HIGHLY EFFICIENT RECYLABLE ZnO NANOPARTICLES CATALYST BIO-DERIVED FROM SOLANUM XANTHOCARPUM BERRY EXTRACT FOR THE SYNTHESIS OF SOME SCHIFF BASE DERIVATIVES

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ABSTRACT

The green, ecofriendly production of ZnO nano partricles using Solanum xanthocarpum Berry Extract and their use as a nanocatalyst in the synthesis of substituted Schiff base derivatives. Bio-synthesized nanoparticles were characterized by XRD, SEM, EDX, IR and TEM techniques. Bio- derived ZnO nanoparticles are efficiently utilized in the synthesis of Schiff base derivatives (3a-e) from 2-amino-5-fluorobenzonitrile and substituted benzaldehydes in the presence of ultrasound irradiation with high yields. The catalyst can be removed and recycled several times without marked loss of activity.

KEYWORDS: ZnO nanopartricles, Solanum xanthocarpum Berry Extract, nanocatalyst, Schiff base, SEM and TEM

INTRODUCTION

Among diverse metal oxides, ZnO nanoparticles have attained to the shine for its semiconducting properties, unique antibacterial, antifungal, wound healing and UV filtering properties, valuable catalytic and photochemical activity[1]. Over the past several forever and ever, plants and different natural sources have come up as a low cost, energy-efficient, eco-friendly and non-toxic approach for synthesis of nanomaterials[2]. These synthesized nanoparticles have the advantage of useful polydispersity, dimensions and stability by all of a lesser synthesizing cost. Here and there the combination of nanoparticles utilizing plants or parts of plants can demonstrate invaluable over other organic procedures by dispensing with the detailed procedures of maintaining cell cultures and can further be correctly scaled up for large nanoparticles synthesis[3] . Many examples are found in literature for ecofriendly synthesis of ZnO nanoparticles utilizing leaf extract, for example, Corriandrum Sativum with $Zn(CH_3CO)_2$ $2H_2O$ as starting material[4] , Calotropis procera[5] , ocean growth, for example, green Caulerpa peltata, red Hypnea Valencia and brown Sargassum myriocystum[6], squeezed orange[7] , Calotropis procera latex[8] , aqueous leaf extract of Acalypha indica[9] , and Calotropis Gigantea leaf extract[10] . Solanam xanthocarpum (Solanaceae), a herb (Fig. 1), develops as wild plant in numerous parts of India, especially in slopes and valley of Manipur. Organic products are palatable and neighborhood individuals of Manipur utilize organic products for treatment of different infirmities as customary society medication. India is one of the crude material-delivering countries of South Asia. Solanum xanthocarpum contains alkaloids, phenolics, flavanoids, sterol, saponins and their glycosides, and has an extensive variety of therapeutic qualities. S. xanthocarpum yield natural organic substance solanocarpidine and a sterol, carpesterol. Root is one of the constituents of Dasamulasava[11]. Seeds are used as diuretic. Juice of berries is represented to be useful for sore throat. A decoction of plant is used as a piece of gonorrhea and it as well said to promote conception in females. Kantakari is reported to be supportive in Kasa Roga (hack) moreover in Tamakwasa (bronchial asthma). In Chattisgarh, it is considered as a most vital

herb for traditional healers in treatment of more than 100 common diseases alone or in blend with other nearby and striking herbs.

Figure 1 Solanum xanthocarpum Berries

Schiff bases derived from aromatic amines and aromatic aldehydes are also a very important class of organic compounds because of their applications in many fields including biological[12,13], inorganic[14], and analytical chemistry[15].

Several synthetic methods have been reported for the synthesis of Schiff bases. However, most of them have limitations including long reaction times, need for a special catalyst, low yields, and extensive recrystallization[16]. Therefore, the pursuance of more convenient and practical synthetic methods for preparation of these compounds still remains an active research area. Recently, the use of several catalysts, like inorganic salts[17] and zeolites[18], in organic synthesis.

Utilization of heterogeneous catalysts in different areas of organic synthesis has now reached significant levels, not only for the possibility to perform environmentally benign synthesis but also for the good yields and excellent selectivity that can be achieved[19]. In general, heterogeneous catalysts offer higher surface area, lower coordinating sites, high atom efficiency, easy product purification, and simple reusability.

Herein, a novel method is presented for the synthesis of some Schiff base derivatives catalyzed by biologically synthesized zinc oxide. Zinc oxide is a unique material that has prompted much interest in the past decade. Different morphologies and a wide range of particle sizes for ZnO have led to diverse investigations in academic and industrial societies[20].

In this present examination we prepared ZnO nanoparticles, a green and minimal cost technique utilizing berries of Solanum xanthocarpum . This technique is actually favorable for preparation of very much described nanoparticles without usage of cruel, poisonous and costly chemicals. Additionally, this method is more significant because of its cost suitability. Other than the green synthesis, explore the catalytic action of ZnO NPs prepared from the fruit extract of S. xanthocarpum.

2. Experimental Section

2.1. Materials

Materials used for the synthesis of ZnO nanoparticles are Zinc nitrate [$Zn(NO_3)_2.2H_2O$] and all other chemicals were purchased from Merck, India and used without further purification. Solanum xanthocarpum Berries were collected in and around Chidambaram, Cuddalore district, Tamil Nadu, India. Solanum xanthocarpum Berries were washed, shade dried and finely powdered. The 100g powder, was suspended in 250 ml of water for two hours and then heated at 60-65ºC for 30 minutes. The extract was collected separately and the processes were repeated thrice with the residual powder, each time collecting the extract. The collected extracts were pooled and passed through a fine cotton cloth. The filtrates were evaporated at 40-50ºC in a rotavapour under reduced pressure. The dark semisolid material (yield-14%) obtained was stored at 0-4ºC until use[21].

Preparation of zinc nanoparticles

For the mix nanoparticle 50 ml of Solanum xanthocarpum Berry extract was taken

and heated to 60-80 degree Celsius using a stirrer hotter. 5 grams of Zinc Nitrate was added to the solution as the temperatures achieved 60 degree Celsius. This mix is then bubbled until it condensed to a significant yellow colored paste. This paste was then gathered in an ceramic crucible and heated in an air heated furnace at 400 degree Celsius for 2 hours. A light white shaded powder was obtained and this was meticulously accumulated and stuffed for depiction purposes. The material was pounded in a mortar pestle in order to get a better nature for characterization.

General procedure for synthesis Schiff base derivatives catalyst by ZnO nanoparticles from plant sources

2-amino-5-fluorobenzonitrile (0.01mol), substituted benzaldehyde (0.01mol) mixed with ZnO nanoparticles (5mol %) and 95% Ethanol (20 ml) were taken into a 100 ml conical flask. The mixture was irradiated by an ultrasonic generator in a water-bath at 30-35°C for 30 min. The product was filtered with suction on a Buchner funnel, washed with cold water then with ethanol. The crude product was recrystallized from ethanol to afford light brown shiny crystals. The ZnO catalyst could be used consecutively for five times for the condensation of acetophenone and benzaldehyde. After washing the filtrate the separated organic layer was concentrated under reduced pressure and the product was purified by column chromatography using hexane/ethyl acetate as solvent system in different concentration to get the pure compound.

2.3. Characterization

Ultraviolet and visible (UV-vis) absorbance spectra were measured over a range of 800-200 nm with a Shimadzu UV-1650PC recording spectrometer using a quartz cell with 10 mm of optical path length. High resolution Scanning Electron Microscopy (HRSEM) as well as Elementary Dispersive X-ray (EDX) evaluation experiments were performed on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25^0C. XRD spectrum was recorded on the X'PERT PRO model X-ray diffractometer from Pan Analytical instruments operated at a voltage of 40 kV and also a current of 30 mA with Cu Ka radiation. The nanoparticles size and structure verifications were done by Transmission Electron Microscopy (TEM) making use of PHILIPS CM200. The ^{1}H & ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ solution on a Bruker 400 spectrometer as well as chemical shifts were reported relative to $SiMe_4$.The progress of reaction was monitored by TLC.

Results and Discussion

3.1. Characterization of ZnO nanocatalyst

OPTICAL ABSORPTION

UV visible absorption spectra have been examined by dispersing Nano catalyst in the high purity at room temperature Fig 2. The UV absorption for plant mediated synthesized ZnO observed in wavelength 377nm. which is good agreement with the previous work[22].

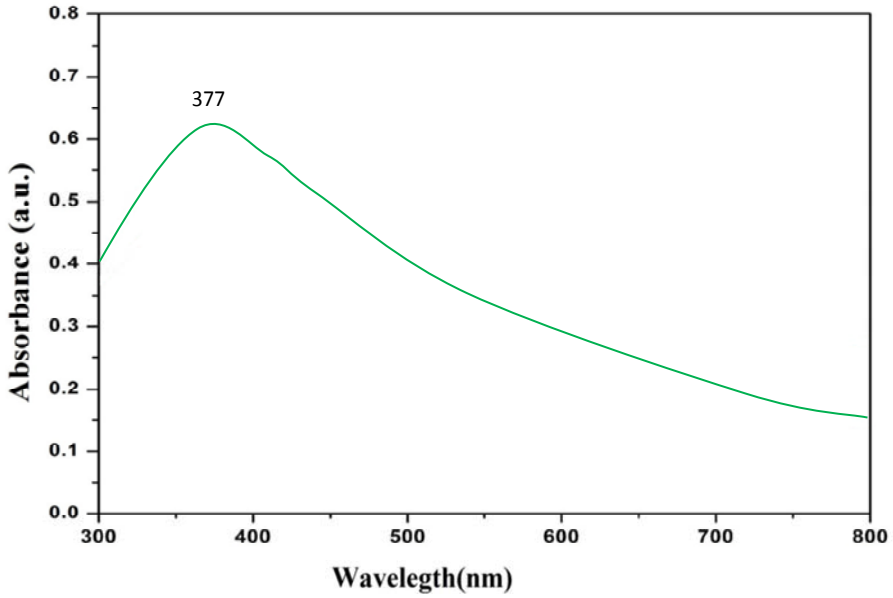


Figure 2 UV-vis absorption spectrum of ZnO nanoparticles.

XRD ANALYSIS

Fig.3 shows XRD diffraction pattern of ZnO nanoparticles. It is found that there exist strong diffraction peak with 2θ values of 31.73°, 36.23°, 47.48°, 56.58°, 62.83°and 67.88°. corresponding to the crystal planes of (100),(101), (102), (110), (103) and (112) respectively. All diffraction peaks of sample correspond to the characteristic hexagonal wurtzite structure of zinc oxide nanoparticles. Similar, X-ray diffraction pattern was reported by C. Chenn et.al. [23] and Y. Pung.et.al. [24]. Using the Scherer equation[25] the average crystalline size of ZnO NPs is found to be 20 nm. Diffraction pattern corresponding to impurities are found to be absent. This proves that pure ZnO nanoparticles were synthesized.

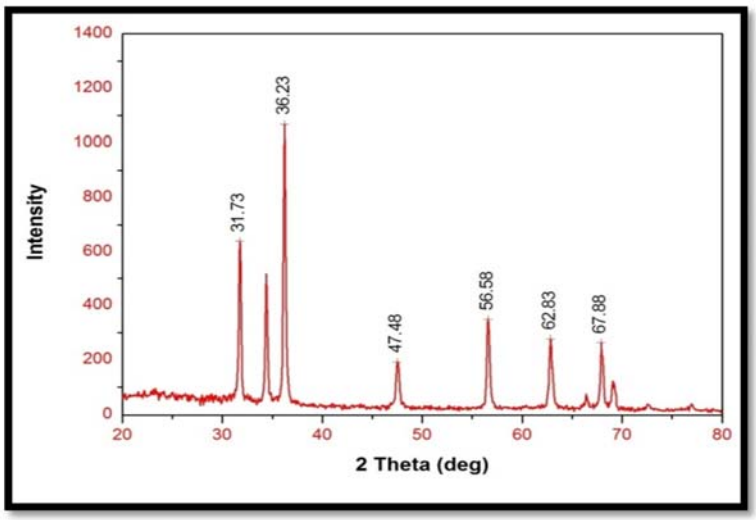


Figure 3 XRD pattern of bio derived ZnO nanoparticles.

SEM WITH EDX ANALYSIS

Thus the surface morphology and size of the zinc oxide nanoparticles were analyzed by Scanning Electron Microscope. SEM image had shown individual ZnO nanoparticles as well as number of aggregates. Fig.4a illustrates the particles are predominantly spherical in shape and aggregates into larger particles with no well-defined morphology The chemical purification of samples as well as their stoichiometry was tested by EDX studies. As shown Fig 4b zinc and oxygen are the only elementary components of the prepared nanoparticles.

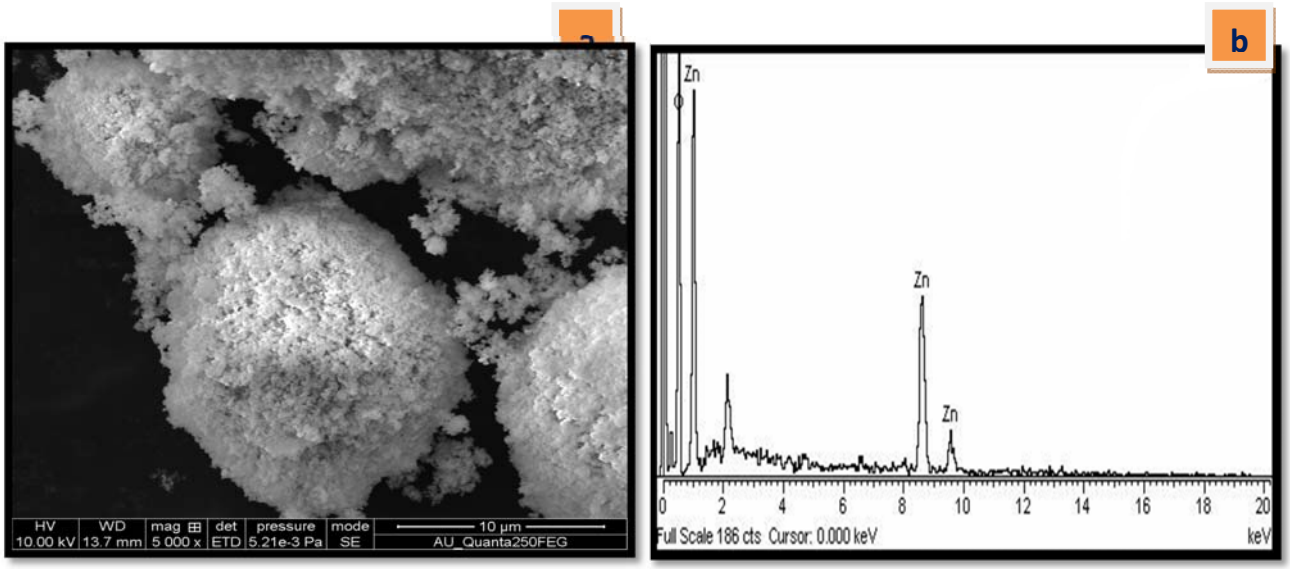


Figure 4 SEM image (a) and EDX (b) of bio derived ZnO nanoparticles**.**

In FT-IR spectrum of ZnO NPs (Figure 5) the band at 619 cm^{-1} is assigned to the stretching vibrations of (Zn–O) bond. The broad band with low intensity at 3422 cm^{-1} is related to vibration mode of (OH) group, indicating the presence of little amount of water adsorbed on the zinc oxide nanoparticles surfaces.

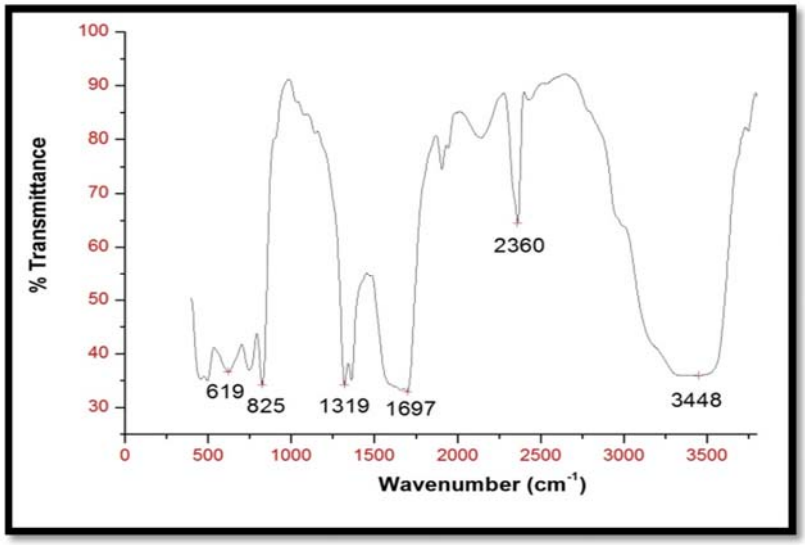
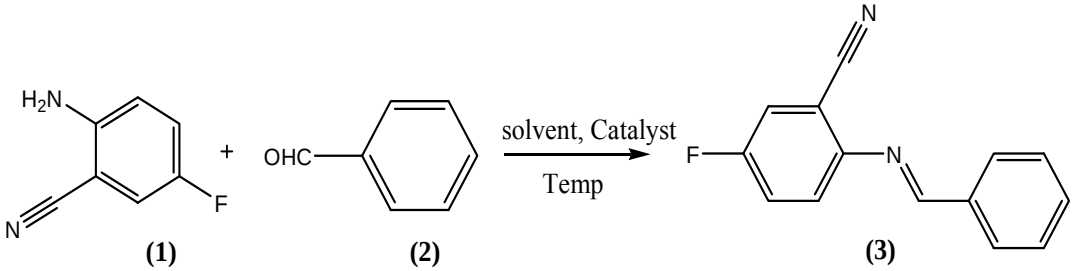


Figure 5 IR spectrum of bio derived ZnO nanoparticles.

Optimizing reaction condition, Schiff base derivatives of 2-amino-5-fluorobenzonitrile (1) (0.01mol), benzaldehyde (2) (0.01mol) and 5 mol% of catalyst were used as a standard model reaction for the synthesis of compound 3(Scheme 1).



Scheme 1 standard model reaction

Reaction optimization model with various experimental parameters such as solvents, catalyst and temperature as shown in Table 1

Table 1 Optimization of reaction conditions for synthesis of (E)-2-(benzylideneamino)-5-fluorobenzonitrile[a]

Entry	Catalyst	Solvent	Temp (^{0}C)	Time (h)	Yield(%)[b]
1	Bio-ZnO Nps	Ethanol	Reflux	3	85
2	Bio-ZnO Nps	Methanol	Reflux	3	80
3	Bio-ZnO Nps	Water	Reflux	8	Trace
4	Bio-ZnO Nps	Toluene	Reflux	4	32
5	Bio-ZnO Nps	Acetonitrile	Reflux	6	44
6	ZnO bulk	Ethanol	Reflux	5	52
7	ZnO Nps (commercial)	Ethanol	Reflux	3	78

a Reaction condition : Aromatic amine (1mmol)(1), benzaldehyde (1mmol)(2), 5 mol% of catalyst; b yields are related to isolated pure products

Initially, the reaction was catalysed by ZnO Nps in different solvents at reflux temperature. The reaction in water, toluene and acetonitrile gives the expected Schiff base derivatives only traces

with several side products and unreacted material(Table 1 Entry 3-5).To observe the catalytic effectiveness of bulk ZnO, Bio ZnO and commercial ZnO nanoparticles, the reaction was carried out in ethanol as a solvent at reflux temperature. The biologically derived ZnO nanoparticles shows better catalytic activity over bulk ZnO and commercially available ZnO nanoparticles (Table 1, Entry 5-6)

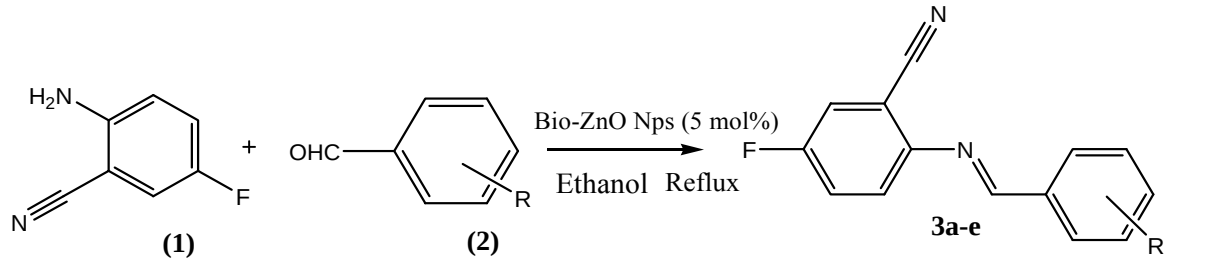
The effect of catalyst loading on the synthesis of model reaction was investigated by varying the catalyst amount from 0 to 10 mol% (Table 2). It was found that 5 mol% of the catalyst was sufficient to get optimum yields in less reaction time while less than 5 mol% of the catalyst increased the reaction time. Use of more than 5 mol% of the catalyst did not show any profound effect on the reaction rate as well as the yield this may be attributed to the coagulation of ZnO nanoparticles which decreased the effective surface area of the catalyst[26].

Table 2 effect of catalyst loading on the model reaction

Entry	Catalyst (mol%)	Time (h)	Yield (%)[a]
1	2.5	3	72
2	5	3	85
3	7.5	3	85
4	10	3	85

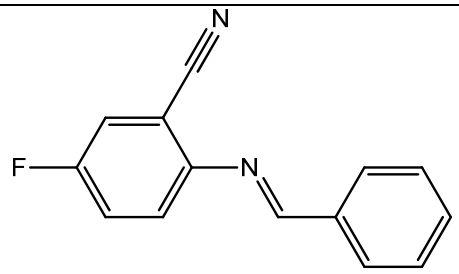
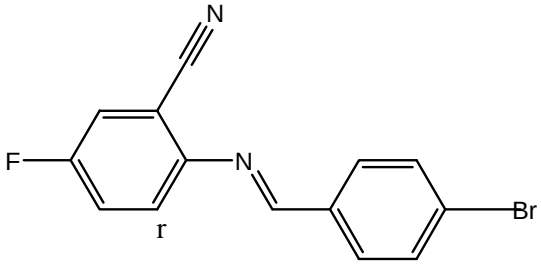
[a] Reaction condition : Aromatic amine (1mmol)(1), benzaldehyde (1mmol)(2), 5 mol% of catalyst; b yields are related to isolated pure products ; [b] yields are related to isolated pure products

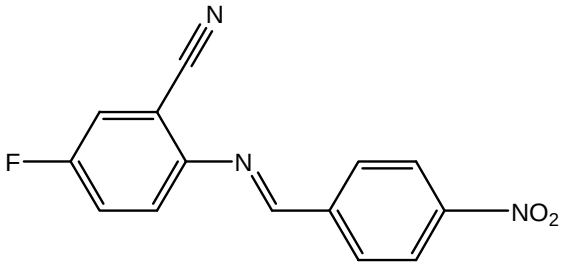
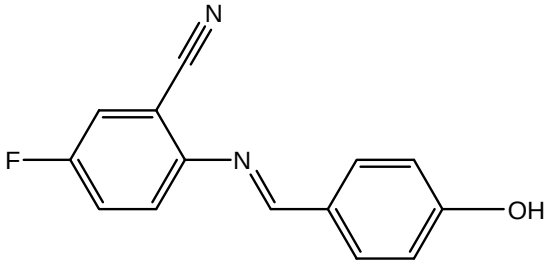
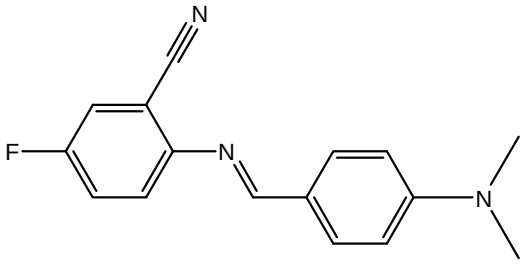
In particular , the developed protocol (scheme 2) was executed to all substrates listed in the Table 3



Scheme 2 Synthesis of (E)-2-(benzylideneamino)-5-fluorobenzonitrile **3a-e**

Table 3 Synthesis of (E)-2-(benzylideneamino)-5-fluorobenzonitrile derivatives[a]

Entry	Product	Yield (%)[b]	Mp(^{0}C)	References
3a		85	91(90)	27
3b		85	135	--

3c		83	148	--
3d		90	110	--
3e		89	129	--

[a] Reaction condition : Aromatic amine (1mmol)(1), substituted benzaldehyde (1mmol)(2), 5 mol% of catalyst; b yields are related to isolated pure products ; [b] yields are related to isolated pure products

Table 4 Spectroscopy data of synthesized Schiff base derivatives (**3a-e**)

	IR Frequency (cm^{-1})			**1H NMR Spectral data (ppm)**			
Entry	**CH=N**	**C-F**	**C-CN**	**CH=N**	**Aromatic Protons**	**OH**	**CH_3**
3a	1592	1185	2268	8.70	7.09-8.04	-	-
3b	1591	1197	2227	8.87	6.86-7.82	-	-
3c	1589	1199	2220	7.91	6.91-7.89	-	-
3d	1562	1172	2058	8.36	6.56-7.90	11.84	-
3e	1598	1247	2198	8.36	7.16-8.09	-	3.48

Table 5 Recycling potential of biologically derived ZnO nanocatalyst

No of cycle	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
Yield (%)	85	82	82	79	78	72	69	65
Time(h)	3	3	3	3	3	3	3	3

The reusability of the catalyst was checked out by repeating the model reaction making use of Bio-ZnO NPs 5 mol% nanoparticles under optimized reactions. The outcomes of these experiments revealed that the catalytic activity of biologically synthesized nano ZnO did not reduce dramatically after five catalytic cycles. We have actually checked the reusability of bio derived ZnO nanocatalyst in condensation reaction of benzaldehyde and 2-amino-5-fluorobenzonitrile. The bio-ZnO nanocatalyst was recouped by filtration and was cleaned with warm water/ethanol to eliminate any kind of absorbed products. The catalyst was reused without noticeable loss of their catalytic activity, up to 5 cycles and also effectiveness

continue to be nearly very same (First recycle 85%, Second recycle 82% and also Third recycle 82%, Fourth recycle 79% and Fifth recycle 78% Schiff base was obtained) (Table 5). The recovered catalyst reserved the most of its activity still after at least 5 times of reusing (Fig 6).

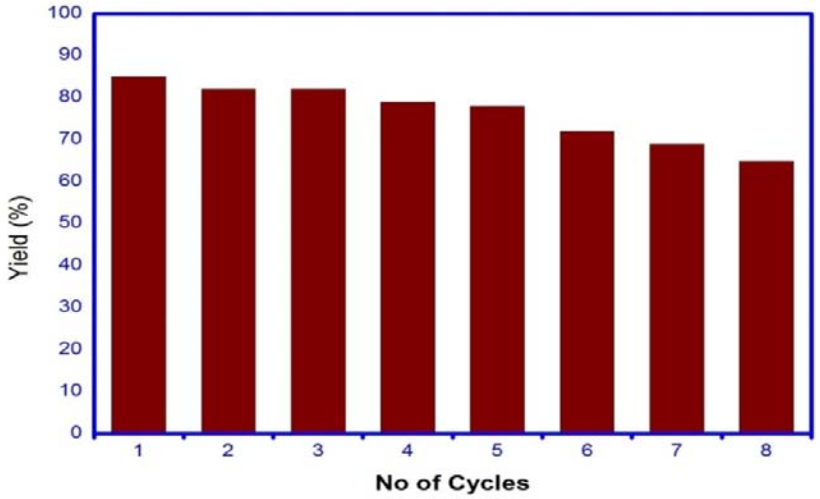
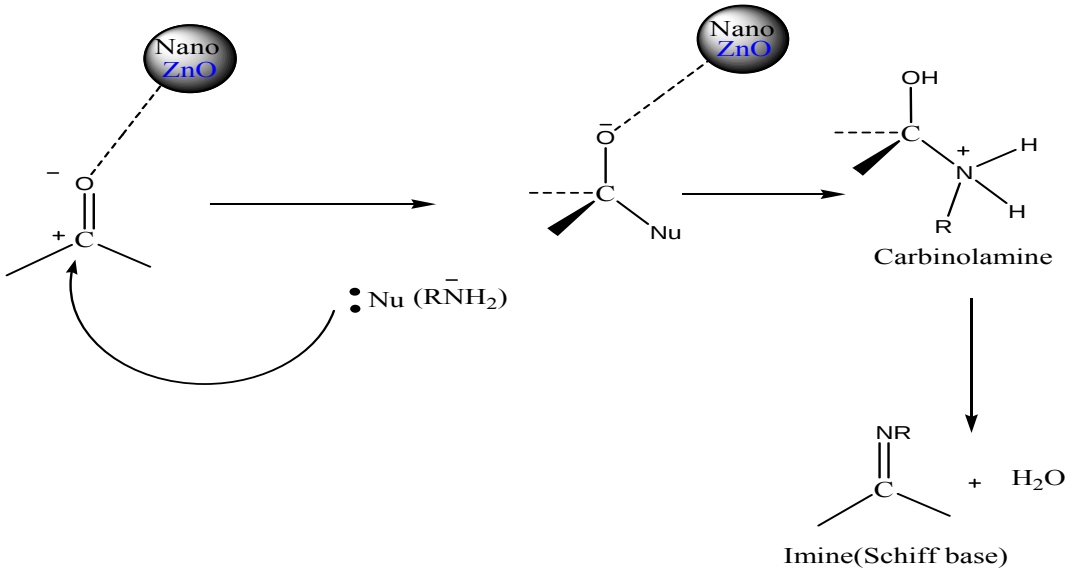


Figure 6 Studying reusability of biologically derived ZnO nanoparticles in the preparation of Schiff base derivatives

In order to identify the catalytic behavior of zinc oxide nanoparticles, the possible mechanism for the coupling of aldehydes, and amines in the existence of bio-ZnO NPs as an effective catalyst is displayed in Scheme 3. To the very best of our understanding, bio-ZnO NPs catalyzes the reaction by nucleophilic activation of the carbonyl groups of aldehyde; this makes them prone to nucleophilic attack. In the possible mechanism, it has actually been observed that biologically synthesized nano-ZnO triggers the aldehyde and react with the amine form of hemiaminal product carbinolamine. One water molecule was removed from the carbinolamine to form Schiff base and its derivatives (Scheme 3)



Scheme 3 Proposed Catalytic mechanism of the formation of Schiff base derivatives.

CONCLUSION

In summary, we have developed a new green, simple, and efficient methodology for the synthesize of Schiff base derivatives with high product yield and excellent selectivity, using biologically synthesized zinc oxide using berry extract of Solanum xanthocarpum as a cheap and effective catalyst. Biologically synthesized ZnO nanoparticles is a unique catalyst among all other reported catalysts considering conversion percentage, environmental safety, stability, reaction time, catalyst mol percentage,

and reusability. The mild reaction conditions, easy work-up, clean reaction profiles render this approach as an interesting alternative to the existing methods.

REFERENCE

1. E. Selvarajan, V. Mohanasrinivasan, Mater. Lett. 2013,112, 180–182.
2. J. Huang, T. Kunitake, J. Am. Chem. Soc., 2003, 125 (39), 11834–11835
3. C. Krishnaraj, E.G. Jagan, S. Rajasekar, P. Selvakumar, P.T. Kalaichelvan, N. Mohan, Colloids Surf. B: Biointerfaces 2010, 76, 50-56.
4. D. Gnanasangeetha, S. Thambavani D, Res. J. Material Sci. 15 2013, 1, 1-8.
5. P.S. Ravindra, K.S. Vineet, S.Y. Raghvendra, K.S. Prashant, K.S. Prashant, C.P. Avinas, Adv. Mat. Lett., 2011, 2, 313-317.
6. S. Nagarajan, K. A. Kuppusamy, J. Nanobiotech. 2013, 11, 39.
7. A.K. Jha, V. Kumar, K. Prasad. J. Bionanosci., 2011, 5, 162– 166.
8. R.P. Singh, V.K. Shukla, R.S. Yadav, P.K. Sharma, P.K. Singh, A.C. Pandey, Adv. Mat. Lett. 2011, 2, 313-317.
9. D. Gnanasangeetha , D. SaralaThambavani , J. Chem. Bio.Phy. Sci. Sec. B, Nov. 2013-Jan .2014, 4, 238-246.
10. C. Vidya, S. Hiremath, M.N. Chandraprabha, M.A. Lourdu Antonyraj, I.Venu Gopal, A. Jain, K. Bansal, Int. J. Current Eng. Tech. 2013, 1, 118-120
11. Neelapu Neelima et al / IJRAP 2011, 2 (3) 845 – 850
12. Ramla, M. M.; Omar, A. M.; Tokudo, H.; El-Diwoni, I. H. *Bioorg. Med. Chem.* **2007**, *15*, 6489-6496.
13. Mohamed, G. G.; Omar, M. M.; Hindy, A. M. *Turk. J. Chem.* **2006**, *30,* 361-382.
14. Canpolat, E.; Kaya, M. *Turk. J. Chem.* **2005**, *29*, 409-415
15. Croot, P. L.; Johansson, M. *Electroanalysis* **2000**, *12,* 565-576
16. Dos Santos, J. E.; Dockal, E. R.; Cavalheiro, E. T. G. *Carbohydr. Polym.* **2005**, *60*, 277-282.
17. Mobinikhaledi, A.; Steel, P. J. *Syn. Reac. Inorg. Met-org. Chem.* **2009**, *39*, 133-135
18. Mobinikhaledi, A.; Foroughifar, N.; Zendehdel, M.; Jabbarpour, M. *Syn. Reac. Inorg. Met-org. Chem.* **2008**, *38*, 390-393.
19. M. Sabbaghan, A. Anaraki Firooz, V. Jan Ahmadi, The effect of template on morphology, optical and photocatalytic properties of ZnO nanostructures, J. Mol. Liq. 175 (2012) 135–140.
20. Y. D. Jin, J. P. Yang, P. L. Heremans et al., "Single-layer organic light-emitting diode with 2.0% external quantum efficiency prepared by spin-coating," Chemical Physics Letters, vol. 320, no. 5-6, pp. 387–392, 2000.
21. C. Chena, B. Yu, P. Liu, J. F. Liu, L. Wang, *Journal of Ceramic Processing Research*
    12 (2011) 420-425.
22. Swee-Yong Pung, Wen-Pie Lee, Azizan Aziz, *International Journal of Inorganic Chemistry* 2012 (2012) 1-9
23. B. D. Culity, *Elements of X-ray diffraction 2nd ed*, Addison-Wesley, USA,
    1987
24. Bhattacharyya, P., Pradhan, K., Paul, S., Das, A.R., 2012. Tetrahedron Lett. 53, 4687–4691
25. Farhadi, S.; Babazadeh, Z.; Maleki,. Acta Chim. Slov. 2006, 53, 72.
26. Tayebee, R.; Ahmadi, S. J.; Rezaei Seresht, E.; Javadi, F.; Yasemi, M. A.; Hosseinpour, M.; Maleki, B. Ind. Eng. Chem. Res. 2012, 51, 14577.
27. C.gopi and N.Santhi, International Letters of Chemistry, Physics and Astronomy Online: 2014, 36, 50-66.