Photo degradation of Methyl Orange & Rhodamine B Dyes Using Green Synthesized ZrO_2 Nano catalyst

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Abstract: In this review, we examine the photo catalytic degradation of organic dye pollutants in the presence of nanocatalyst. Green synthesis has now become a vast developing area in research .Degradation of Methyl Orange (MO) and Rhodamine B (RhB) dyes were studied under UV-Vis irradiation using a simple and eco-friendly green synthesized Zirconium oxide (ZrO_2) nanocatalyst under direct exposure of sunlight. ZrO_2 nanocatalyst was prepared by green method using *Gossypium herbaceum* (cotton plant) flower extract which act as reducing agent. The synthesized nanocatalyst was characterized by UV-vis, FT-IR, X-ray diffraction and SEM. The comparison study of photo catalytic degradation of dyes were carried out using UV-Visible radiation and the photo catalytic activity were found to be 88.89%, 85.9% for Methyl Orange (MO) and Rhodamine B dyes respectively after 30 minutes duration. The report emphasizes that the ZrO_2 nanocatalyst are observed to be an excellent on reduction of hazardous dyes, which is confirmed by a decrease in absorbance maximum values.

Keywords: *Green synthesis, Gossypium herbaceum, Zirconium Oxide (ZrO_2) nano particle, Photo catalytic degradation, Methylene Orange (MO) and Rhodamine B (RhB).*

1. Introduction

The rapid growth of the textile industry has led to the pile up of various organic pollutants[1] .The expanding needs for water and declining supply has made the treatment and recycle of industrial effluents has an attractive option [2]. The waste dyes and their byproducts contaminate the water sources and produce toxic nature; some of this color is usually present in food, cosmetics, painting etc., [3]. Cationic and anionic dyes are the major chemicals with the maximum variety of colors have been used widely in textile, dyeing and paper painting. These dyes cannot be easily degraded [4]. The accumulation of these dyes in the water bodies causes eutrophication, reduces the reoxygenation capacity and makes severe damage to the aquatic organisms by hindering the infiltration of sunlight [5]. Several combinations of treatment methods have been developed so far for efficiently process textile wastewater decolorization being among the main targets to achieve. They are environmental friendly techniques since they produce no solid wastes. Methyl Orange and Rhodamine B dyes are water soluble, distinctly used in textile industries. The "Green-chemistry" concept is the inspiring enthusiasm to exploit the novel, high-efficient and eco-friendly photo catalysts for waste water cleaning [6]. Photo degradation offers a promising method for the degradation of organic pollutants in water. Among the various metal oxide nanoparticles, ZrO_2

Nanocatalyst is become the most important nanoparticles in different industries because of their specific properties such as high thermal and chemical stability, low thermal conductivity [7] which is used as refractory material, cutting tools thermal barrier coating and catalyst support, sensors, fuel cells, advanced ceramics, transparent and optical devices, metallic glass etc., [8]. Green synthesis have now been applied to design of a wide range of chemical products and process with the aims of minimizing chemical hazards to health and the environment reducing waste and prevents pollution . Here, a ZrO_2 nanoparticle was prepared in green synthesis method by using *Gossypium herbaceum* (cotton plant) extract. The ZrO_2 nano catalyst promising that its size dependant catalytic potential in the reduction of hazardous dyes in various environment-related applications [9].The degradation of Methyl Orange and Rhodamine B with ZrO_2 nanocatalyst was studied using UV-Vis radiation.

2. MATERIALS AND METHODS

2.1 Materials

Gossypium herbaceum (cotton plant) was collected from Aundipatti nearby Theni district. Zirconyl chloride octahydrate [$ZrOCl_2.8H_2O$] was used. All the glass wares were washed with de-ionized water.

2.1 Preparation of *Gossypium herbaceum* (Cotton plant) extract

Gossypium herbaceum (cotton plant) was washed thoroughly with distilled water in order to remove the dust particle.About10 grams of *Gossypium herbaceum* (cotton plant) weighed and cut into small pieces and refluxed with 200 ml of de-ionized water for 40 minutes and filtered using whatman no.1 filter paper filtrate used as reducing agent.

2.3 Green synthesis of ZrO_2 Nanoparticles

For the synthesis of ZrO_2 nanoparticle, 200 ml of the *Gossypium herbaceum* flower extract was added to the 100ml of Zirconyl chloride octahydrate solution. The solution was stirred for 30 minutes. Nanoparticles formed by the color change of the solution from yellow to honey yellow.

3. RESUSLTS AND DISCUSSION

3.1 UV-Visible spectrum

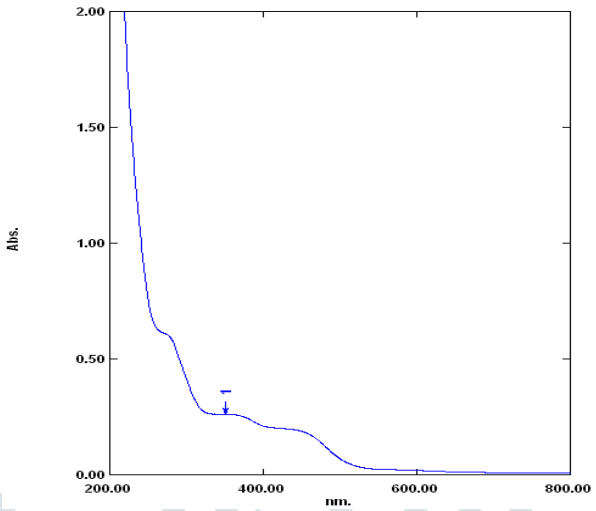

Fig1. UV-Visible spectrum of ZrO_2

In these spectra λ_{max} for ZrO_2 was observed as 350 nm.This indicates the absorption shift towards the shorter wavelength, because of the particle size reduction. From these spectra, it is evident that resultant nanoparticle was embedded in silica matrix and exhibited the significant blue shift.

3.2 FT-IR Spectrum of ZrO_2

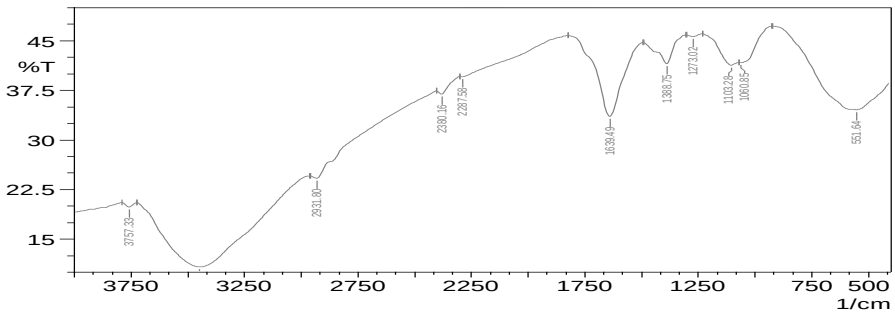

Fig.2 FT-IR Spectrum of ZrO_2

The FT-IR spectra of metal sample show specific stretching vibrations for the different structural forms of metal. The stretching frequency of ZrO_2 is 551.64cm^{-1} was absorbed, IR absorption is due to the vibrations.

3.3 X-Ray Diffraction Pattern

The average particle size is determined using **Debye –Scherer's equation** applied to major, peaks corresponding to maximum intensity in the XRD pattern of the samples. The size of the synthesized ZrO_2 Nanoparticles was calculated from powder XRD pattern using Scherer's formula.

$$D = K\lambda/\beta\cos\theta$$

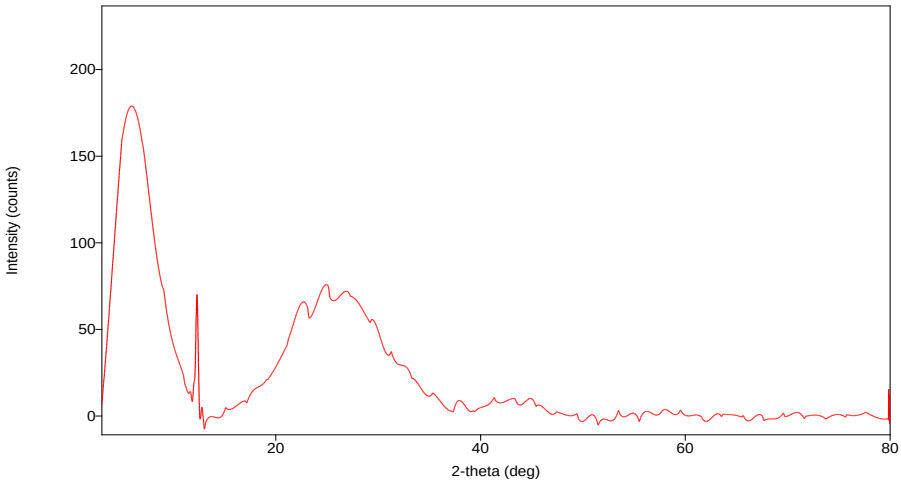

Fig.3 XRD Spectrum of ZrO_2 nanopartical

Fig.3 Shows the XRD pattern of ZrO_2. The observed "2θ" values come in good agreement with standard "2θ" values .This confirms that powder prepared was ZrO_2 nanoparticles thus estimated was found to be 7.64 nm.

3.4 Scanning Electron Microscopy (SEM)

The SEM is recorded by JEOL Model 6390 computer – controlled microscope. The image obtained by SEM of the samples for ZrO_2 (fig.4) shows flake like morphology. The ZrO_2 Nanoparticles have been distributed well within the range of ~100 nm which is the favorable for SEM other purpose. From this, the synthesized ZrO_2 sample having particle size in the nano scale.

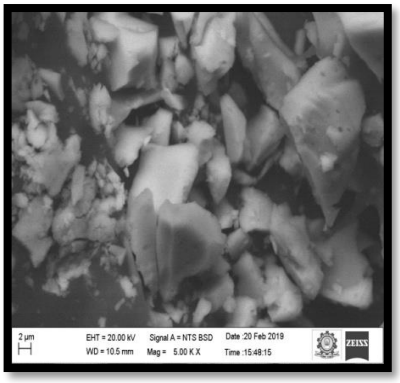

Fig.4 SEM image of ZrO_2 Nanoparticle

3.5 Photo catalytic degradation studies

Effect of variation of initial concentration of Methyl Orange and Rhodamine B dyes

The mixture of dye solution and the nanoparticle were exposed to sunlight and its effect on rate bleaching was studied. The extent of degradation of the dyes in the presence of nanocatalyst were studied at definite intervals of time [30 minutes] using UV-Visible spectrum .The variation in absorbance are represented in fig.5,6. If more concentration of dyes are taken, it imparts a darker color to the solution and it may act as filter to the incident light reaching the semiconductor surface as a consequence, the rate of photo catalytic bleaching of methyl orange and rhodamine B dyes decrease. The extent of removal of dyes has been calculated using the following relationships.

$$\text{Percentage removed} = 100(C_0 - C)/C_0$$

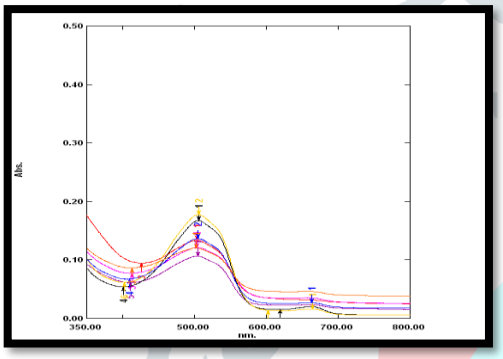

Fig5.UV- visible spectrum of Methyl Orange with ZrO_2

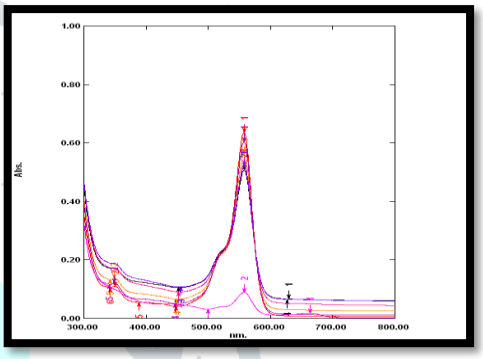

Fig6.UV- visible spectrum of Rhodamine B with ZrO_2.

ZrO_2 nanoparticles offered 88.89% for Methyl Orange and 85.9% for Rhodamine B dyes shows greater efficiency of reaction time. The observed photo catalytic degradation activity is higher.

3.6 Photo degradation studies:

The studies of Photo degradation of dyes in the presence of nanocatalyst were studied using ZrO_2 nanocatalyst. The percentage removal of Methyl Orange, Rhodamine B dyes on 30 minutes time interval to 150 minutes were given in the table no.1

S.no	Time duration in minutes/hour	Percentage% removal	
		Methyl orange	Rhodamine B
1	30	22%	19.5%
2	60	33.6%	29.3%
3	90	56%	49%
4	120	68.3%	65%
5	**150**	**88.89%**	**85.9%**

Table no.1 represented the decolorization efficiency of methyl orange and rhodamine b dyes

It reported that the adsorption between the dyes and the ZrO_2 nano catalyst under UV-irradiation shows both methyl orange and rhodamine b dyes has better enhance of photo catalytic efficiency.

4. CONCLUSION

The green synthesis method has been used for the synthesis of ZrO_2 nanocatalyst using *Gossypium herbaceum* (cotton plant) extract. The sample obtained by the green synthesis was characterized by UV-Visible ,FT-IR ,XRD and SEM instrumental methods. The UV-Visible spectra gives the peak at 360 nm ,it shows the presence of oxide peak .The FT-IR analysis of the spectra shows broad band between 551.64 cm^{-1}, characteristic of ZrO_2 band. The image obtained by SEM of samples ZrO_2 shows flake like morphology. From the XRD results the size of ZrO_2 nanocatalyst were calculated to be 7.68 nm .The ZrO_2 nanoparticles have been distributed well within the range of $\approx$ 100 nm which is the favorable property to exhibit better photo catalytic activity. The photo catalytic degradation of the dyes was carried out with UV-Visible radiation .So we conclude that photo catalytic degradation of the dyes was carried out with UV-Visible radiation and the photo degradation were found to be 88.89% for Methyl Orange and 85.9% for Rhodamine B with ZrO_2 nanocatalyst in 30 minutes duration. The green synthesized nano catalysts have good photo catalytic properties for the degradation of organic pollutants like Methyl Orange and Rhodamine B dyes.

REFERENCES:

1. Bayoumi, R.A1., Musa,S.M.2, Bahobil,A.S.3, Louboudy,S.S.4 and El-Sakawey,T.A, *Biocoloration and Biodegradation of azo dyes by some bacterial isolates*, J. Appl. Environ. Biol. Sci., 1(1) 1- 25 , page 1-3(2010).

2. Y. M. Slokar and A. M. L. Marechal, Dye Pigmen. 37, 335 doi:10.1016/S0143-7208(97)00075-2 (2013).

3. A. Baban, A. Yediler, N.K. Ciliz, Integrated water management and CP implementation for wool and textile blend processes, Clean 38 (2010) 84–90.

4. T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent:a critical review on current treatment technologies with a proposed alternative, BioRes. Technol. 77 (2011) 247–255.

5. Li. Huang, D. Gu, L. Yang, L. Xia, R. Zhang, and H. Hou, J. Environ. Sci. 20, 183 (2008)

6. Malvina arrarte –garu color pollution by "encyclopedia of color science and technology"

7. Jannatul Ferdous Rumky1, Zainal Abedin2, Hafizur Rahman2, Ali Hossain2 *Environmental Treatment of Dyes: Methyl Orange Decolorization Using Hog Plum Peel and Mix-Bacterial Strains* (2013)

8. J. Ma, W. Ma, W. Song, C. Chen, Y. Tang, J. Zhao, Y. Huang, Y. Xu, and L. Xang, Environ. Sci. Technol. 40, 618 doi:10.1021/es051657t (2006).

9. Hongjun Donga,b, Gang Chena,∗, Jingxue Suna, Chunmei Li a, Yaoguang Yua, Dahong *A novel high-efficiency visible-light sensitive Ag2CO3 photocatalyst with universal photodegradation performances: Simple synthesis, reaction mechanism and first-principles study*(2013).

10. R C Meena and Ram Babu pachawarya *"Photo catalytic degradation of Model textiles Azo dyes in textile waste water using methylene blue immobilized resin Dowex-11" Journal of scientific and industrial Research* vol.68,P.No.730-73, (2010)

11. Chandra, N.; Singh, D.K.; Sharma, M.; Upadhyay,R.K.; Amritphale, S.S. and Sanghi S.K. *Synthesis and characterization of nano-sizedzirconia powder synthesized by singl emulsion-assisted direct precipitation*, J. Colloid Interface Sci., 342: 327-332. (2010).

12. Huang, L.; Cao, Z.; Meyer, H.M.; Liaw, P.K.; Garlea,E.; Dunlap; J.R.; Zhang, T. and W. Responses of *Bone-Form Cells on Pre-Immersed Zr-Base Bulk Metallic Glasses: Effect of Composition and Roughness. Acta Biomater*, 7: 395-405(2011).

13. V.Vincenzo Balzani, Nanoscience and Nanotechnology: *A personal view of a chemist, small*, Vol.3,P.278-285(2007).

14. Mohammed Taher Eassa, Republic of Iraq Ministry of Higher Education and Scientific Research University of Kufa – Faculty of Science Chemistry Department, *Photocatalytic Degradation of Light Green Dye Using TiO2 and Nano TiO2 as Catalysts*(2012).

15. Azarmidokht Hosseinnia, Mansoor Keyanpour-Red and Mohammad pazouki *"photo catalytic degradation of organic dyes with different chromospheres by synthesized Nanosize TiO2 particles" word applied science journal* 8(11): 1327-1332(2010).

16. M.Ghane, B. Sadeghi, A.R. Paknejhad *" synthesis and charterization of a Bi-oxide Nanoparticles ZNo/CuO by Thermal Decomposition of Oxalate precursor method"*(2010).

17. Batista, Carlos A. Silvera; Larson, Ronald G.; Kotov, Nicholas A. *"Nonadditivity of nanoparticle interactions"*. *Science*. 350 (6257): 1242477(2015).

18. J. Fowsiya , G. Madhumitha , Naif Abdullah Al-Dhabi , Mariadhas Valan Arasu "Photocatalytic degradation of Congo red using Carissa edulis extract capped zinc oxide nanoparticles

19. Bhagavanth Reddy Ganapuram1, Madhusudhan Alle1, Ramakrishna Dadigala1,Ayodhya,Dasari1Venkatesham Maragoni1 Veerabhadram Guttena "Catalytic reduction of methylene blue and Congo red dyes using green synthesized gold nanoparticles capped by salmalia malabarica gum".

20. Bhakya S1, Muthukrishnan S2*, Sukumaran M1, Muthukumar M2, Senthil Kumar T3 and Rao MV2 **"**Catalytic Degradation of Organic Dyes using Synthesized Silver Nanoparticles: A Green Approach".

21. M. Vanaja, K. Paulkumar, M. Baburaja, S. Rajeshkumar, G. Gnanajobitha,C. Malarkodi, M. Sivakavinesan, and G. Annadurai "Degradation of Methylene Blue Using Biologically Synthesized Silver Nanoparticles".

22. Kumari Jyoti, Ajeet Singh "Green synthesis of nanostructured silver particles and their catalytic application in dye degradation".

23. Vani Mamillapalli1, Amukta Malyada Atmakuri1, Padmalatha Khantamneni Department of Pharmacognosy and Phytochemistry, *Nanoparticles for Herbal Extracts,Asian Journal of Pharmaceutics* (Suppl) • 10 (2) | S54 Apr-J

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