Enhancement of Visible Light Photocatalytic Activity of ZnO/ MnO_2 nanocomposites

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***Abstract*: ZnO nanoparticle and ZnO/MnO_2 nanocomposite were synthesized by using simple sol-gel method and were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared (FT-IR) spectroscopy. X-ray diffraction reveals that the prepared ZnO/MnO_2 nanocomposite exhibit hexagonal ZnO and ortho rhombic MnO_2. The strong peaks of the Zn, Mn and O elements were observed in the EDX spectrum. The FT-IR spectra shows the characteristic peaks of Zinc Oxide (stretching Zn-O) between 400cm^{-1} to 590cm^{-1}and absorption peaks in 1633cm^{-1} described to the OH bending vibrations combined with Mn atoms. The photocatalytic performances of ZnO/MnO_2 nanocomposite was investigated for the degradation of methylene blue (MB) aqueous solution in direct sun light. The antibacterial activity of the prepared ZnO nanoparticle and ZnO/MnO_2 nanocomposite were carried out against both Staphylococus aureus, Klebsilla pneumonia, Bacillus subtilis, and E.coli bacteria and the antibacterials activity of ZnO/MnO_2 nanocomposite was reported to be better than ZnO nanoparticle. So ZnO/MnO_2 can be considered as strong antibacterial agent.**

***Keywords*: Antibacterial, Methylene blue, Nanocomposite, Photocatalytic, Sol- gel.**

I. INTRODUCTION

In the field of nanocomposite synthesis, from different metal oxide notable improvements have been recently accomplished and lots of efforts have been done to control their size, composition and uniformity[1]. A Nanocomposite is a composite material in which one of the component has at least one dimension that is around 10^{-9}m[2]. Nanosized ZnO is a very important material with a wide range of applications[3]. Zinc oxide based nanocomposites are very interest of researchers for the direct band gap of 3.2 ev, and exciton binding energy of 60 Mev[4]. which means that it can only absorb ultra violet lights and the utilization of solar energy is low. Zinc oxide based nanostructures have wide range of high tech applications ***eg :*** Surface acoustic wave filter, Photo detectors ,Photo diodes , gas Sensors ,optical Modulators wave guide, Electrochemical Super Capacitors , fuel cell and Batteries[5]. ZnO has Potential applications in the production of UV Light emitters, transparent high power electronics, piezoelectric transducers and solar cells. The merits of zinc Oxide is, it has low maintenance cost, high surface to adsorption ratio and it remove heavy metal ions and it has high stability.

In recent years MnO_2 has considerable research interest due to their physical and chemical properties and broad applications in catalysis, Ion exchange and energy storage devices. MnO_2 has also been widely used in Duracell (alkaline) based barriers, Photo catalytic activities and electrolysis[6]. MnO_2 has been also found to have important applications in water cleaning [7]. MnO_2 is an important functional metal oxide which has several applications in various fields such as artificial oxidase, Inorganic Pigment in ceramies and electrodes for super capacitors[8]. MnO_2 with the advantages of environment friendliness, natural abundance, low cost and efficient charge discharge carriers to be promising electrode materials for super capacitors[9]. ZnO and MnO_2 nanoparticles are two kinds of technologically important semiconductors because of potential application in advanced systems. ***eg :*** photonic devices, sensors, solar cells etc[10]. ZnO/MnO_2 based composites are also antibacterial agent under UV Light. Several types of Zinc oxide nanostructures such as nanowires, nanobelts, nanoribbons, nanorods, nanotubes were prepared by various hydrothermal synthesis, chemical vapour deposition, spray pyrolysis and sputter deposition. However ZnO/ MnO_2 nanocomposite were prepared by solgel method, solution mixing process, melt blending process, Hydrothermal method, wet chemical method, micro emulsion synthesis, spray drying and solution method[11]. The Sol- gel technology has more advantages than other techniques for preparation of mixed oxide nanocomposites. It is an environmental friendly method. It is a wet chemical technique widely used in the formation of nanocomposits. Sol – gel process involves the conversion of precursor solution usually metal salts (or) (Metal alkoxide) into nano structured inorganic solid through inorganic polymerization reactions catalyzed by water. The ZnO – MnO_2 nanocomposite has been wide applications in photocatalytic studies which Composed of two parts photo and catalysis which used light to activate a substance which modifies the rate of a chemical reaction without being involved itself. The sunlight is applied in the dye solution toxic substances are Destroyed (or) neutralized. The positive hole of zinc oxide break water molecule to form Hydrogen gas and Hydroxyl Radical. The negative – electron reacts with oxygen molecule to form superoxide anion. The ZnO act as a very good photo catalyst[12]. It has high ability to break molecular bonds, it is inexpensive and abundant. Photocatalyst Reaction kill the bacteria inside the water with oxidation process. Photocatalyst convert Hazardous Oxygenic contaminants and Bacteria into Harmless substance CO_2 and H_2O.

II. EXPERIMENTAL METHOD

The nanosized ZnO & ZnO/MnO_2 nanocomposite were prepared by sol-gel method.About0.9M NaOH solution Was heated at 55^0c and the same volume of 0.45M solution of zinc nitrate tetrahydrate was added dropwise with vigorous stirring. After complete mixing the ZnO nanoparticles were allowed to preceipitate. ZnO nanoparticles were separated and purified by repeated washing with water and ethanol. The powdered ZnO nanoparticles were calcinated at 500^0c for 2 h[13].

About 2:3 M ratio of $KMnO_4$ and $MnSO_4$ solution was stirred for an hour. Next ZnO nanoparticles were added to the solution. The solution was heated at 160^0c for 3h for the formation of ZnO – MnO_2 Nanocomposite [14].

III. CHARECTERIZATION

The crystal structure of the ZnO & ZnO / MnO_2 nanocomposites was investigated by X-ray Diffraction using ultra Microtome L: Leoca UCT X-ray diffractometer. The surface morphology and compositional analysis of the nanocompositional analysis of the nanocomposites were studied by scanning Electron Microscopy (SEM) Joel 6390La/OXFORD XMXN filament: tungsten, EDAX resolution 136 ev EDAX detector area $30mm^2$ Elemental mapping. the Molecular vibration of ZnO / MnO_2 nanocomposites were analyzed with Fourier Transformer Infrared (FTIR) on Thermo Nicolet Avtar 310 $4000cm^{-1}$ to $400cm^{-1}$ Resolution $4Cm^{-1}$.The optical transmittance was recorded using A gilent cary 5000, 200nm to 3000nm DRS integrating sobere diameter 150mm angle of incidence 8^0. The optical properties of the samples were investigated by measuring the UV – Vis absorbance spectra at room temperature.

The photo catalytic activities of ZnO, ZnO/ MnO_2 powders were evaluated by measuring the degradation of Methylene Blue (MB) in water under the UV region. The potential toxicity of nano – sized ZnO and ZnO/ MnO_2 were investigated using both Gram positive and Gram negative bacteria as test organisms.

IV RESULTS AND DISCUSSION

A. X-ray Diffraction studies

The X-ray diffraction patterns of the ZnO nanoparticle and ZnO/MnO_2 nanocomposite was shown in Fig. 1 from the XRD pattern the sharp peaks indicate that the ZnO/MnO_2 nanocomposite were crystalline in nature. Average particle size was 25nm to 30nm. The ZnO/MnO_2 nanocomposite shows hexagonal ZnO and Orthorombic $MnO_{2.}$ The crystalline size (D) is calculated using scherrer's equation $D=\frac{0.9\lambda}{\beta Cos\theta}$Where D is the grain size of the wavelength of the X-ray radiation, β is the full width at half maximum (FWHM) intencity of the diffraction peak and θ is the diffraction angle. Crystalline size of the prepared ZnO-MnO_2 nanocomposite is

6-14nm range. From the diffraction patterns it was seen that, Most peaks observed are matching with hexagonal structure of ZnO and some matched with MnO_2 to Orthorhombic structure The diffraction peaks of ZnO nanoparticle located at 31.781,34.448,36.266,47.559, 56.585,62.850 and the corresponding planes are 100,002,101,102,110,103,112 and the diffraction peaks of ZnO–MnO_2 nanocomposite are located at 31.54,32.949,34.350,36.351,38.459 etc and the corresponding planes are100,110,002,101,220
respectively.

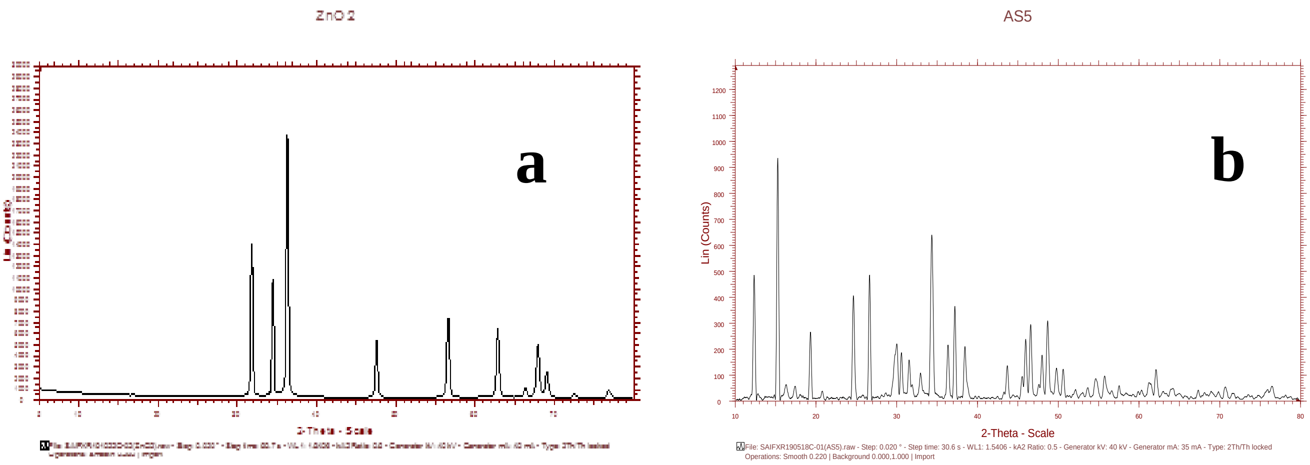

Fig . 1 (a) XRD Patterns of ZnO (b) XRD Patterns of ZnO / MnO_2

B. Morphological property of ZnO, ZnO/MnO_2 nanocomposite

SEM images of the samples are shown in Fig. 2 It can be seen that the powder was composed of primary particles are spherical shape and also some hollow shape[15].The morphology of ZnO-MnO_2 nanocompositbecomes more smooth and homogenous.

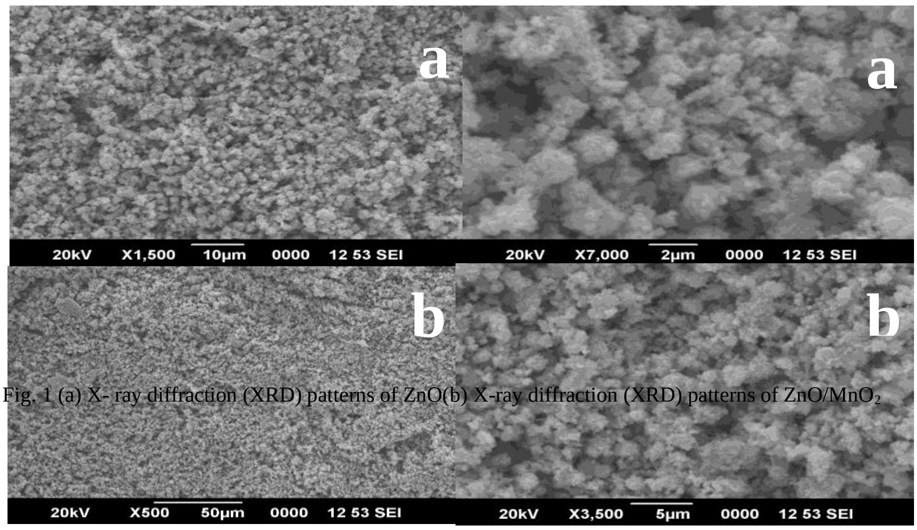

Fig . 2 (a) Scanning electron microscope (SEM) images of ZnO (b)Scanning electron microscope (SEM) image of ZnO/MnO_2

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C. Energy dispersive X-ray spectroscopy

The chemical composition of the films was examined by using (EDX) analysis for confirming the presence of manganese, Zinc and Oxygen[16]. Fig. 3(a) shows the EDX spectrum of ZnO, ZnO/MnO_2 prepared by Sol-gel method. The main peaks observed in the spectrum related to Zn and Oxygen. The elemental analysis of ZnO with two sharp peaks was found to have weight percentage of 85.85 of Zinc and 15.15 percentage of Oxygen. The EDX spectrum of ZnO/MnO_2 nanocomposite, the elemental mapping of ZnO/MnO_2 with major peaks was found to have weight percentage of 31.8 percentage of Zinc and 28.8 percentage of Oxygen. 25.49 of Manganese. This confirmed the formation of ZnO nanoparticles and ZnO/MnO_2 nanocomposite in Sol-gel method.

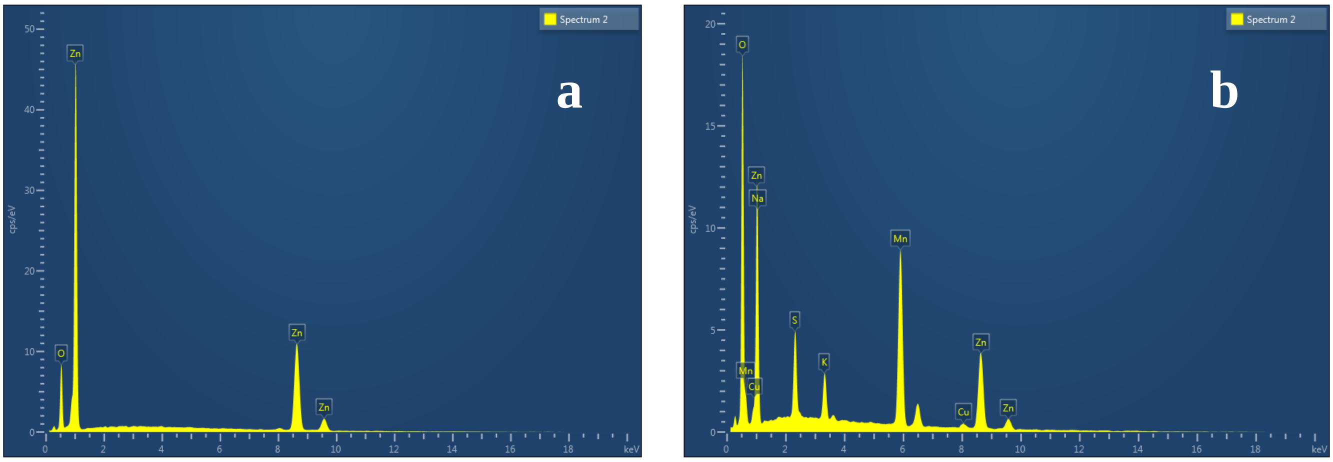


Fig . 3 (a) energy dispersive X-ray spectroscopy (EDX) pattern of ZnO, (b) energy dispersive X-ray spectroscopy (EDX) pattern of ZnO/MnO2

TABLE I

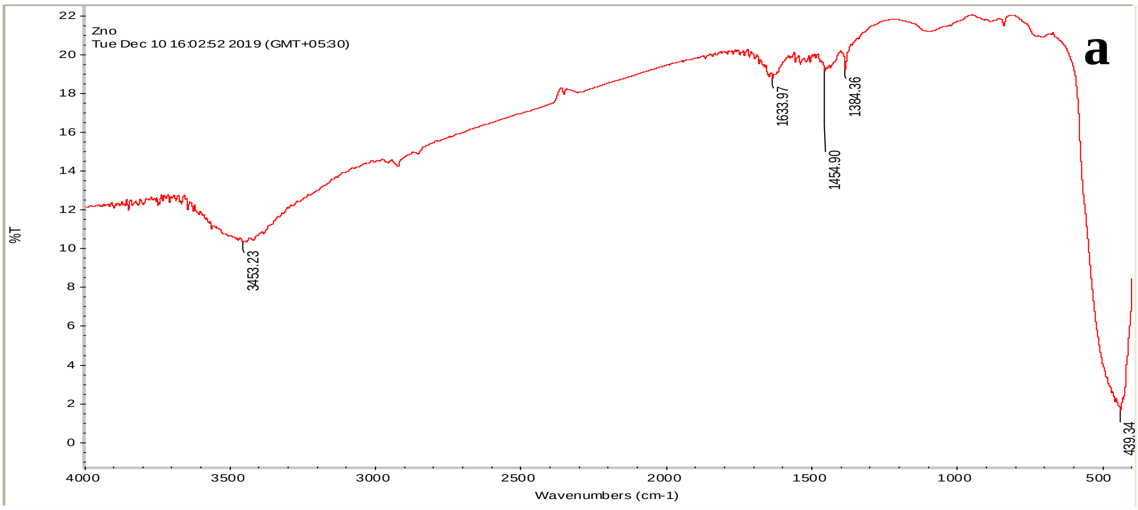
Nanoparticles	Element	Weight%	Atomic%
ZnO	O	15.15	42.18
	Zn	85.85	57.82
ZnO+MnO_2	O	28.8	55.96
	Na	5.62	7.6
	S	4.15	4.02
	K	2.75	2.18
	Mn	25.49	14.43
	Cu	1.4	0.68
	Zn	31.8	15.12

Table I EDX data of ZnO &ZnO/MnO_2 Nanoparticles

Table I shows that the synthesized nanocomposite is associated with small amount of impurities of Na, S, K and Cu.

D. FT – IR Spectral Study

The Fig. 4 illustrate a series of absorption of bands in the range of 400-4000cm^{-1}.The region below 1500$cm^{-1}$is important for metal oxides absorption bands due to inter atomic vibration .The absorption bands of MnO_2 nanoparticle occurs at 525cm^{-1} which correspond to MnO stretching vibration. Whereas the sharp peak at 439cm^{-1} is ascribed to ZnO stretching bonds. The peaks at 1633cm^{-1}and3453cm^{-1} which corresponds to O-H bending and stretching for ZnO-MnO_2 nanocomposite respectively. The peak at 1384cm^{-1} is attributed to symmetric C-H bending vibration .The band at 3412cm^{-1} indicates the presences of asymmetric stretching OH band. This shows FT IR results of ZnO/MnO_2 nanocomposite respectively[17].



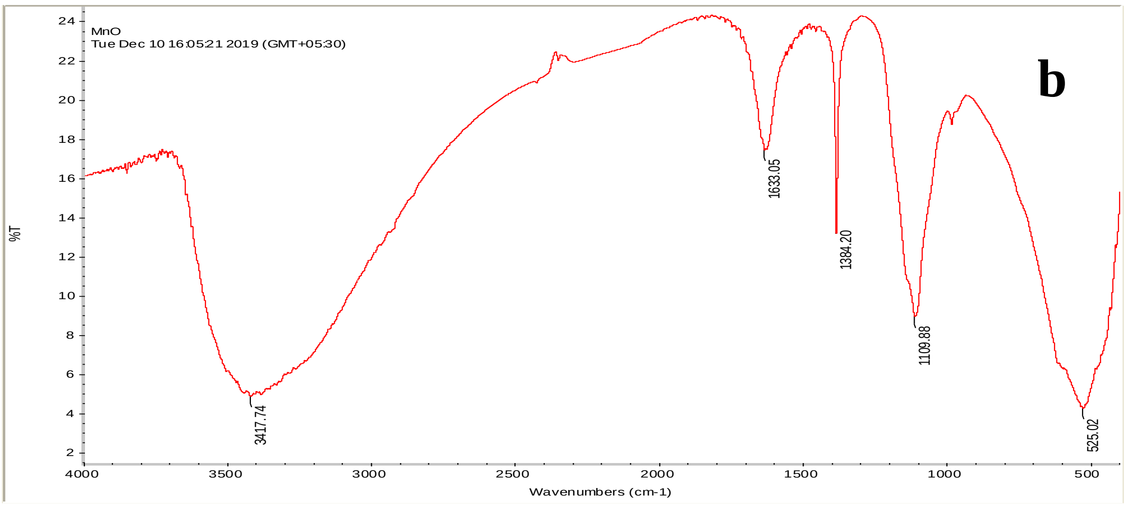


Fig .4 (a) FT-IR spectra for ZnO, (b) FT-IR spectra for ZnO/MnO_2

E. Photocatalytic Dye degradation

The photo degradation of Methylene Blue(MB) by ZnO nanoparticle and ZnO/MnO_2 Nano composite are shown in Fig. 5 The photo catalytic activity of ZnO, ZnO/MnO_2 Nanocomposite were carried out using methylene blue dye under direct sunlight .The concentration of MB decreased with increased visible light irradiation time and it confirms that the degradation of MB dye has taken place in the presence of ZnO/MnO_2 Photo catalyst. About 80% of the dye effluent was degraded within 60 minutes using ZnO/MnO_2 Nanocomposite whereas ZnO nanoparticle degrade it by 50 min and hence the ZnO nanoparticle degrade the dye effectively than the nanocomposite. However both ZnO nanoparticle & ZnO / MnO_2 nanocomposite are good photo catalyst under sunlight [18].

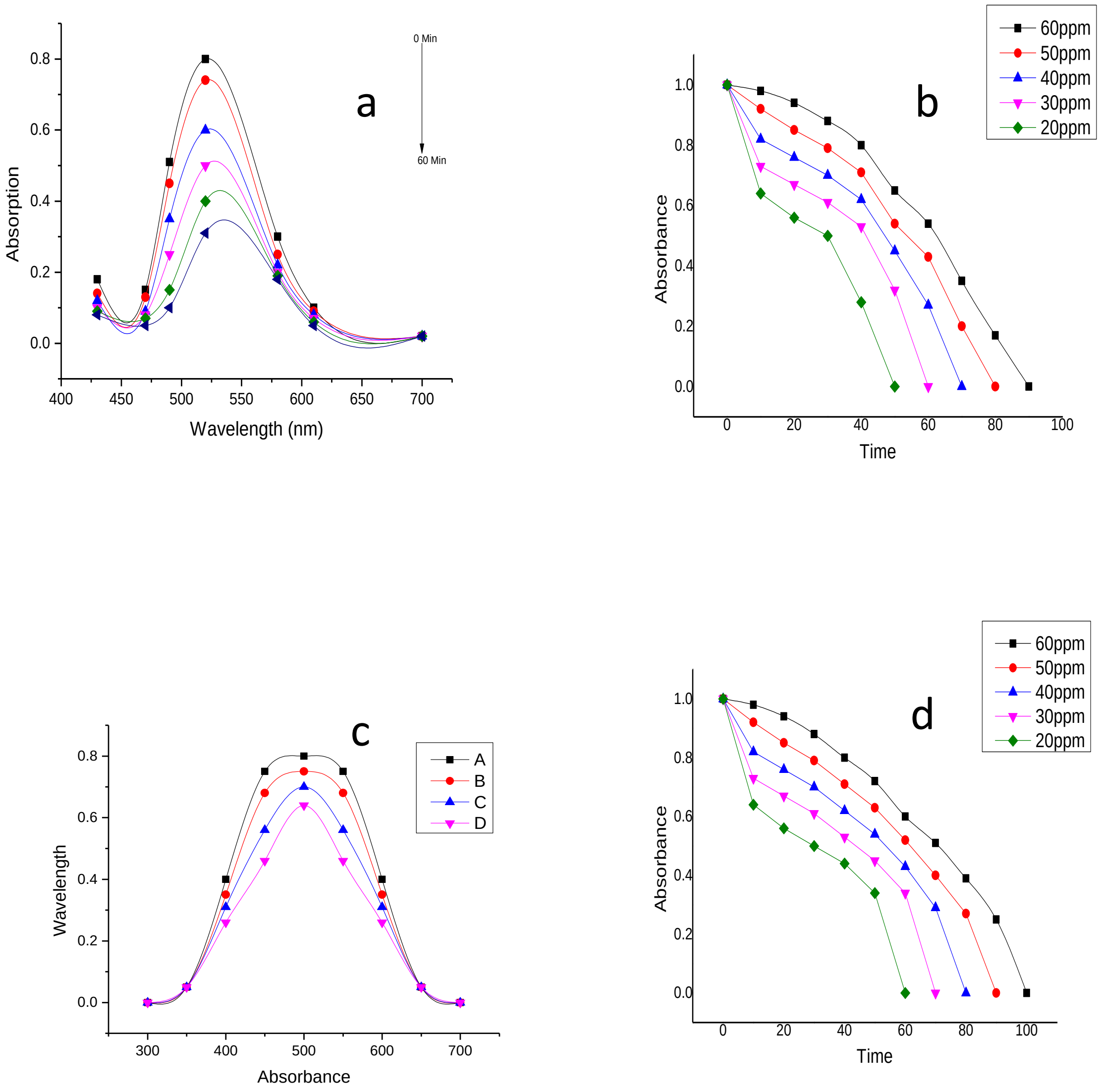


Fig. 5 Photodegradation of MB by ZnO, ZnO / MnO_2 using sun light

F. Anti bacterial activity

There is a considerable interest in the expansion of antibacterial agents for usage in the hygiene industry biomedical food and health. Metal based nanocomposite display high-biological activity against different fungi, bacteria and viruses. ZnO nanoparticle and ZnO –based nanocomposite have been extensively used for diverse biomedical applications, including antidiabetic, anticancer, drug delivery and anti-inflammatory applications.

Fig . 6 Anti Microbial activity of ZnO, MnO_2 & ZnO/MnO_2 Nanocomposite

Table II *ANTIMICROBIAL RESULTS*

Sample Code	Bacteria Strains Name			
	Staphylococcus Aureus (G+)	Bacillus Subtilis (G+)	Klebsilla Pneumonia (G-)	E – Coli (G-)
ZnO	15	11	12	10
MnO_2	18	12	14	12
$ZnO+MnO_2$	25	15	18	14
PC	20	19	26	16
NC	-	-	-	-

Table II Antimicrobial Results of ZnO,MnO_2, ZnO/MnO_2

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Keys

PC	-	Positive Control (Streptomycin)
NC	-	Negative Control
	-	No Zone
Mm	-	Millimetre
G+	-	Gram Positive Organism

From the table it is clear that the ZnO/ MnO_2 nanocomposite shows more activity than the ZnO and MnO_2 nanoparticles. The Zno / MnO_2 nanocomposite inhibits the bacterial growth by disrupting cell morphology changes and function leading to cell death. The reason for the antibacterial activity is that when the $Mn^{2+}$and Zn^{2+} released by ZnO/MnO_2 comes into contact with the cell membranes of the microbe, the cell membranes with negative charge and Mn^{2+} and Zn^{2+} with positive charge mutually attract, and the Mn^{2+} and Zn^{2+} penetrates into the cell membrane and reacts with sulfhydryl groups inside the cell membrane. As a result the microbe becomes so damaged that the cells lose the ability of growth through cell division, which leads to the death of the microbe.

V CONCLUSIONS

ZnO-MnO_2 nanocomposite was synthesized and characterized by XRD, SEM-EDX and FT-IR techniques. The crystalline structure of the samples was studied through the XRD pattern. The Morphology of the samples was analysed by SEM. The EDX technique which was employed to ensure the presence of Zn and Mn in the prepared samples. The photo catalytic activity of ZnO and ZnO/MnO_2 can decompose Methylene Blue. It can be depend with suitable metals at different concentrations. It is clear that doping of Manganese in ZnO enhances immobilized photocatalysts for water and environmental detoxification from organic compounds ,inorganic compounds like arsenic and bacteria also, the antibacterial activity of the prepared ZnO, MnO_2 base nanocomposite against both S.Aureus and E.Coli bacteria. In comparison the antibacterial activity ZnO/MnO_2 was reported to be better than ZnO. So ZnO/MnO_2 can be considered as a strong antibacterial agent.

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