Copper Doped ZnO Nanoparticles as Photocatalyst for Degradation of Pollutant in Water

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Abstract— Persistent organic pollutants (POPs) are carbon based chemical substances that are resistant to environmental degradation also refractory in nature and hazardous to human being and may not be completely removed through treatment process. So photocatalysis have the abilities decompose dyes, chemicals naturally. So the chemical ZnO has antibacterial and deodorizing property, it's a inorganic compound which is white in colour insoluble in water having molar mass 81.048g/mol and band gap having 3.37Ev and zinc oxide has transcended to use in semiconductors, concrete use, ceramic, glass and even cigarette filter. Zinc oxide is cheap in cost and easily available but it having a band gap of 3.37eV which unsuitable solar photocatalysis because the difference between valence band and covalent band gap is more so to decrease the gap we use cu as a dopant and to bring up to visible radiations, so nanoparticles are prepared with the suitable chemical method which most suitable that is co-precipitation method which is economical, less time consuming and to done photo degradation of POPs, dye degradation from water coming out from industries with improvement of Cu doped ZnO as a photocatalyst. The second objective of this review is to evaluate the immobilization of photocatalyst and suspension system while looking into their future challenges and prospects and the catalyst will characterized by XRD,SEM, FTIR, UV VIS, PH techniques and application test will carried out to quantify photocatalytic degradation of toxic organic dye.

Keywords: Photocatalysis, Degradation, Nanoparticles, Methylene Blue, Cu doped ZnO

I. INTRODUCTION

The annual increase of the world population in 80 million means further annual need of 64 × 109 m3 of drinkable water.About 780 million people around the world can't have safe and clean drinking water which is diminishing by time.[5]In recent years, the contamination of surface and ground water has increased due to population growth. The main sources of environmental contamination are organic dyes used in the food, furniture,leather and textile industries due to their high toxicity and their non-biodegradability, which have carcinogenic effects on humans. MethyeleneBlue (MB) dye is used by different industries, for example, as a dye in silk; as a food coloring additive; and as a dye in wool, leather, cotton, jute, and paper. Methylene blue dyes have strong effects on the immune and reproductive systems and exhibit potential carcinogenic and genotoxic effects. Thus, these hazardous dyes must be removed from industrial effluents. Many methods, such as biological treatment, adsorption and photocatalysis, have been used for removal of these dyes from industrial effluents. The use of photocatalysts to degrade organic compounds in contaminated air or water or to convert them into harmless chemicals has been extensively studied to decrease the damage caused by organic dye pollution to the environment and humans.

To overcome this problem, doping ofZnO with impurity atoms to enhance the activity. Doping of ZnO with transition metal introduces new energy level where electrons are trapped in this level inhibiting electron hole recombination during irradiation. As silver is very expensive metal so doping with copper (Cu) in ZnO is an alternative to modify absorption and emission in visible region. The main objectives of the current review is degradation of pollutant i.e dye with help of copper doped ZnO as a photocatalyst, as well as future challenges and prospects of using doped ZnO nanoparticles in these process. Zinc oxide (ZnO) photocatalysts were synthesized by co-precipitation method using zinc acetate as precursor for degradation of azo dyes under UV irradiation.

The effect of operation parameters on the degradation Results showed that the removal rate of azo dyes increased with the increased dosage of catalyst and decreased initial concentration of azo dyes and the acidic condition is favorable for degradation. Further more, the kinetics of the reactive species during the degradation were also investigated. It was found that the degradation of azo dyes fitted the first-order kinetics and superoxide ions were the main species. The proposed photocatalyst can efficiently and rapidly degrade azo dyes; thus, this economical and environment-friendly photocatalyst can be applied to the treatment of wastewater contaminated with synthetic dyes.

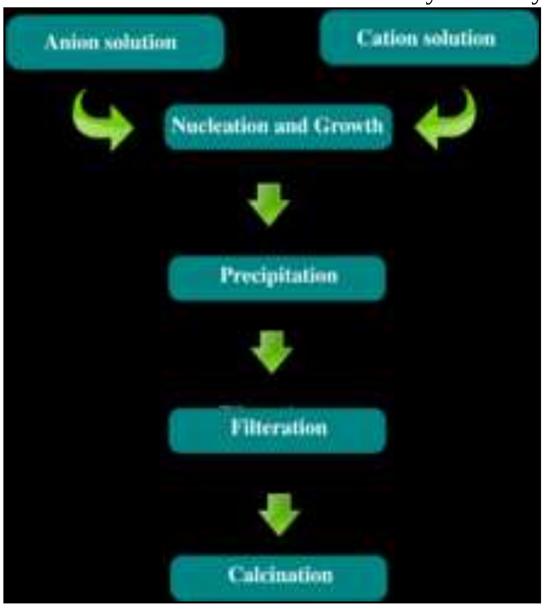


Fig. 1: Process

Fig. 2: Zno powder preparation setup

II. PROBLEM DEFINITION

1) We can decrease the bandgap of ZnO by dopping Cu in ZnO. As bandgap decrease then increase the absorption edge of the ZnO.
2) InTextile, paper and pulp, pharmaceuticals, paint Etcindustries leaves methylene blue are in waste water.So we can try to degrade that pollutant in less time using Cu doped ZnO

III. OBJECTIVE

1) Cu doped ZnO nanoparticles synthesizesuccessfully by simple chemical co-precipitation method.
2) Study of Photocatalytic degradation of Methylene blue (MB) dye under Ultra violet/Visible is irradiation.
3) Photocatalytic efficiency of ZnO increases with Cu doping and increase the photocatalytic performance.

IV. MATERIALS ANDMETHOD

A. *Materials*

1) Apparatus:Conical flask, distilled water, magnetic, stirrer, beaker, heater etc.
2) Chemicals: Zinc acetate, NaOH, Distilled water etc.

To prepare powder the following steps we followed:

1) Centrifuge
2) Drying
3) Grinding
4) Calcinations
5) Stirring

B. *Synthesis of ZnO nanoparticles*

Total 3 batches have been taken at normal temperature, without complexing agent and with complexing agent.

Zinc oxide (ZnO) nanoparticles were prepared by zinc acetate dehydrate (0.1N) and NaOH (0.1N). The solution kept on magnetic Stirring at room temperature for 3.5hr. NaOH added dropwise and maintained pH of the solution. The samples were centrifuged at 10000rpm and 10000rpm for10min and washed with methanol for three times further, it was dried at 60ºc for one night and placed in furnace at 300ºc for 2hr.

Zincoxide (ZnO) nanoparticles were prepared by refluxing operation. Without complexing agent batch was taken at 85ºc for 2hr.NaOH added dropwise and maintained pH of the solution. The samples were centrifuge at10000 rpm and 10000rpm for 10min and washed with methanol for three times further, it was dried at 60ºc for one night and placed in furnace at 300ºc for 2hr. Before reflux operation with complexing agent, NaOH and PEG(0.6ml) was stirred for 30min. With complexing agent batch was taken at 85ºc for 2hr NaOH and PEG solution added dropwise and maintained pH of the solution. The samples were centrifuged at 10000rpm and 10000rpm for 10min and washed with methanol for three times further, it was dried at 60ºc for one night and placed in furnace at 300ºc for 2 hr.

C. *Solar Photo Catalyst Activity*

The methods based on catalysis and photochemistry has been denominated Advanced Oxidation Processes. Among them, those which produce hydroxyl radicals (•OH) have had growing success. As mentioned before, UV light can be used in several ways but direct photolysis can occur only when the chemical compounds absorb incident light efficiently. By contrast, these radicals can also be generated with photocatalysis. Which absorbs UV radiation when this is in contact with the water. In heterogeneous photocatalysis, dispersed solid particles absorb larger fractions of the UV spectrum efficiently and generate chemical oxidants in situ from dissolved oxygen or water. These advantages make heterogeneous photocatalysis a particularly attractive method for environment detoxification. The most important features of this process making it applicable to the treatment of contaminated aqueous effluents are:

- The process takes place at ambient temperature.
- Oxidation of the substances into CO2 is complete.
- The oxygen necessary for the reaction is obtained from the atmosphere.
- The catalyst is cheap, innocuous and can be reused.
- The catalyst can be attached to different types of inert matrices.

Whenever different semiconductor materials have been tested under comparable conditions for the degradation of the same compounds, ZnO has generally been demonstrated to be the most active. Only ZnO is as active strong resistance to chemical and photocorrosion, its safety and low cost limits the choice of convenient alternatives. This semiconductor is of special interest, since it can use natural (solar) UV because it has an appropriate energetic separation between its valence and conduction bands which can be surpassed by the energy content of a solar photon. Other semiconductor particles, absorb larger fractions of the solar spectrum and can form chemically activated surface-bond intermediates, but unfortunately, these photocatalysts are degraded during the repeated catalytic cycles involved in heterogeneous photocatalysis. Therefore, degradation of the organic pollutants present in wastewater using irradiated ZnO suspensions is the most promising process and R&D in this field has grown very quickly during the last years.

To date, evidence supports the idea that the hydroxyl radical is the main oxidizing specimen responsible for photo oxidation of the majority of the organic compounds studied. The first effect, after absorption of near ultraviolet radiation, is the generation of electron/hole pairs,which are separated between the conduction and valence bands. In order to avoid recombination of the pairs generated, if the solvent is Oxido reductive active (water) it also acts as a donor and acceptor of electrons. Thus, on a hydrated and hydroxylated surface, the holes trap •OH radicals linked to the surface. Inany case, it should be emphasized that even trapped electrons and holes can rapidly recombine on the surface of a particle. This can be partially avoided through the capture of the electron by pre-absorbed molecular oxygen, forming a superoxide radical. Whatever the formation pathway, it is well known that O2 and water are essential for photo-oxidation with ZnO. There is no degradation in the absence of either. Furthermore, the oxidative species formed react with the majority of organic substances.

V. RESULT AND DISCUSSION

In this study we have studied pure ZnO and copper doped ZnO nanoparticles were synthesized by co-precipitation method. UV and XRD analysis confirmed the grain size of the pure Cu doped ZnO nanoparticles. The average particle size obtained for pure ZnO particles is 20-25nm and the size was found to decrease in Cu doped ZnO nanoparticles as 10-14nm the optical transmittance of the UV-VIS measurements indicates that the pure ZnO andCu doped ZnO nanoparticles have a bandgap 3.7ev and 3.5ev upto 4% Cu doping after that bandgap increases. The photo catalytic degradation value of methylene blue dye with copper doped ZnO nanoparticles is measured to be 98% after 3hrs of sunlight irradiation therefore the copper doped nanoparticles used as solar photo catalysts for degradation may be a very effective method for the treatment of waste water including removing dye pollutant and improving the water quality of various naturalsources.

A. Experimental Work:

Fig.Mixing

Fig.Titration

Fig.Centrifuge

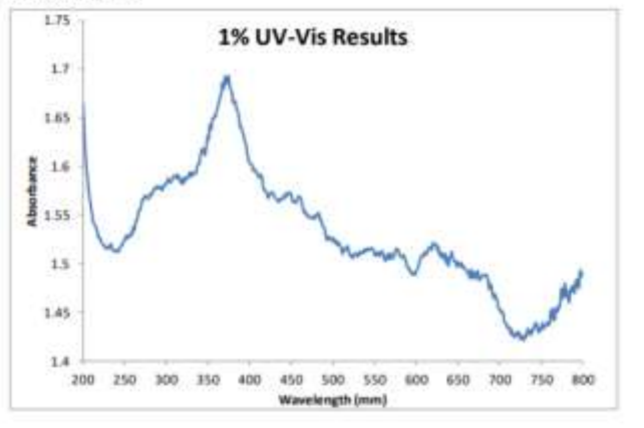
Fig.Oven

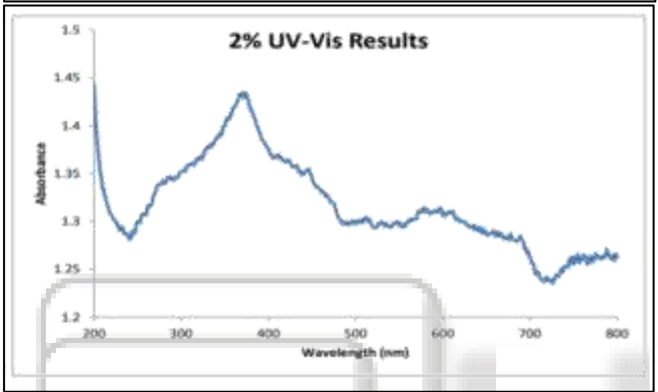
Fig.Furnace

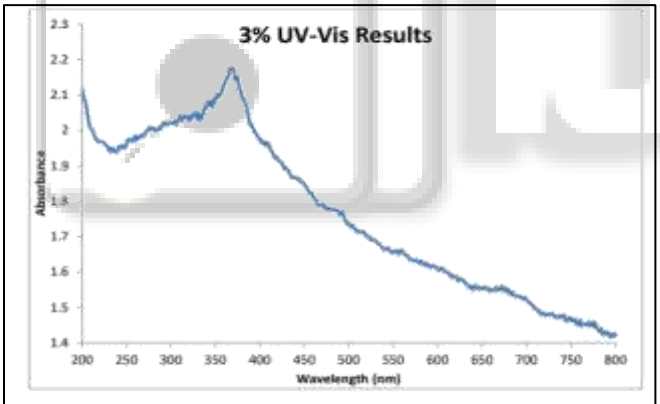
Fig.ZnO Nanoparticles

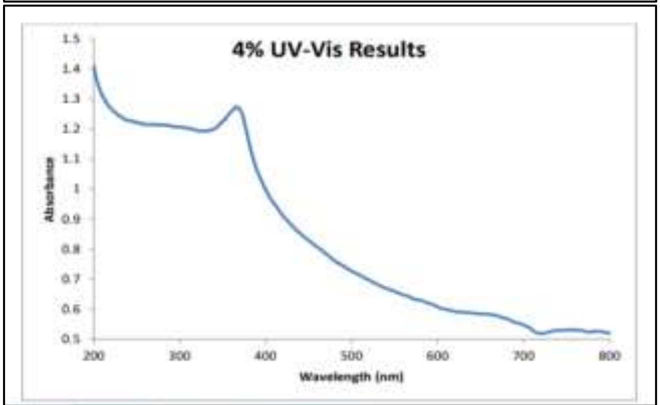
B. Characterization of Cu dopedZnONanoparticles:

UV visible result:









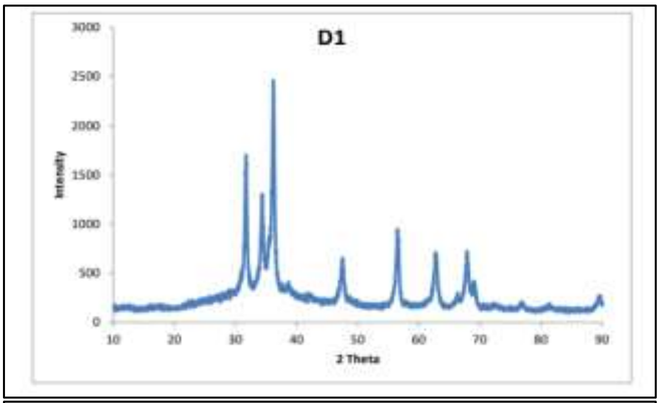
From the above 1st graph we found that wavelength of 1% copper dopped zinc oxide is 360 – 370.

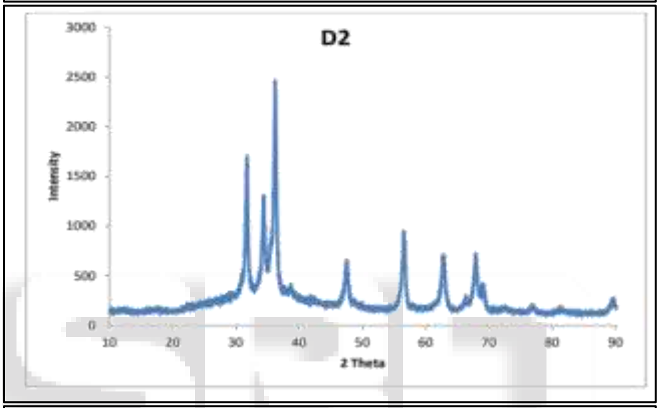
From the above 2nd graph we found that wavelength of 2% copper dopped zinc oxide is 370 – 380.

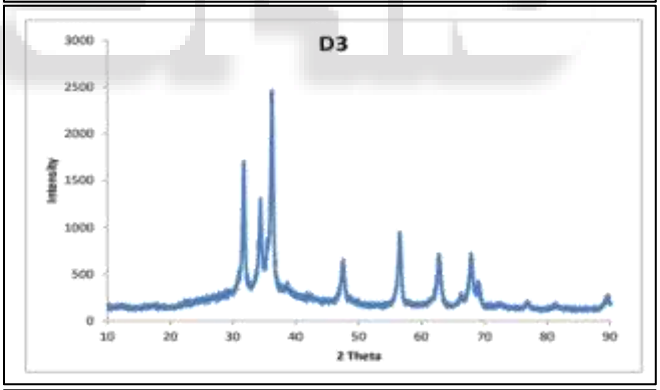
From the above 3rd graph we found that wavelength of 3% copper dopped zinc oxide is 370 – 380.

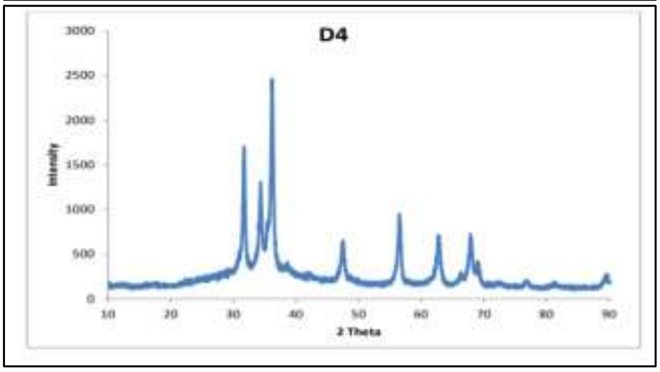
From the above 4th graph we found that wavelength of 4% copper dopped zinc oxide is 380 – 390.

C. XRD Result:









Above graph displays the XRD patterns of undoped and Cu-doped ZnO nanoparticles. All the diffraction peaks can be indexed to the hexagonal wurtzite structure. The diffraction peaks of the Cu-doped ZnO nanoparticles are also in good agreement with those of hexagonal ZnO and are almost identical to that of the pure ZnO, indicating that the Cu atoms have been doped in the ZnO crystal and no new phase has been formed.The crystal size of Cu-doped ZnO nanoparticles can be estimated as 26,25,27 and 28 nm, respectively.

VI. CONCLUSION

In this study we have studied pure ZnO and copper doped nanoparticles were synthesized by co-precipitation method. UV aand XRD analysis confirmed the grain size of the pure Cu doped ZnOnanoparticles. The average particle size obtained for pure ZnO particles is 20-25 nm and the size was found to decrease in Cu doped ZnOnanoparticles as 10-14 nm the optical transmittance of the UV-VIS measurements indicates that the pure ZnO and Cu doped ZnO nanoparticles have a bandgap 3.7 ev and 3.5 evup to 4% Cu doping after that bandgap increases. The photo catalytic degradation value of methylene blue dye with copper doped ZnO nanoparticles is measured to be 98% after 3 hours of sun light irradiation therefore the copper doped nanoparticles used as a solar photo catalysts for degradation may be a very effective method for the treatment of waste water includingremoving dye pollutant and improving the water quality of various natural resources.

REFERENCES

[1] Azo materials https://www.azom.com/azoprofile/.
[2] A review of ZnO nanoparticles as a photocatalysts: synthesis, mechanism, applications http://dx.doi.org/10.1016/j.rser.2017.08.0201364-0321.
[3] Enhancement of photocatalytic activity of cu doped ZnO for the degradation insecticidedoi: 10.1016/j.jenvman.2016.10.04
[4] 4.Mohamed RM1, Mkhalid IA, Al-Thabaiti SA, Mokhtar M. Nano Cu metal doped on TiO2-SiO2 nanoparticle catalysts in photocatalytic degradation of direct blue dye.DOI: 10.1166/jnn.2013.7602
[5] C. Sealy, cleaning up water on the nanoscale, Nano Today 8 (2013)337-338.https://doi.org/10.1016/j.nantod.2013.06.004
[6] Sarmah S, Kumar A (2008) Photocatalytic activity of polyaniline-TiO2 nanocomposites. Indian J Phys. 85: 713–726.
[7] Mittal A (2006) Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers. J Hazard Mater 133: 196-202. [Crossref]
[8] G. Thennarasu, A. Sivasamyn Enhanced visible photocatalytic activity of cotton ball like nanostructured Cu doped ZnO for the degradation of organic pollutant. http://dx.doi.org/10.1016/j.ecoenv.2015.10.030
[9] RahmatollahRahimi*, JavadShokrayian, MahboubehRabbani: Photocatalytic removing of methylene blue by using of Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codopedZnO nanostructures.
[10] Shady Mohamed El-Dafrawy, Salah Fawzy and Shawky Mohamed Hassan Research Article Preparation of Modified Nanoparticles of Zinc Oxide for Removal of Organic and Inorganic Pollutant DOI: 10.3923/tasr.2017.1.9
[11] Thaweesaeng, N., Supankit, S., Techidheera, W., &Pecharapa, W. (2013). Structure properties of as-synthesized Cu-doped ZnOnanopowder synthesized by co-precipitation method.
[12] https://en.m.wikipedia.org/wiki/Coprecipitation
[13] https://www.google.com/amp/s/www.researchgate.net.
[14] Comparison of sol-gel and co-precipitation methods on the structural properties and phase transformation o fγ and α-Al2O3 nanoparticles | SpringerLink https://link.springer.com/article/10.1007/s40436-013-0018-1
[15] https://www.sciencedirect.com/topics/engineering/coprecipitation
[16] Jacob, A. A., Balakrishnan, L., Shambavi, K., & Alex, Z. C. (2017). Multi-band visible photoresponse study of Co2+ doped ZnO nanoparticles. RSC Advances, 7(63), 39657–39665. doi:10.1039/c7ra05429g
[17] Ben Elkamel, I., Hamdaoui, N., Mezni, A., Ajjel, R., &Beji, L. (2018). High responsivity and 1/f noise of an ultraviolet photodetector based on Ni doped ZnO nanoparticles. RSC Advances, 8(56), 32333–32343. doi:10.1039/c8ra05567j
[18] Becheri, A., Dürr, M., Lo Nostro, P., &Baglioni, P. (2007). Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers. Journal of Nanoparticle Research, 10(4), 679–689. doi:10.1007/s11051-007-9318-3
[19] Adam, R. E., Pozina, G., Willander, M., &Nur, O. (2018). Synthesis of ZnO nanoparticles by co-precipitation method for solar driven photodegradation of Congo red dye at different pH. Photonics and Nanostructures - Fundamentals and Applications. doi:10.1016/j.photonics.2018.08.005
[20] Dias, H. B., Bernardi, M. I. B., Marangoni, V. S., de Abreu Bernardi, A. C., de Souza Rastelli, A. N., &Hernandes, A. C. (2018). Synthesis, characterization and application of Ag doped ZnO nanoparticles in a composite resin. Materials Science and Engineering: C. doi:10.1016/j.msec.2018.10.063