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CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 9, Issue, 3(I), pp. 25269-25273, March, 2018

ISSN: 0976-3031

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

EXPLORATION OF VARIOUS NANO ZnO CATALYSTS FOR CONGO RED DYE DEGRADATION

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DOI: http://dx.doi.org/10.24327/ijrsr.2018.0903.1829

ARTICLE INFO

Article History:

Received 15th December, 2017
Received in revised form 25th January, 2018
Accepted 23rd February, 2018
Published online 28th March, 2018

Key Words:

nano ZnO, photocatalysis, titanium dioxide, Congo red, solar radiation

ABSTRACT

Nanosized zinc oxide (nano ZnO) is synthesized using three synthesis procedure namely precipitation, combustion and pyrolytic method. In the precipitation method the raw materials used to prepare nano ZnO is different from other two methods of preparation. This gave three different nano ZnO catalysts of various particle sizes. The prepared catalysts were characterized using XRD, DRS-UV and SEM to elucidate their physico- chemical properties. The efficacies of these synthesised catalysts were tested for the abasement of Congo red dye which is a azo dye. The most common catalyst titanium dioxide and titanium dioxide loaded HY catalysts (1 wt % and 3 wt %) were also tested for the photocatalytic degradation of congo red dye. The pH influence for the dye degradation and recyclability were also studied and the results were discussed.

INTRODUCTION

Nanotechnology has considerably improved and revolutionized several technologies such as industrial, medicine, food safety, and many others. More recently, nano ZnO entered the scientific spot-light, for its semi conducting properties, wound healing and UV filtering properties, high catalytic and photochemical activity. Azo dyes are a well known class of coloured organic compounds which are most widely used for its industrial applications. Congo red dye belongs to a group of azo dyes derived from benzidine (Esther Leena Preethi *et al*., 2015). A photo-catalytic reaction is a promising and emerging process for the purification of water and air and in order to act as photocatalyst, the semiconductor needs to absorb the energy equal to or less than its band gap.

The heterogeneous photocatalysis by semiconductor particles is newly emerging process for removal of global environmental pollutants. Semiconductors (such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) can act as sensitizers for light-induced redox-processes due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band (M. R. Hoffmann*et al*., 1995). In the present study, the catalysts used are TiO_2, TiO_2 loaded HY and nano ZnO. Zinc oxide is an interesting semiconductor material due to its application on solar cells, gas sensors, ceramics, catalyst (Abhulimen I. U *et al*., 2004) and antibacterial cosmetics (Podporska-Carroll *et al*., 2017). In the past photocatalysis by semiconductive materials such as ZnO has become most significant owing to the materials photosensitivity, cost effective, non-toxic, high stability, and the possibility of using sunlight as the source of irradiation (Ahmed *et al*., 2011).

In this present work, the preparation of nano zinc oxide by precipitation, pyrolytic and combustion method were carried out it has been characterized and its activity tested for Congo red dye degradation in detail.

Experimental

Materials

Zinc sulphate heptahydrate (Merck), Zinc acetate dihydrate (Merck), Sodium hydroxide(Merck),, titanium dioxide(Merck), Congo red dye (Merck) was used without further purification.

METHODS

Precipitation Method

Nano ZnO was prepared by the incipient method. $ZnSO_4$.7H2O was used as the starting material and NaOH as the precipitant in the mole ratio 1:2. The resulting slurry was continuously stirred for 5 h, filtered, and washed with deionized water. The wet powder was dried in the oven at 120 °C for 2 h to 4 h and

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finally the ZnO was obtained (Esther Leena Preethi *et al.*, 2015).

$ZnSO_4.7H_2O + 2NaOH \longrightarrow ZnO + 2NaSO_4 + H_2O$

Combustion Method

Zinc acetate dihydrate and sodium hydroxide were taken in 1:1 ($Zn(CH_3COO)_2.2H_2O$: NaOH) concentration. The resulting solution, then kept in an electrical oven at 80°C for 3 hours. The solution containing the precipitate was centrifuged at 2500 rpm for 30 minutes. The precipitate which contains nano ZnO was retrieved by decantation. It was dried and powdered (Dalia Ahmed Mohammed Osman, Mustafa Abbas Mustafa 2015).

Pyrolytic method

Zn $(CH_3COO)_2.2H_2O$ (0.01M) and NaOH (0.02M) were mixed at room temperature. The mixture was calcined at 300°C for 3 hours. The nano ZnO thus obtained was washed with deionised water several times and dried (Sabura Begum*et al.*, 2011).

$(Zn (CH_3COO)_2.2H_2O) + 2NaOH \longrightarrow ZnO + 2NaCH_3COO + H$

Experimental procedure for photodegradation of Congo red dye

100 mL of 1 x 10^{-4} M solution of Congo red was taken with 0.3 g of the prepared catalyst. The degradation reaction was carried out under solar light with the dye solution containing the catalyst being continuously stirred for duration of 180 min using a magnetic stirrer. 3 mL of the sample was withdrawn for analysis. The % degradation was calculated using the below formulae

$$\% \text{ degradation } = \frac{Co - C}{Co} X100$$

Where
Co = initial concentration of dye
C = concentration of dye after photodegradation

Characterization of ZnO nanoparticles

The powder X-ray diffraction (XRD) patterns of nano ZnO were collected on a Philips X'Pert model no. PW 3040/60, using Cu Kα radiation (λ = 1.5060 Å). . The nano materials were examined by UV-Vis Diffuse reflectance spectroscopy. The DRS UV of nano materials was recorded in the range of 200 to 800 nm using JASCO V-550 instrument. The morphology of the catalyst was studied with scanning electron microscopy (SEM) using a Hitachi S-3400N electron microscope.

RESULT AND DISCUSSION

X-ray diffraction

The obtained XRD of the nano ZnO are shown in (Fig. 1(a), (b) and (c)). The precipitation method of nano ZnO (Nano ZnO(p)), showed peaks at 30.32, 36.40, 39.92, 62.36 and 69.48 of miller indices (100), (002), (101), (102), (110), (103) and (201). The combustion method of ZnO (Nano ZnO(c)) peaks at 31.44, 34.24, 36.30, 47.54, 56.70, 62.89 and 67.94 and the pyrolytic method of nano ZnO (Nano ZnO(py)) peaks at 31.80 34.43, 36.30, 47.54, 56.53, 63.68, 68.32 and 69.26 of the same miller indices respectively. The three samples of nano ZnO exhibited a diffraction pattern of FCC crystal structure.

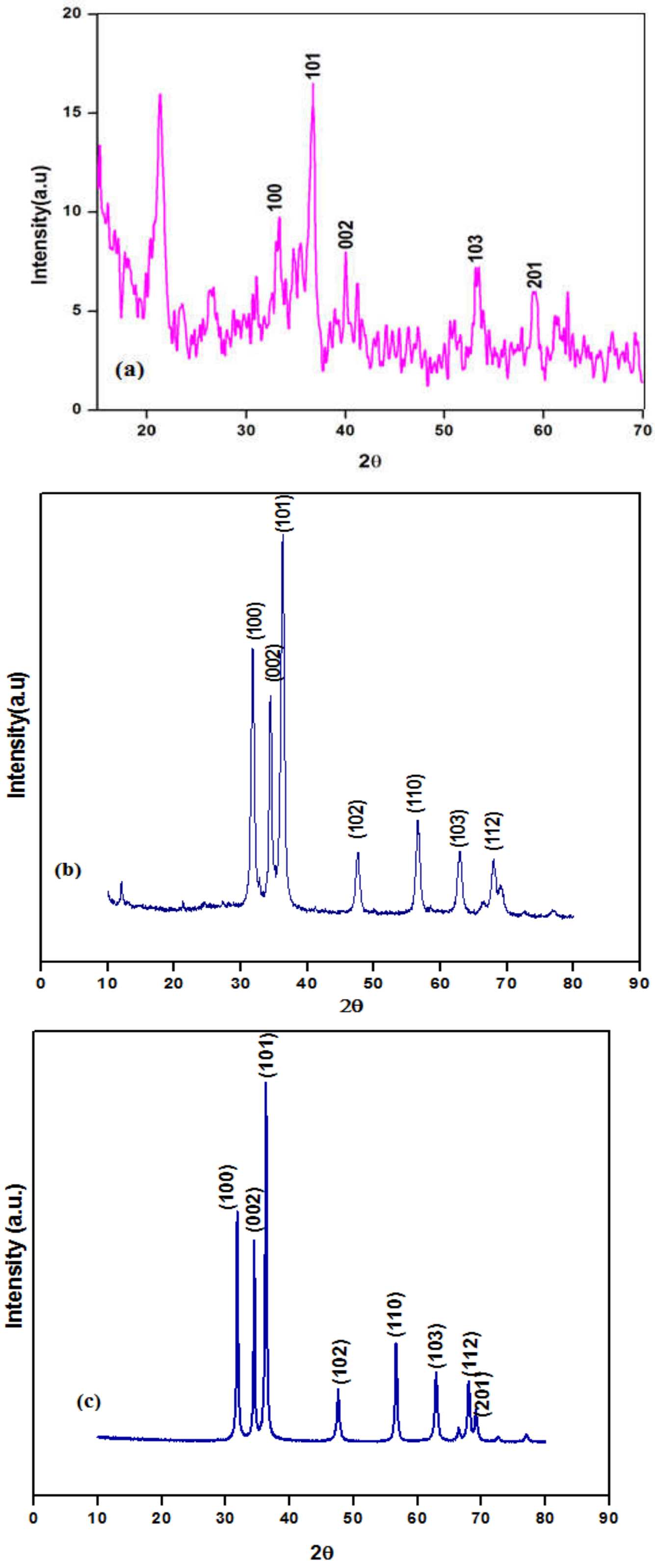


Fig 1 XRD images of nano ZnO (a) Precipitation Method (b) Combustion Method (c) Pyrolytic method

The average crystallite sizes of the nano ZnO crystallites have been estimated by Scherer's formula:

D = Kλ/βcosθ

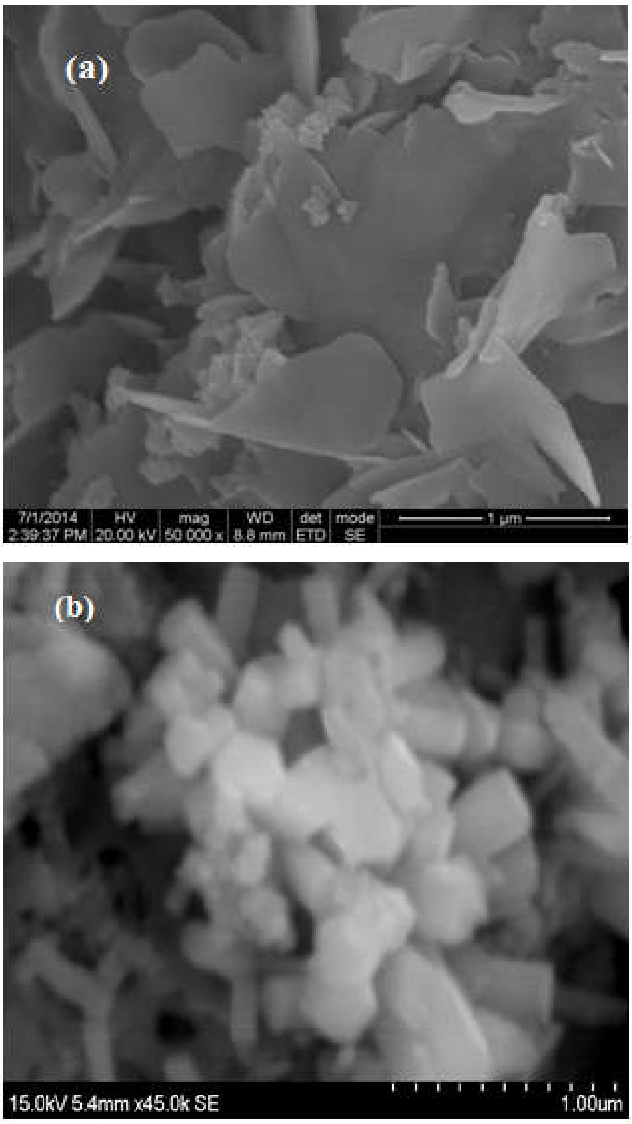
Where K =0.9 is the shape factor, λ is the X-ray wavelength of Cu Kα radiation (1.5402 nm), θ is the Bragg angle, and β is the experimental full-width at half-maximum (FWHM) of the respective diffraction peak. The average particles diameters of the ZnO nanoparticles were calculated to be 3.85nm, 3.56nm and 3.06nm for samples Nano ZnO(p), Nano ZnO(c) and Nano ZnO(py) respectively it is given in Table 1.

Table 1 Analysis of XRD result in the assignments of a range of reflections of Nano ZnO

Samples	d values (nm)	FWHM	Crystallite size (nm)
ZnO(p)	1.2836	0.45	3.852
ZnO(c)	1.301	0.48	3.568
ZnO(py)	1.300	0.56	3.060

Scanning Electron Microscope

The surface morphology of the nano ZnO was shown in (Fig.2) the size of the synthesized ZnO was found to be in nano range. The SEM images of nano ZnO samples showed that the agglomerations of particles in to flower shape for the nano ZnO synthesised using combustion method. The pyrolytic method prepared nano ZnO showed very less particle size as seen from the SEM image, which reconfirms the result obtained from the XRD, that among the three different synthesis methods adopted to prepare nano ZnO, the pyrolytic method resulted comparatively small sized nano ZnO.



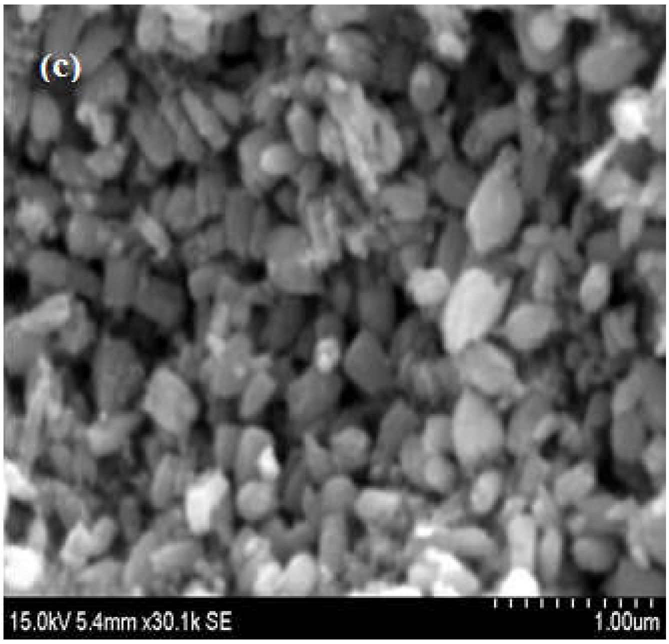


Fig 2 SEM images of nano ZnO (a) Precipitation Method (b) Combustion Method (c) Pyrolytic method

DRS- UV

The diffuse reflectance spectroscopy in UV-Vis range of 200-800 nm in the exaction absorption is at about 350 - 410nm (Fig. 3). Therefore it could easily harness solar radiation to produce free radicals for photocatalysis reaction. The prepared nano ZnO catalysts could be used as ideal catalysts for photodegradation

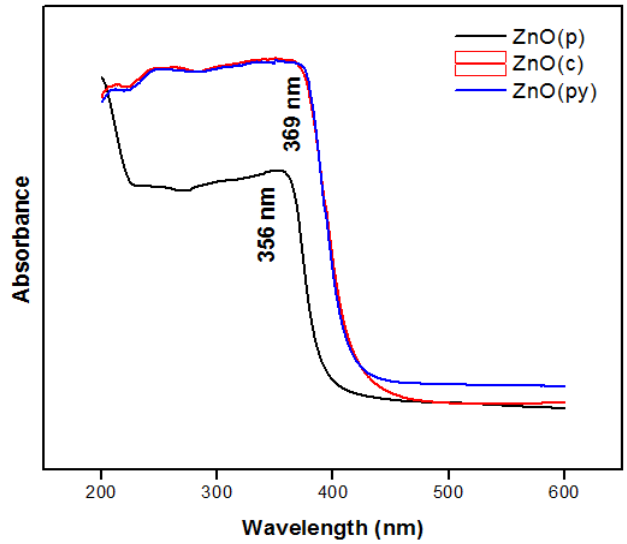


Fig 3 DRS-UV of nano ZnO (a) Precipitation Method (b) Combustion Method (c) Pyrolytic method

Photocatalytic activity of various catalysts

The degradation of Congo red dye was studied using different catalysts and the results are shown in (Fig. 4). It has been observed that the titania loaded HY catalysts showed very less activity. This observation evidently confirmed that the active element of the photocatalysis is the semiconductor metal oxide and its quantity is less in TiO_2 loaded HY catalyst.

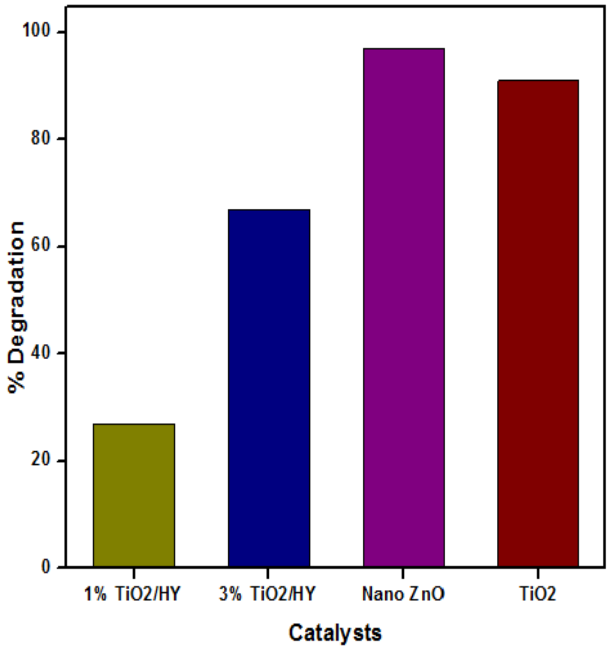


Fig 4 Photocatalytic activity of various catalysts in Congo red dye [Dye] = 1 x 10^{-4}M, Time = 3h, under solar light

Among the catalysts tested nano ZnO prepared by using precipitation technique displayed high activity. The degradation process is studied over nano ZnO prepared using various synthesis technique and the results are showed in (Fig.5). Although all nano ZnO showed very high activity in the degradation of Congo red dye, nano ZnO prepared using pyrolytic method exhibited 100 % .Hence pyrolytic method of preparation of nano ZnO is most effective which agrees well with its small crystallite size as shown in XRD and SEM.

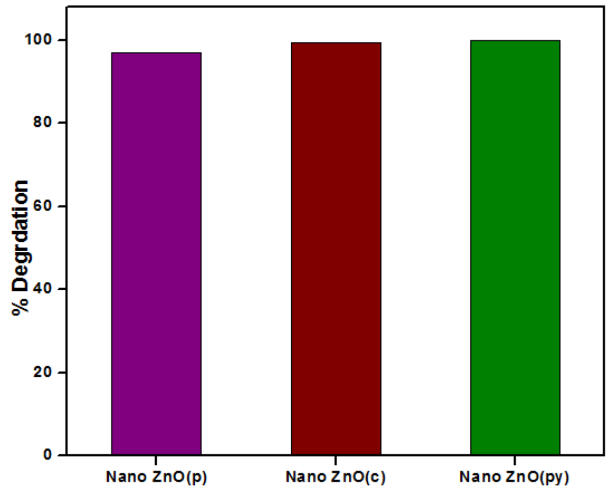
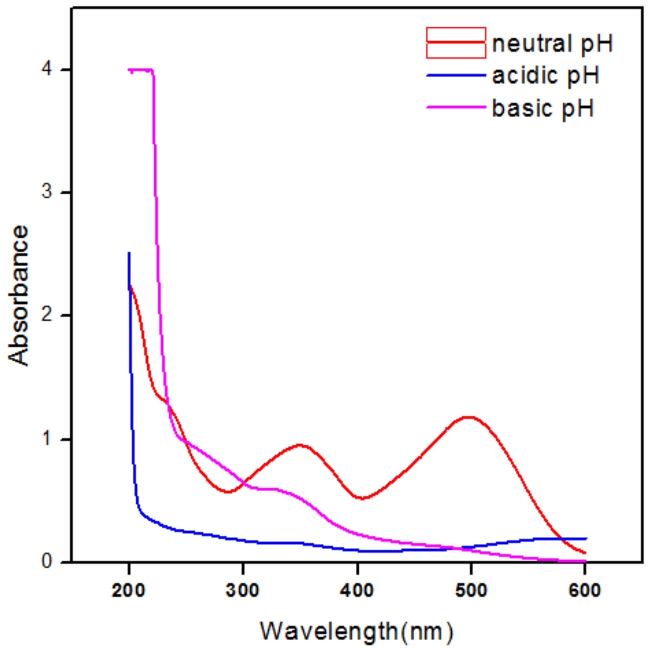


Fig 5 Photocatalytic activity of various nano ZnO catalysts in Congo red dye [Dye] = 1 x 10^{-4}M, Time = 3h, under solar light

Effect of pH on degradation of Congo red dye with nano ZnO photocatalyst

The pH of the dye solution in the present study is adjusting concentration of acid, neutral and base. The effect of pH on the efficiency of photo catalytic degradation of Congo red dye was studied in the pH range in acidic value of 3, neutral value 7 and alkaline solution of pH values in 12 and the results are shown in Fig.6. It is evident that neutral pH condition is ideal for degradation of Congo red dye.



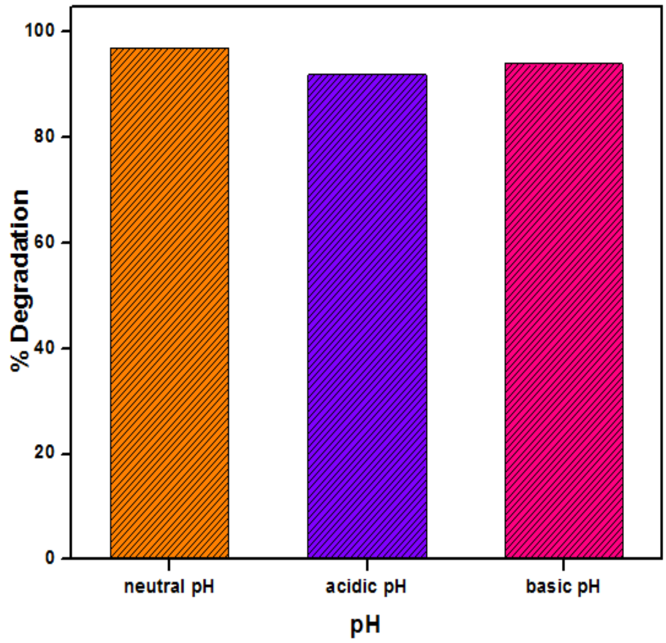


Fig 6 Effect of pH on Congo red dye [Dye] = 1 x 10^{-4}M, Time = 3h, under solar light.

Recyclability

The degradation of Congo red dye over nano ZnO was tested for its activity in recyclability and the results are shown in (Fig.7). The activity was almost retained when it is reused for the first time. After the first run, the catalyst is filtered, dried and calcined at for hand reused. But when it is reused the second time its activity was observed to be hampered slightly.

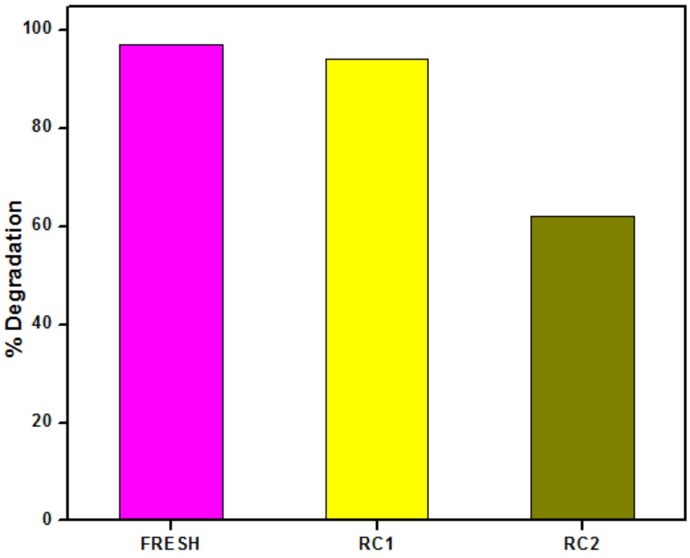


Fig 7 Effect of catalyst recycling on the degradation of Congo red dye [Dye] = 1 x 10^{-4}M, Time = 3h, under solar light.

CONCLUSION

In this study, a simple and convenient method is developed for the preparation of ZnO nanoparticles. Nano zinc oxides could be successfully prepared by precipitation, combustion and pyrolytic methods and their yield is high. These synthesized ZnO nanoparticles were used as catalysts in the process of degradation of hazardous dyes in a cost effective behavior. The synthesized catalysts could interact with sun light as its band gap is found to be 3.2 eV as confirmed by DRS UV. The XRD and SEM technique showed that the synthesized material is in nano size and are crystalline. Among the three different synthesis methods, pyrolytic method is proved to be most active, its comparatively less particle size could be the contributing reason for its high activity

Acknowledgements

The authors acknowledge DST-SERB New Delhi for supporting the above work.

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How to cite this article:

Esther Leena Preethi M., Umasankari A and Rekha C.H.2018, Exploration of Various Nano ZnO Catalysts for Congo Red dye Degradation. *Int J Recent Sci Res.* 9(3), pp. 25269-25273. DOI: http://dx.doi.org/10.24327/ijrsr.2018.0903.1829

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