Ag-Cuo Nanorods As Photocatalyst For Degradation of Organicdye Congo Red

Sravani.k*, Jhansi.S, Jagadeesh babu.M, Venkataramana.CH, Muralikrishna.R

Abstarct:

A novel and efficient synthesis of Crystalline Ag-CuO nanorods were prepared by hydrothermal technique using organic solvents. Chemical route used for the preparation of Ag-CuO nanorods is simple , time saving and cost effective. The phase, morphology of the resulting material were deduced from characterization details using SEM, XRD,EDX. The resulting product is employed as photocatalyst and is monitored in degradation of congo red dye. The % of degradation was calculated from the c/co values and is found to be 93% in the present case. Rate constant value is also calculated from ln c/co values and is found to be 3.7x104. From the results it can be deduced that employing Ag-CuO nanostructures improves the rate photodegradation of congo red dye when compared with pure CuO nanostructures.

Keywords: Ag-cuo nanorods, congo red dye, % of degradation.

Introduction:

Now-a-days many industries uses dyes and pigments to color their products. As a result they often discharge a large amounts of colored effluents in various activities [1] Color is the major contaminant to be recognized in water and it should be removed from water before it is discharged into water bodies [2]. Various techniques were available for removing dyes from effluents , these includes electrochemical treatment [3,4], sonochemical treatment [5], photo catalytic oxidation [6,7] adsorption [8,9], etc. Congo red (CR) (sodium 3,3 (1E,1E)-biphenyl-4,4diylbis(diazene-2,1-diyl)bis(4-aminonaphthalene-1-sulfonate)) is the most frequently used secondary diazo dye. Benzidine is quite toxic metabolite of Congo red dye, causes cancer of the bladder in humans [10]. The effluents of congo red dye are highly colored, have low biological oxygen demand (BOD) and high chemical oxygen demand(COD) as they contain high amounts of dissolved solids [11]. So it is utmost important in order to treat these dyes by a definite process which is environment friendly.

Since lastdecade,nanoparticles constructed from more than one metallic phase has attracted a great intrest. Nanoparticles with different morphologies has caught the attention of scientists because of their potential applications in various fields [12]. Among the various metal Oxides available, cupricoxide(CuO) is a p-type semiconductor with a band gap of 1.2eV at room temperature[13]. The dimensions of CuO and morphology of Nanomaterials play a critical role for each specific application[14]. CuO due to its wide range of applications like gas sensors [15], solar energy conversion[16], lithium ion batteries [17],] and is well known as heterogeneous catalyst [18]. Due to the size and morphology dependent properties of CuO nanostructures, different types of CuO morphologies has been synthesized such as nanorods, nanosheets, nanodendrites, honey comblike, urchin like and dumb bell like nanostructures [19–21]. Using Hydro thermal growth technique for synthesis of Ag-CuO nanorods seems to be a competitive alternate. Separation of the catalyst remains as a challenge for many industries and magnetic recovery of these nano catalyst makes an inexpensive and effective separation, which is far better than conventional techniques. Furthermore owing to the special properties, magnetic segregation properties of these nanocatalysts we focused on some pertinent applications like photo catalytical degradation of dyes and organic pollutants. The physical and chemical properties of these nano catalysts has potential use , due to the availability of large number of reactive sites on the curved surface of these nano hybrids, favours the adsorption of the

reactant molecules, which improves the chemical reactivity, interest is primarily concerned to the promising properties of the nanomaterials.

The effects of various operating parameters such as initial concentration of dye, catalyst dosage, bufferic pH and irradiation time on photocatalytic degradation have been studied . Usually it takes nearly 2 hours for the dyes for photo cataltical degradation however the degradation time varies depending on the conc. Of the dye, catalyst added and PH factors. Degradation of potent dyes like Congored is found to be done in presence of these core shells and Ag-cuo heteromer when the dye concentration is matained even at 25 to 30 ppm addition of 50mg of catalyst at neutral pH degrades the dye in nearly 80 mins which can be measured subsequently using UV-Visible spectrophotometer. Hence a combination of Ag with cuo is carried out in a hydrothermal method using an autoclave. Ag-cuo nanorods prepared is tested for its photocatalytic performance using an organic dye congored. The relative degration was found to be 93% and is much more effective with in a short duration of time. Various parameters were studied inorder to evaluate the activity of photocatalyst and is found that the catalyst is found to be very effective even in minute concentrations.

Materials and methods:

Silver nitrate (99.9%), Oleic acid(OAc, 90%), Oleyl amine(OAm,80%), 1-dodecanol, Copper acetate were purchased from sigma Aldrich. All these reagents were used without any purification and double distilled water is used in all the process when required.

Method of preparation:

a) Synthesis of Ag nanoparticles:

1ml of OAc, 1ml of OAm, 10ml of 1-dodecanol were added in a clean sterilized 50ml beaker and the mixture is heated to 220oc for 10mins with constant stirring and after attaining the temperature 100mg of silver nitrate is added and is allowed to stand for 1hr at the same temperature in an autoclave, upon reaching the above said condition it is left to cool and the resulting dark brown solution is checked for the formation of Ag nanoparticles by UV-Visible spectrophotometer.

b) Synthesis of Ag-CuO Nanorods:

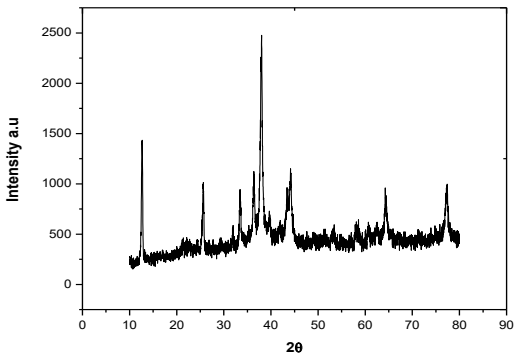
Ag nanoparticles solution, (dark brown solution) formed by the above process is added with 300mg of copper acetate and is heated to 160oc for 2hrs. After completion of the reaction the solution is allowed to stand to attain the room temperature. The resulting solution is washed several times with ethanol and hexane alternatively, centrifuged and the product obtained is calcinated at 400oc for 1hr to form Ag-CuO nanorods.

Charecterization details:

Prior to the phase and morphology studies UV-Visible spectra analysis was performed for Ag nanoparticles and Ag-CuO nanorods. XRD, SEM, EDX were also measured in addition to this.

XRD:

By comparing the XRD data of Ag-CuO nanorods with the XRD data of pure Ag and Pure CuO nanorods (16,17), hkl values the phase of the catalyst is determined.



SEM:

The distinctive sem images of Ag-CuO nanorods are shown in the following figures. The cataytical effect of these were investigated through degradation of organic dye congored.

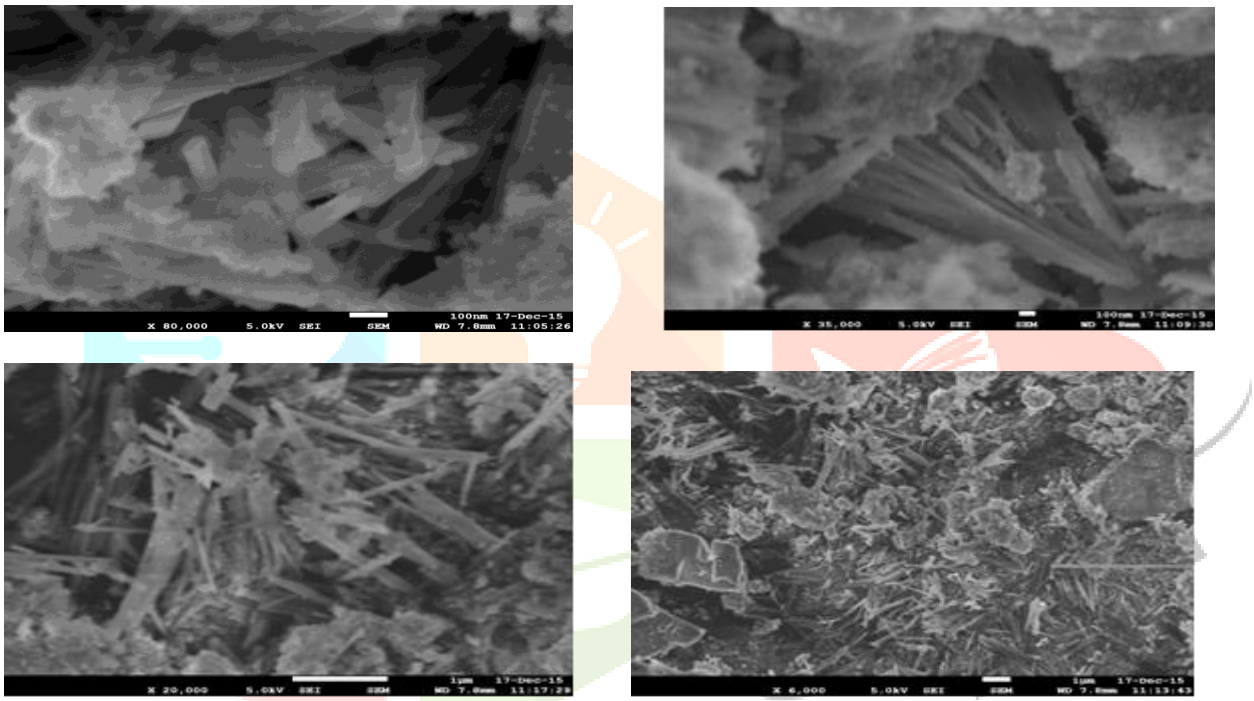


Fig 2: SEM images of Ag-CuO nanorods

EDX:

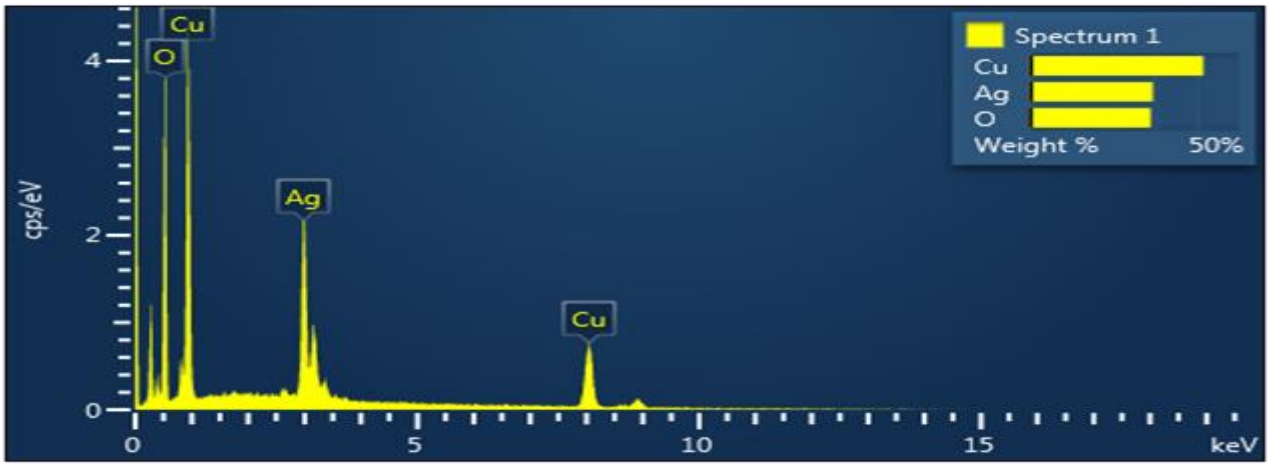
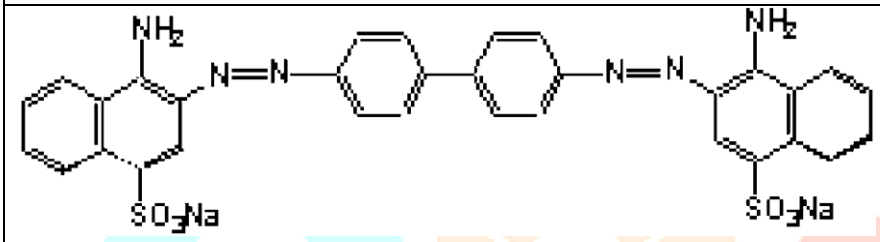


Fig 3: EDX spectra and elemental composition details

Element	Wt%	Wt% Sigma
O	28.97	0.41
Cu	41.55	0.48
Ag	29.48	0.44
Total:	100.00	

Photocatalytic performance of Ag-CuO Nanorods for the degradation of Organic dye CongoRed:

Photocatalytic activity of Ag-CuO nanorods was observed for the degradation of congored dye at room temperature using UV-Visible spectroscopy.

Structure	Molecular formula	Wavelength
	696.68g/mol	510nm

Experimental section:

CongoRed dye of 1000ppm is prepared by using doble distilled water and serial dilutions of 100ppm, 50ppm, 25ppm were prepared. 50ml of 25ppm concentrated dye is taken in a 100ml beaker and 25mg of catalyst is added to the solution and is stirred in dark for 30mins. The samples were collected for every 10mins and the absorbance was recorded eventually using UV-Visible spectroscopy. Various graphs C/Co Vs Time, ln(C/Co) Vs Time, % of degradation Vs Time were reported below.

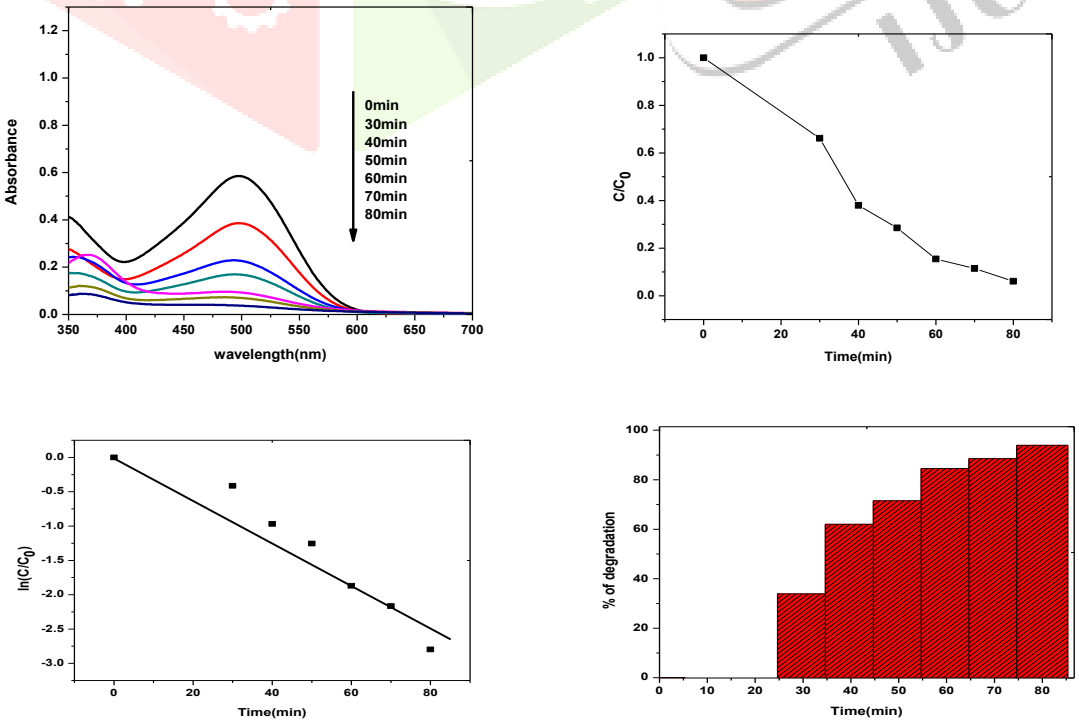


Fig 4: a) Absorbance Vs Wavelength b)C/Co Vs Time c)ln(C/Co) Vs Time d) % of degradation Vs Time.

Results and discussions:

From the graphs observed above the time required for the degradation of congored was found to be 80 mins which is found to be very effective as only minute concentration of the catalyst has been used.

ln C/Co graph is plotted in order to caliculate the rate constant value. The rate constant value k is found to be 3.7x10-4. The regression coefficient value R is found to be 0.912. The bar graph is constructed for the % of degradation Vs Time and the degradation is found to be 93% which is very effective.

Conclusion:

In summary, Ag-CuO nanorods were obtained under different conditions in a hydrothermal technique. These nanostructures were charecterised by XRD, SEM, EDX techniques. The major and potential application of the synthesized nanostructures for the degration of organic dye, congo red was observed and the results suggest better Photocatalytic properties of nanorods compared to the other morphologies due to its high surface area.

References:

[1] S.C.R. Santos, R.A.R. Boaventura, Adsorption modeling of textile dyes by sepiolite, Appl. Clay Sci. 42 (2008) 137–145.

[2] M.S. Chiou, P.Y. Ho, H.Y. Li, Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads, Dyes Pigments 60 (2004) 69–84.

[3]B.K. Körbahti, Response surface optimization of electrochemical treatment of textile dye wastewater, J. Hazard. Mater. 145 (2007) 277–286.

[4] Z.M. Shen, D. Wu, J. Yang, T. Yuan, W.H. Wang, J.P. Jia, Methods to improve electrochemical treatment effect of dye wastewater, J. Hazard. Mater. B131 (2006) 90–97.

[5] S. Wang, Z.H. Zhu, Sonochemical treatment of fly ash for dye removal from wastewater, J. Hazard. Mater. B126 (2005) 91–95.

[6] H.Y. Zhu, R. Jiang, Y.J. Guan, Y.Q. Fu, L. Xiao, G.M. Zeng, Effect of key operational factors on decolourization of methyl orange during H2O2 assisted nanosized CdS/TiO2/polymer composite thin films under simulated solar light irradiation, Sep. Purif. Technol. 74 (2010) 187–194.

[7] R. Jiang, H.Y. Zhu, Y.J. Guan, Y.Q. Fu, L. Xiao, Q.Q. Yuan, S.T. Jiang, Effective decolorization of azo dye utilizing SnO2/CuO/polymer films under simulated solar light irradiation, Chem. Eng. Technol. 34 (2) (2011) 17–185.

[8] L. Lian, L. Guo, C. Guo, Adsorption of Congo red from aqueous solutions onto Ca-bentonite, J. Hazard. Mater. 161 (2009) 126–131.

[9] E. Bulut, M. Özacar, I˙.A. S¸engil, Equilibrium and kinetic data and process design for adsorption of congo red onto bentonite, J. Hazard. Mater. 154 (2008) 613–622.

[10] M. Boeniger, Carcinogenecity and metabolism of azo dyes, especially those derived from benzidine, USDHHS (NIOSH) Tech. Rep. (1980) 80–119.

[11] S. Maiti, S. Purakayastha, B. Ghosh, Production of low-cost carbon adsorbents from agricultural wastes and their impact on dye adsorption, Chem. Eng. Commun.195 (2008) 386–403.

[12] S. Rackauskas,A.G.Nasibulin,H.Jiang,Y.Tian,V.I.Kleshch,J.Sainio, E.D. Obraztsova S.N.Bokova, A.N.Obraztsov, E.Kauppinen, Nano- technology 20(2009)165603.

[13] M. Yin,C.K.Wu,Y.B.Lou,C.Burda,J.T.Koberstein,Y.M.Zhu, S. O'Brien, Copperoxidenanocrystals,J.Am.Chem.Soc.127(2005) 9506–9511.

[14] J.Y. Xiang, J.P.Tu,L.Zhang, Y.Zhou,X.L.Wang,S.J.Shi, Self- assembled synthesis of hierarchical nanostructured CuO with various morphologies and their application as anodes for lithium ion batteries, J.Power Sour.195(2010)313–319.

[15] D. Li,J.Hu,R.Wu,J.G.Lu,Conductometric chemical sensor based on individual CuOnanowires,Nanotechnology21(2010)485502.

[16] Y. Xu,D.Chen,X.Jiao,Fabrication of CuO pricky microspheres with tunable size by a simple solution route,J.Phys.Chem.B109(2005) 13561–13566.

[17] S. Venkatachalam,H.W.Zhu,C.Masarapu,K.H.Hung,Z.Liu, K. Suenaga,B.Q.Wei,In-situformation of sandwiched structures of nanotube/CuxOy/Cucomposites for lithium battery applications, ACS

Nano 3(2009)2177–2184.

[18] C.T. Hsieh,J.M.Chen,H.H.Lin,H.C.Shih, Field emission from various Cuo nanostructures,Appl.Phys.Lett.83(2003)3383–3385.

[19] D.P. Singh, A.K.Ojha, O.N.Srivastava, Synthesis of different Cu(OH)2and CuO(nanowires, rectangles, seed-,belt-,and sheet like)nano structures by simple wet chemical route,J.Phys.Chem.C113(2009)3409–3418.

[20] Y. Liu,Y.Chu,Y.J.Zhuo,M.Y.Li,L.L.Li,L.H.Dong,Anion-controlled construction of CuO honey comb sand flowers-like assemblies on copperfoils,Cryst.GrowthDes.7(2007)467–470.

[21] Y. Zhao,J.Zhao,Y.Li,D.Ma,S.Hou,L.Li,X.Hao,Z.Wang,Room temperature synthesis of 2DCuO nano leaves in aqueous solution, Nanotechnology 22(2011)115604.