The Synthesis and Characterization of Metal Oxide Nanoparticles and Its Application for Photo catalysis

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Abstract- In the present study different metal oxide nanoparticles (Magnesium, Zinc and Copper) were synthesized using two different methods wet chemical method and hydrothermal method. These nanoparticles were characterized using FESEM, EDAX and XRD to investigate their structural and morphological properties. Their potential for dye degradation is experimentally verified. **XRD** data was used to calculate the particle size using Debye Scherrer formula and it was found to be in the nano-range. **SEM** analysis also supported that metal oxide particles are in the nano-range with varying morphology. **EDAX** confirms the presence of metals Zn, Mg and Cu in the respective oxides. The dye degradation **activity** of ZnO, MgO and CuO nanoparticles were investigated by the degradation of methylene blue (MB) and Eriochrome black-T(EBT) dye   in aqueous medium under natural sunlight. Results indicate that MgO nanoparticles have better photocatalytic efficiency under natural sunlight as compared to ZnO and CuO nanoparticles for methylene blue dye and ZnO nanoparticles higher dye degradation for Erichrome Black-T dye.   Such photocatalytic activity was not observed for metal oxides in bulk and also was not observed in dark conditions. Wet chemical route for synthesis of nano-metal oxides was found to be very simple, cost-effective technique for development of metal oxide nano-particles This can be developed as effective method for dye degradation thus reducing organic dye waste load from effluents of industries.

Index Terms- Hydrothermal Method, Metal oxide nanoparticles, Photocatalysis, SEM, Wet-Chemical Method, XRD

I. INTRODUCTION

Transition metals due to their variable oxidation states form oxides of different stoichiometry. These metal oxides have various geometrical structures which in turn lead to different chemical and electronic properties. Metal oxide nanoparticles due to their smaller size have properties different than those in the bulk. Out of large number of metal oxides present in nature; some of the metal oxides are most useful in accordance with their applications to day to day life in science and technology. Physico-chemical properties of metal oxides have special relevance in chemistry mostly related to the industrial use of oxides as sensors, ceramics, adsorbents and catalysts.

Dye can be colored, ionizing and aromatic organic compound which shows an affinity towards the substrate to which it is being applied. It is generally applied as a solution that is aqueous or oil base and requires a mordant to improve the fastness on the material on which it is applied. Dyes have many functional variations like acidic, basic, disperse, azo, anthra-quinone based and metal complex and others.

Dyes are used in industry on large scale for various applications from production of plastics /textiles/ fabrics and many more things. After the use when plastic/textile is scraped what happens to the dye needs to be examined. In the present study dye degradation ability of Mg, Zn, Cu oxide nanoparticles has been studied. This has direct industrial application like after use toxic organic dyes can be degraded using nano metal oxides so that they do not enter local water body; they will be separated, disposed or recycled.

The textile industry is the largest consumer of dye stuffs. During the coloration process, a large percentage of the synthetic dye does not bind and is lost to the waste stream (Weber and Adams, 1995). Approximately 10-15% dyes are released into the environment during dyeing process making the effluent highly colored and aesthetically unpleasant (Ratna and Padhi, 2012). Dyes have been applied in many industries such as textiles, printing, leather, pulp, food and plastics, etc. The effluent from these industries normally contains presence of these dyes. About 10,000 different commercial dyes and pigments exist and more than $7x10^5$ tons are produced per year worldwide (Shah et al., 2010). Approximately 10-15% of these dyes are released after dying process (Al-Degs et al. 2008).

Many organic dyestuffs are harmful to human being and toxic to animals and microorganisms. Hence now a days it has been made mandatory to remove the spent dyes before its release in to natural water bodies. Various dye removal process have been used such as coagulation, chemical oxidation, membrane separation, electrochemical process, biological treatment and adsorption techniques (Durai and Rajasimman 2011). Adsorption was recognized to be an effective process for the removal of dyes from waste water which are the easiest for separation and highly effective in dye removal (Orthman et al., 2003). Different kinds of adsorbents have been developed for various applications such as activated carbon (Iqbal et al., 2007), active carbon from pyrolysis of bagasse (Lori et al., 2008), spent activated clay (Weng et al., 2007),, soil(Cheng et al. 2008), kaolin (Nandi et al., 2009), CuO NPs and carbon-encapsulated super magnetic colloidal NPs (Wang et al. 2013). (Ghulam et al 2013).

In the present work, CuO, ZnO, MgO nanoparticles have been synthesized by two simple methods and their potential for dye degradation is experimentally verified and utilized as nano adsorbents for the removal of organic   dyes. The XRD and morphological study of oxide- naoparticles was observed by scanning electron microscopy (SEM).

ZnO nanoparticles are used for many applications including an activator of accelerator in the vulcanization process as a form

control in lattices and photocatalyst. Using ZnO particles show a high degree of transperancy, making them useful in sunscreens, paints, varnishes, plastics and cosmetics especially for broad UV A(315-400nm) and UV B(280-315nm) blocking.(S. Sultana 2013)

The oxides of transition metals are an important class of semiconductors having applications in multiple technical fields like solar energy transformation, magnetic storage media, electronics and catalysis among the oxides of transition metals. Copper oxide nanoparticles are of special interest because of their efficiency as nano-fluids in heat transfer application. CuO is the basis of several high Tc semiconductors. CuO is a semiconducting material with a narrow band gap and used for photoconductive and photothermal applications opposite to n type semiconducting metal oxides. CuO is p-type semiconductor with a band gap of 1.2-1.9 eV .(S. Raja ,2015) Zinc oxide is the one of the most important n-type semiconductor materials with a 3.37 eV band gap at room temperature and that is in the UV region and makes this nanoparticle as an efficient UV absorber. NanoMgO is a functional material which is used in various areas like photocatalysis, antibacterial activity etc.

In the present   paper, we report the comparative study of these three metal-oxide nanoparticles done for the first time.

II.   EXPERIMENTAL MATERIALS AND METHODS

A. Chemicals

All chemicals used in the experiment were of analytic reagent grade. Copper nitrate, Zinc nitrate, Magnesium nitrate, sodium hydroxide, zinc acetate, methanol. methylene blue(MB) and Eriochrome black-T(EBT) dyes. De-ionized water was used throughout the experiment.

B. Synthesis Of Metal Oxide Nanoparticles

In the preparation by **wet chemical method,** Metal oxide nanoparticles were synthesized by using 0.2 M solution of $M(NO3)2$ and 0.4M NaOH The nitrates of the respective metals were dissolved in water to which sodium hydroxide was added drop-wise with continuous stirring at room temperature leading to generation of metal hydroxides. The stirring was continued for 6 hrs at 85^0C.The reaction mixture was then filtered and dried in oven at 60^0C. These   hydroxides are calcined in furnace at 600^0C and oxide nanoparticles were obtained. The product was characterised by SEM, EDAX and XRD.
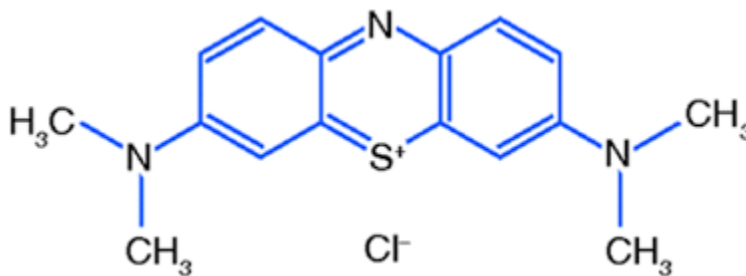
In the **hydrothermal** method acetate salt of the metal dissolved in methanol was reacted with   sodium hydroxide in a Teflon lined sealed autoclave and heated under autogenous pressure at 110 ^{0}C for 6 hours in an oven. The product was then filtered, washed, dried and characterise**d.**
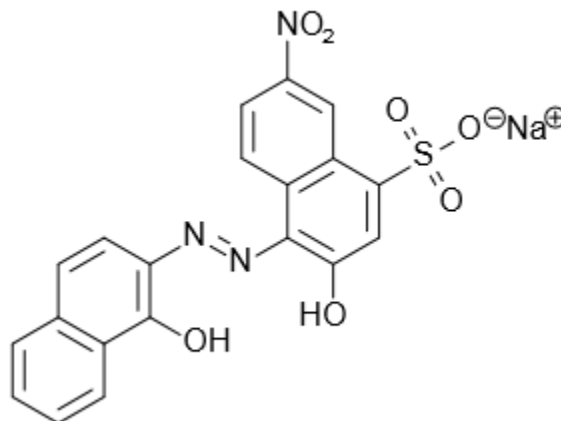
C. Characterisation

The powder X-ray diffraction (XRD) analysis was performed by using X-ray diffractometer   Bruker D advance in the scanning range from 20 to 80 at average rate. Surface morphology of synthesized products was carried out by SEM analysis using Model SIGMA HV with resolution 20KV to 1KV and magnification x50-10,00,000 and accelerating range 0.1-30 kV

D. Measurement Of Photocatalytic Activities

Frequently used organic dyes, namely, Eriochrome black-T (EBT) and Methylene blue(MB) were degraded photochemically using metal oxide nanoparticles.

Methylenebluedye
Figure 1.Structure of Methylene blue dye

Eriochrome black-T
Figure2: Structure Of Eriochrome black-T dye

The photocatalytic activity of as synthesized MgO, CuO and ZnO was performed using Methylene blue dye and Eriochrome black-T dye as degraded materials under natural sunlight irradiation.2.5 ml dye solution was mixed with desired concentrations of catalysts. Before irradiation, suspension was stirred magnetically for 30 minutes in dark conditions until adsorption-desorption equilibrium was established. Then suspensions were irradiated by light sources without stirring. Under natural sunlight irradiation, all experiments were done inside the laboratory in an open atmosphere between 10:00am to 4:00 pm.

III.   RESULTS AND DISCUSSION

A. Structure And Morphology
X-ray studies

XRD data was used to confirm the phase formation and calculate the particle size. Average particle size for different specimens was obtained from the main peaks using the **Debye Scherrer equation D=0.89λ/βcosθ.** Where D=crystallite site, k=shape factor =0.89, **θ** =diffraction angle at maximum peak intensity. **β**=full width at half maximum of diffraction angle in radians. **λ= x ray wavelength.** (In X-ray diffraction, some prominent peaks were considered and corresponding d-values were compared with the standard.)

Figure 3 is the X-ray diffractogram of MgO nanoparticles obtained by calcining $Mg(OH)_2$.The product had peak at 44^0 assigned to 111 plane indicating complete transformation to MgO. The crystallite sizes were calculated using diffraction maxima from the half-width of diffraction peaks using Debye Scherrer equation. d-values were compared with standard JCPDS files and showed presence of pure oxides.

Figure 4 X-ray diffraction pattern of ZnO nanoparticles show sharp and well defined peaks.It indicates. the good crystallinity of synthesized material. The observed 2θ values are consistent with the standard JCPDS values(JCPDS No.80-0075) which specify the wurtzite structure of ZnO nanoparticles d-values were compared with standard JCPDS files and showed presence of pure oxides.

Figure 5 X-ray diffraction of synthesized copper oxide nanoparticles. is shown. X-ray diffraction pattern of pure copper oxide indicated that copper oxide in the form of CuO . (In X-ray diffraction, some prominent peaks were considered and corresponding d-values were compared with the standard [JCPDS file No. 05-661] X-ray diffraction shows that metal oxide is pure CuO**.**
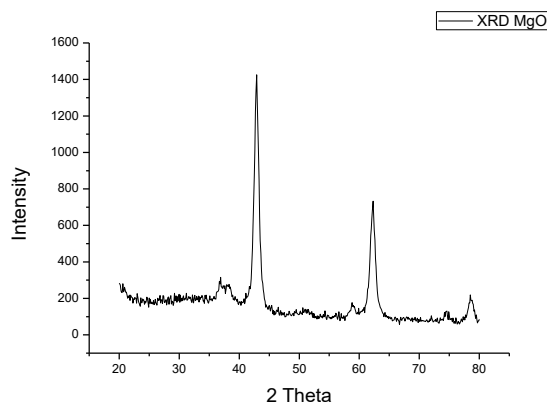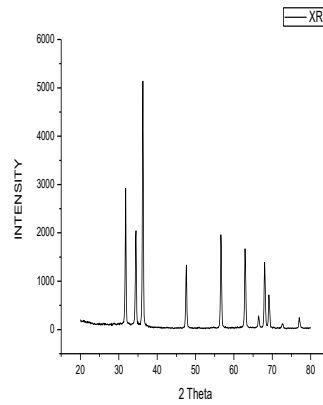

Figure 3: XRD pattern of MgO nanoparticles
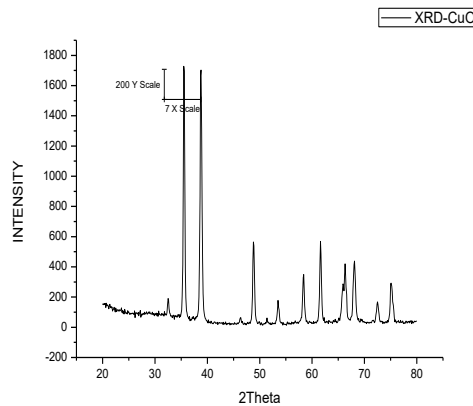
Figure4: XRD pattern of ZnO nanoparticles

Figure5: XRD pattern of CuO nanoparticles

Table 1: Crystallite Size Calculation from XRD

Sr No	Area	Centre	Height	CrystalliteSize	Lattice Strain
For MgO					
1.	1246.70	42.88	1164.70	10.44	0.0095
2.	559.90	62.245	541.27	11.75	0.0060
For ZnO					
1.	793.15	31.78	2734.00	37.3	0.0035
2.	1561.37	36.27	4960.00	34.79	0.0033
3.	653.00	34.45	2028.00	33.84	0.0036
4.	403.34	47.58	1263.00	35.63	0.0025
5.	631.77	54.64	1888.00	35.00	0.0023
6.	569.60	62.93	1536.00	32.91	0.0021
7.	485.87	68.027	1272.00	32.88	0.0020
For CuO					
1.	593.92	35.54	1744	32.08	0.0037
2.	702.13	38.78	1665	26.17	0.0042
3.	196.32	48.83	529	30.8	0.0028
4.	187.857	61.62	506	32.67	0.0022
5	247.439	66.191	298.38	14.96	0.0044

6	195.21	66.074	379.76	24.41	0.0026

SEM studies
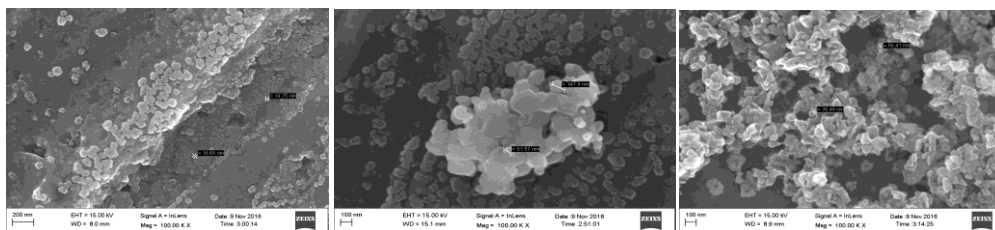

Figure 6: SEM MgO   Figure7: SEM ZnO   Figure8 : SEM CuO

SEM image shows the surface morphology of the oxide nanoparticles.

Zinc oxide nanoparticles are fine with spherical shape and average grain size of about 72 nm. MgO most of the particles are in the range 10-20 nm with spherical morphology. CuO particles showed rod shaped/ellipsoid morphology. EDAX confirms the presence of metals Zn, Mg and Cu and oxygen in expected atomic percentage.

IV.   MECHANISM OF DYE DEGRADATION

Degradation of dyes is due to the reason that nanoparticle catalysts used are semiconductor in nature which upon photo-illumination generate electron-hole pairs. The generation of electron-hole pairs is responsible for the photo-degradation of different dyes. Further the photo-degradation of dyes was found to be dependent on initial dye concentration.

Since initially it is the adsorption of dye on the nanoparticles followed by the photo-catalytic degradation process, therefore the possible explanation could be that at this dye concentration maximum number of active sites on the surface of catalyst is available for adsorption of dyes. As the concentration increases, the active sites for adsorption present on nano-particles get blocked thus the rate of dye degradation decreases.

V.   CONCLUSION

- Among two methods of preparation the hydrothermal method seemed to be better than the wet chemical method with respect to particle size. Photo-degradation of all the dyes was found to be dependent upon the concentration of the catalyst (In this case metal oxide nanoparticles)..
- EBT degradation was faster by ZnO than MgO whereas MB degradation was faster by ZnO nanoparticles.90% MB is adsorbed at 665nm by MgO in 6 hrs Whereas 80-85% EBT was adsorbed by ZnO at 620nm during a time interval of 4hrs.

VI.   ACKNOWLEDGEMENT

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