JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Green Synthesis of Iron Oxide Nanoparticles from Syzygium Cumini Extract and Their Catalytic Activity in Heterocyclization

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Abstract: This study focused on green synthesis of iron oxide nanoparticles (FeONPs) using syzygium cumini leaves extract. Here the syzygium cumini leaves extract acts as reducing and stabilizing agent to facilitate the iron oxide. The synthesized S. cumini FeONPs are supported on activated modified clay and they are characterized by using FTIR and XRD. The newly developed NPs are screened for their catalytic property in the formation of thiazole derivatives. It is found that the bentonite supported S. cumini FeONPs give a high rate of conversion and give more than 90% product in water, at a fairly low temperature. It shows potential for the environmentally friendly synthetic pathway for prime organic molecules.

Keyword: **Nanoparticles, Syzygium cumini, bentonite clay, thiazole**

I. INTRODUCTION

Nanotechnology has revolutionized material science by enabling the design of nanoscale materials with unique physicochemical and catalytic properties. Metal and metal oxide nanoparticles, in particular, have been extensively investigated owing to their high surface-to-volume ratio, tunable size, and functional versatility in catalysis, sensors, drug delivery, and environmental remediation [1,2]. Among them, iron oxide nanoparticles (Fe_3O_4) have attracted special interest due to their superparamagnetic behavior, biocompatibility, non-toxicity, and recyclability [3]. Conventional chemical and physical routes for synthesizing iron oxide nanoparticles, such as co-precipitation, hydrothermal, and sol–gel methods, often require hazardous reagents, high temperature/pressure, and energy-intensive conditions [4]. These drawbacks have led to the exploration of sustainable and environmentally benign alternatives.

Green synthesis of nanoparticles using plant extracts has emerged as a promising strategy because phytochemicals present in leaves, fruits, seeds, and barks act as natural reducing, stabilizing, and capping agents [5]. This approach eliminates toxic chemicals, reduces waste, and enhances biocompatibility. Several plants such as Azadirachta indica, Moringa oleifera, and Camellia sinensis have been reported for the biosynthesis of iron oxide nanoparticles [6,7]. Syzygium cumini is a medicinally significant plant belonging to the Myrtaceae family. Its leaves are rich in flavonoids, anthocyanins, tannins, ellagic acid, and other phenolic compounds, which exhibit strong antioxidant and reducing properties [8,9]. These phytoconstituents provide an effective reducing medium for metal precursors while simultaneously stabilizing the nanoparticles, leading to controlled morphology and enhanced stability.

To further improve the catalytic activity and stability of green-synthesized nanoparticles, they are often immobilized on solid supports. Bentonite clay, a naturally occurring alumino silicate with high surface area, layered structure, cation-exchange capacity, and mechanical stability, is an attractive support for nanomaterials [10]. Incorporation of iron oxide nanoparticles into the bentonite framework prevents agglomeration, increases active surface sites, and enhances reusability, making the composite highly suitable for heterogeneous catalysis [11]. Reports have shown that clay-supported metal nanoparticles exhibit remarkable efficiency in promoting organic reactions under mild conditions [12].

Catalytic applications of such hybrid nanomaterials are particularly relevant in heterocyclic synthesis. Heterocycles constitute the core of numerous natural products, pharmaceuticals, and agrochemicals. Among them, thiazoles and their derivatives are of great significance owing to their broad spectrum of biological activities such as antimicrobial, anticancer, anti-inflammatory, antioxidant, and antiviral properties [13,14]. Specifically, 4-phenylthiazol-2-amine derivatives have been identified as promising pharmacophores in medicinal chemistry [15]. However, conventional synthetic methods often involve harsh conditions, prolonged reaction times, and toxic catalysts [16]. The use of green nanocatalysts provides an eco-friendly and efficient pathway for synthesizing these biologically valuable scaffolds.

In this study, we report the green synthesis of bentonite clay-supported iron oxide nanoparticles using Syzygium cumini leaf extract as a reducing and stabilizing agent. The synthesized nanocomposite was characterized using standard physicochemical techniques and subsequently employed as a heterogeneous catalyst for the synthesis of 4-phenylthiazol-2-amine derivatives. This work highlights a sustainable approach to nanoparticle synthesis and demonstrates their catalytic efficacy in promoting thiazole synthesis under environmentally benign conditions.

Material and Methods:

Melting points were determined by open capillary method and were uncorrected. The chemicals and solvents used were of laboratory grade and were purified prior to use. Completion of the reaction was monitored by thin-layer chromatography on precoated sheets of silica gel-G (Merck, Germany) using UV lamp for detection. IR spectra were recorded (in KBr pallets) on Shimadzu spectrophotometer. 1H NMR and 13C NMR spectra were recorded (in DMSO) d6 on Bruker Avance-400 MHz spectrometer using TMS as an internal standard. The mass spectrum was recorded on EI-Shimazdu-GC-MS spectrometer.

Preparation of FeONPs on Activated Bentonite:

Leaves of Syzygium cumini, free of any infection, were picked and cleaned under running tap water and double distilled water. The leaves are crushed and boiled with 200 ml double distilled water in round bottom flask for about 2 hrs. After cooling it is filtered and used for further procedure.

Bentonite clay is activated by 15 ml Syzygium Cumini leaves extact. The activated bentonite clay is treated with $FeCl_3$ and Syzygium Cumini leaves extract. Coversion of Fe^{+3} to Fe_2O_3 can be identified by color changes brown to black. The formation of S.cumini FeONPs@bentonite is also confirmed by XRD analysis.

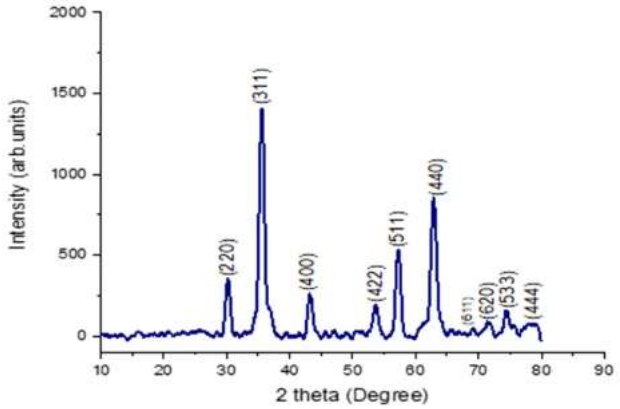


Fig. 2: XRD of S.cumini FeONPs@bentonite

XRD analysis:

XRD analysis generated ten peaks for the biosynthesized Fe_3O_4-NPs positioned at 2θ angles of 30.2°, 35.5°, 43.2°, 53.8°, 57.3°, 62.95°, 69.0°, 71.4°, 74.3°, and 78.1°. The observed lattice spacing at 30.2°, 35.5°, 43.2°, 53.8°, and 57.3° matched well with the (220), (311), (400), (422), and (511) planes of Fe_3O_4 crystals. The crystal structure data was in close agreement with the reported data and can be assigned to the magnetite phase of iron oxide. This XRD pattern for magnetic nanoparticles is cross referenced with ICDD—International Centre for Diffraction Data (ICDD) file number: 00–019-0629. The peak intensity ranged from 240 to 1,400 arbitrary units for the synthesized Fe_3O_4-NPs.

General procedure for the synthesis of phenylthiazol-2-amine derivative (3a-k):

A mixture of substituted Aldehyde (1 mmol), and urea (1.5 mmol), was stirred in water at 80^0C on magnetic stirrer using S.cumini FeONPs@bentonite as a catalyst. The reaction progress was confirmed by TLC. After completion of reaction, the catalyst was removed by external magnet. Then the reaction mixture was poured in ice cold water. The product was precipitated out was filter by simple filtration method. For further purification, the product was recrystallize in ethanol. The conformation of the formed product is carried out by spectral characterization.

Spectral Data:

4-phenylthiazol-2-amine (3a):

M.P. 158-160 0C; Yield: 85 %; IR (KBr, cm-1): 3319 (-NH_2), 3146 (Ar- C-H), 1562 (C=C); 1H NMR (400 MHz, DMSO-d6, TMS, δ, ppm): 7.72-6.97 (m,7H, Ar-H), 6.38 (s, 2H, NH2); 13C NMR (100 MHz, DMSOd6):δ 171.2, 148.0, 134.9, 130.2, 129.7, 128.1, 127.8, 127.1,116.3;EIMS (m/z): 176

4-(4-bromophenyl)thiazol-2-amine (3c):

M.P. 186-188 0C; Yield: 89 %; IR (KBr, cm-1): 3289 (-NH_2), 3182 (Ar- C-H), 1602 (C=C); 1H NMR (400 MHz, DMSO-d6, TMS, δ, ppm): 7.89-7.09 (m,7H, Ar-H), 6.51 (s, 2H, NH2); 13C NMR (100 MHz, DMSOd6):δ 170.9, 150.4, 139.3, 130.7, 128.8, 128.0, 127.4, 126.2, 114.8;EIMS (m/z): 255

4-(3-nitrophenyl)thiazol-2-amine(3f):

M.P. 188-190 0C; Yield: 90 %; IR (KBr, cm-1): 3323 (-NH_2), 3160 (Ar- C-H), 1592 (C=C), 1524 (N=O); 1H NMR (400 MHz, DMSO-d6, TMS, δ, ppm): 7.90-7.17 (m,7H, Ar-H), 6.38 (s, 2H, NH2); 13C NMR (100 MHz, DMSOd6):δ 170.3, 150.1, 140.7, 130.2, 129.5, 128.4, 127.6, 126.1, 109.2; EIMS (m/z): 221

4-(4-methoxyphenyl)thiazol-2-amine (3g):

M.P. 206-208 0C; Yield: 88 %; IR (KBr, cm-1): 3339 (-NH_2), 3207 (Ar- C-H), 2980 (C-H), 1567 (C=C); 1H NMR (400 MHz, DMSO-d6, TMS, δ, ppm): 7.84-7.10 (m,7H, Ar-H), 6.49 (s, 2H, NH2), 2.8 (s, 3H, OCH3); 13C NMR (100 MHz, DMSOd6):δ 170.6, 149.4, 142.3, 131.7, 129.9, 128.6, 126.2, 126.8, 60.4; EIMS (m/z): 206

4-(4-hydroxyphenyl)thiazol-2-amine (3i):

M.P. 176-178 0C; Yield: 90 %; IR (KBr, cm-1): 3279 (-NH_2), 3134 (Ar- C-H), 1597 (C=C); 1H NMR (400 MHz, DMSO-d6, TMS, δ, ppm): 7.84-6.88 (m,7H, Ar-H), 6.82 (s, 2H, NH2), 5.89 (s, 1H, OH); 13C NMR (100 MHz, DMSOd6):δ 172.4, 150.8, 140.7, 130.4, 128.6, 126.3, 112.9,; EIMS (m/z): 192

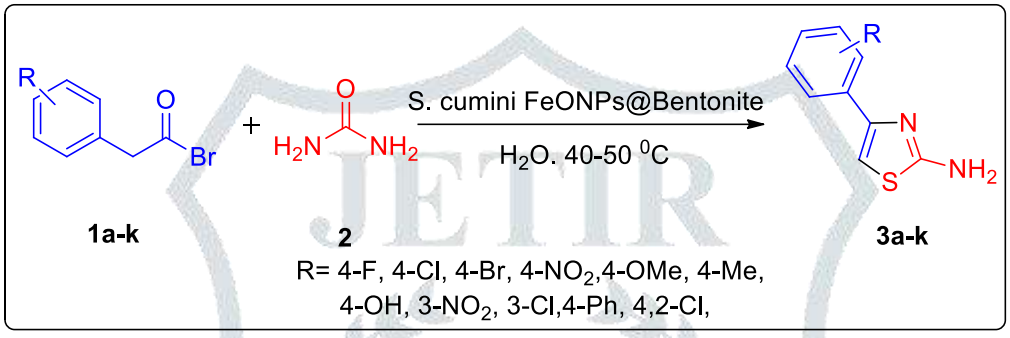
4-([1,1'-biphenyl]-4-yl)thiazol-2-amine (3k):

M.P. 208-210 0C; Yield: 86 %; IR (KBr, cm-1): 3279 (-NH_2), 3242 (Ar- C-H), 1614 (C=C); 1H NMR (400 MHz, DMSO-d6, TMS, δ, ppm): 7.04-8.34 (m,10H, Ar-H), 6.78 (s, 2H, NH2); 13C NMR (100 MHz, DMSOd6):δ 171.3, 152.2, 144.5, 131.3, 129.9, 129.2, 127.8, 127.1, 126.8, 126.0, 1060.7; EIMS (m/z): 252

Result and Discussion:-

The present study describes the efficient synthesis of phenylthiazol-2-amine derivatives catalyzed by bentonite-supported iron oxide nanoparticles (FeONPs@bentonite). The results clearly demonstrated uniform dispersion of iron oxide nanoparticles on the bentonite surface, providing a high surface area and abundant active sites for catalytic activity. To follow our interest in the synthesis of thiazole derivatives, we investigated here the iron oxide nanoparticles catalysed by activated bentonite clay is one-pot synthesis through two component condensation of an phenacyl bromide and thiourea.

Initially, the 4-bromophenacylbromide **(1)** with thiourea **(2)** using FeONPs@bentonite catalyst as model reaction and the reaction was monitored in the absence of solvent and catalyst at room temperature. The reaction did not go to completion even after 24 hours of stirring. The same reaction was examined at elevated temperature, the reaction takes place in the forward direction but the yield of the product obtained was low. Inspired by these results, the model reaction was carried out in the presence of solvent such as ethanol, acetonitrile, THF and toluene. The reaction proceeds successfully but it reaches to about 30-35% yield of the product at higher temperature. In order to modify the reaction path in the light of the "Green Chemistry", water was used as green reaction media due to its advantages over conventional organic solvents. The results obtained using water was superior as compared to the organic solvents.

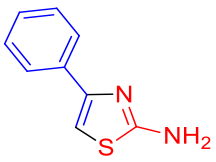


Scheme 1: General scheme for the synthesis of phenylthiazol-2-amine derivative (**3a-k**)

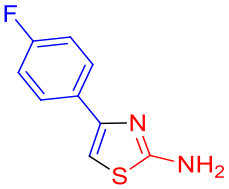
The structures of all the synthesized compounds were established on the basis of IR, NMR and Mass spectral analysis. The IR spectrum of compound **3c** shown a band at 3289 cm^{-1} for the –NH_2, a band at 1602 cm^{-1} due to presence of C=C. The ^{1}H NMR of the compound **3c** showed characteristic singlet for NH_2 at δ 6.51, and all aromatic protons were observed in their respective aromatic region. Mass spectra of all the compounds gave expected M^+ peak corresponding to their molecular mass. The natural chlorine and bromine ratio were observed whenever present in the compounds.

We investigate the reaction by using different substituted phenacylbromide containing both electron donating and electron withdrawing groups as a suitable substrate for this reaction.

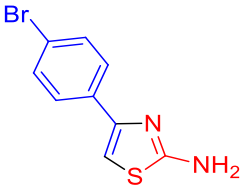
Table 1: Synthetic derivatives of phenylthiazol-2-amine (**3a-k**)



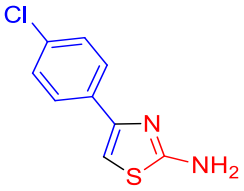
3a
Melting Point: 158-160^{0}C
Yield: 85%



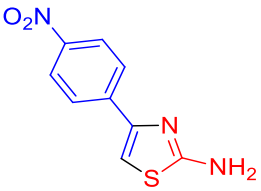
3b
Melting Point: 222-224^{0}C
Yield: 88%



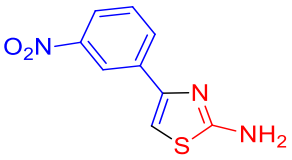
3c
Melting Point: 186-188^{0}C
Yield: 89%



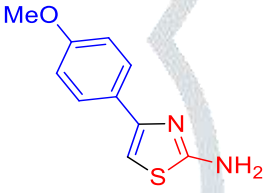
3d
Melting Point: 170-172^{0}C
Yield: 90%



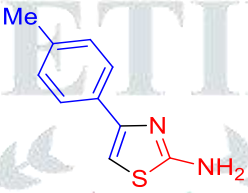
3e
Melting Point: 186-188^{0}C
Yield: 86%



3e
Melting Point: 190-192^{0}C
Yield: 87%

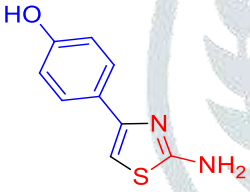


3f
Melting Point: 188-190^{0}C
Yield: 90%

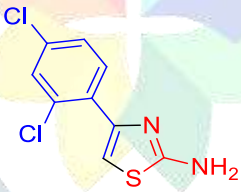


3g
Melting Point: 136-138^{0}C
Yield: 85%

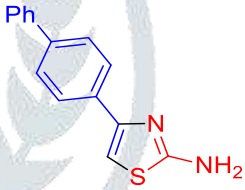
3h
Melting Point: 170-172^{0}C
Yield: 89%



3i
Melting Point: 176-178^{0}C
Yield: 90%



3j
Melting Point: 16o-162^{0}C
Yield: 89%



3k
Melting Point: 208-210^{0}C
Yield: 86%

Conclusion:

This work highlighted the green synthesis FeONPs from Syzygium Cumini leaf extract supported on bentonite clay and it was efficaciously implemented for lipase immobilization. Iron oxide nanopartilele have been intensively studies for a variety of application within numerous fields ranging from medicine and pharmaceutics to micro electronics and analytical chemistry. Therefore, the intensive research work investigating the synthesis of iron oxide nanoparticles must further continue. The distinct characteristics, size, and shape of Fe_2O_3 nanoparticles were identified using FTIR & XRD spectroscopic technique

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