different functional groups such as -NH and -OH (Table 3, entry 12, 14,). Similarly, no chemoselectivity was observed for the compounds containing -SH and -NH respectively (Table 3, entry 13).

Table 3: Substrate scope variation of the acetylation reaction products with Ac_2O under solvent free conditions[a] in the presence of $CuFe_2O_4$ MNPs.

S.No	Substrate	Product	Time	Yield[b] (%)
1			5	98
2.			5	98
3.			5	97
4			5	95
5			5	95
6			30	95
7			30	95

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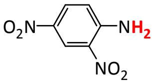
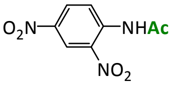
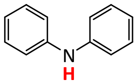
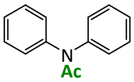
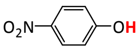
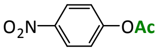
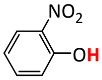
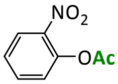
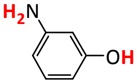
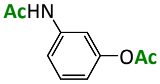
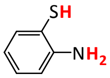
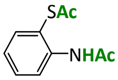
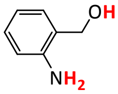
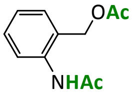
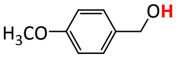
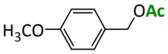
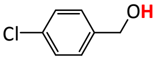
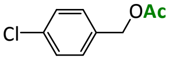
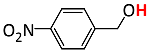
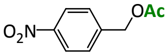
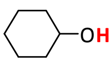
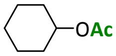
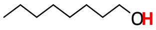
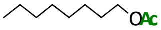
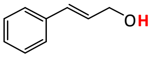
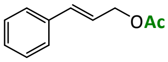
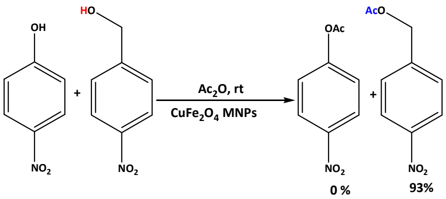
8			35	90
9			30	95
10			60	93
11			60	93
12			45	96
13			60	96
14			45	90
15			45	92
16			45	94
17			60	93
18			90	95
19			60	90
20			60	95

[a]Reaction conditions: alcohols/phenols/anilines (1mmol), $CuFe_2O_4$ MNPs (0.0107 mmol) in acetic anhydride (2mmol)at room temperature

[b]Isolated Yield.

By using a mixture of substituted benzyl alcohol and phenol the chemoselectivity was evaluated. An equimolar mixture of 4-nitro benzyl alcohol and 4-nitro phenol was reacted with acetic anhydride in presence of biogenic $CuFe_2O_4$ MNPs catalyst. The result of this reaction revealed that it proceeded with absolute chemoselectivity towards 4-nitro benzyl alcohol (Scheme 2).



Scheme 2: Chemoselectivity in the presence of $CuFe_2O_4$ MNPs

3.3 Recyclability:

An important characteristic of a true heterogeneous catalyst is its recyclability. To study the recyclability of the catalyst we performed the reaction of Phenol with acetic anhydride under similar reaction conditions. The catalyst could be separated from the reaction mixture after completion of the reaction with the help of an external magnet and it can be reused for successive experiments (4 times). The product yield was found to remain same, which indicated the reusability and the recyclability of the catalyst without loss of activity (figure 8a). There is no change in morphology in the nanoparticles as observed by the TEM image taken after the 4th cycle in the recycling process (figure 8b). The bright rings of the SAED image in figure 8(c) confirmed the crystalline nature of recycled $CuFe_2O_4$ MNPS. The VSM result of recycled catalyst retained its magnetic property upto its 4th cycle as shown by the fig8(d).

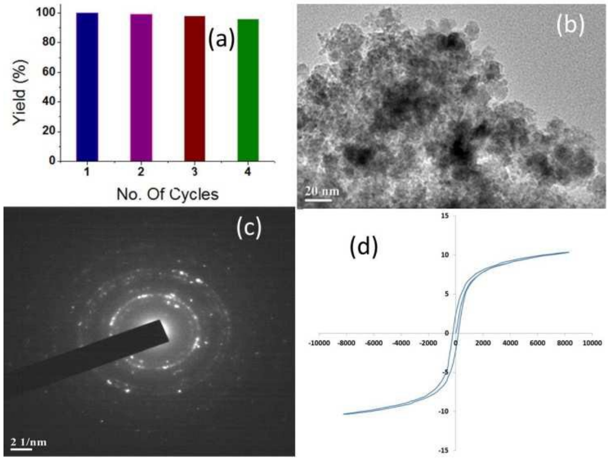


Fig.8: a) Recyclability of $CuFe_2O_4$ MNPs, b) TEM image of recyclable $CuFe_2O_4$ MNPs (4th cycle), (c) SAED pattern of recycled $CuFe_2O_4$ MNPs, (d) VSM of recycled catalyst of 4th cycle.

4. Mechanism:

The mechanism of acetylation reactions with the nanocatalyst is not exactly known. However, a proposed mechanism has been suggested, which indicates the activation of the carbonyl group of acetic anhydride by coordinating to $CuFe_2O_4$ MNPs[43] (figure 9). The activated carbonyl then reacts with the substrates to give the corresponding acetates.

In order to compare the efficiency of the synthesized MNPs with previously reported catalyst for acetylation reaction we performed the reaction of aniline with acetic anhydride as shown in table 4, the previously reported nanocatalyst suffered one or more disadvantages which included toxicity, low yield of products, non-usability and longer reaction time.

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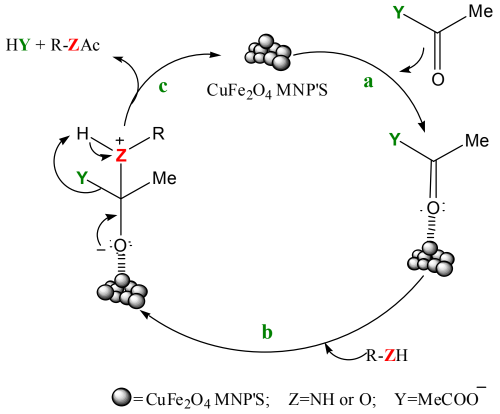

Fig 9: Proposed mechanism for acetylation of alcohols, phenols, aniline.

Table 4: Comparison efficiency of $CuFe_2O_4$ MNPs with some reported catalysts for the acetylation reactions of aniline:

Entry	Reaction Conditions	Time (min)	Catalyst (mol %)	Yield (%)	Ref
1	$HClO_4$–SiO_2	15	1mol	80	44
2	Zeolite H-FER	120	150 mg	99	45
3	$BiFeO_3$	5	100 mg	98	43
4	EtOAc	20 h	0.1 M (70°C)	16	21
5	RHA/TiO_2	9	20 mol	93	23
6	Fe_3O_4@PDA-SO_3H	30	2 mol	96	30
7	Zinc Acetate (Microwave)	20	0.045 mmol	91	46
8	$CuFe_2O_4$MNPs r.t.	5	2 mol	98^a	This Work

^{a}Reaction conditions: aniline (1 mmol), $CuFe_2O_4$ MNPs (0.0107 mmol) in acetic anhydride (2 mmol)at room temperature.

5. Conclusion:

In the investigation, we have synthesized biogenic $CuFe_2O_4$ MNPs using *Camellia sinensis* var. Assamica (Tea) for the first time. Moreover, we have shown the catalytic applicability of the synthesized nanoparticles for the acetylation of various alcohols, phenols, and amines at room temperature under solvent free conditions with excellent yields. The reaction proceeded within a very short reaction time and the products obtained also gave good to excellent yields. Recyclability up to 4 times is one more advantage of the prepared catalyst. The easy preparation, biogenic synthesis of the catalyst, no harsh reaction conditions are the advantages of this protocol.

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