Journal of Basic and Environmental Sciences 2 (2015) 19 – 35 **ISSN 2356-6388**

Physical and antimicrobial studies on paper coated with nano ZnO

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Article Information

Received; 12 May. 2014
In Revised form; 28 May 2014
Accepted; 28 May 2014

Keywords:

Nano ZnO
Antimicrobial
paper

Abstract

Zinc oxide (ZnO) is a potential pigment material for paper coating to impart brightness and better printing properties. Nano–ZnO, due to its extremely small size, gives paper coating pigment a high covering power. In this work, zinc oxide -soluble starch nano composites was prepared by a simple method using zinc acetate and oxalic acid and soluble starch as stabilizing agent. The properties of paper before and after coating with nano zinc oxide were studied. The brightness and tensile of nano zinc oxide coated paper showed significant improvement than that of bulk –ZnO coated paper. In addition, the nano-ZnO coated paper showed excellent anti-fungal and luminescence properties and resistance to absorb paraffin oil than that the paper treated by bulk ZnO that are much essential to enhance the life of paper.

Abstract

Key words:-.

1-Introduction

The surface and coating colours improve the printing properties of paper. Ink absorption, surface strength, opacity, stiffness and gloss are all improved through a desirable spatial arrangement of pigment coating components in the coating layer. This is achieved by using appropriate combinations of pigment, binder and thickener as well as additives for control of pH, friction, brightness and pigment dispersion. The most commonly used pigments are calcium carbonate and kaolin clay. Latex is used as a water-insoluble binder and carboxymethylcellulose (CMC) is commonly used as a co-binder and thickener. Recently, ethyl hydroxyethyl cellulose (EHEC) has been investigated as a co-binder and thickener [1].

The creation of water-repellent barrier layers is essential for packaging materials including porous and absorbent textiles, non-wovens, paper or paperboard. The surface properties and wettability of those substrates can be influenced by physical (drying, calendaring) and chemical (impregnation, coating) treatments, forming a first barrier against water adsorption. Hydrophobic barrier coatings are most likely applied by means of extrusion [2], lamination [3] or dispersion coating [4]. The latter methodology is preferred due to better repulpability and compatibility of the aqueous system.

Paper and paperboard have been increasingly used as a packaging and printing material since they are renewable, recyclable and biodegradable. Now days more than 2.5 million tons of paper and paperboard are used worldwide in food packaging. Packaging for food not only provides a long shelf life and good protection, but also prevents food from various risks including microbial spoilage. At present, antimicrobial packaging materials are being developed to solve many problems associated with food distribution and safety. In fact, antimicrobial packaging is considered as active packaging that can be defined as a mode of packaging in which the package, the product and the environment interact to prolong shelf life or enhance safety or sensory properties, while maintaining the quality of the product [5].

Due to the organic, fibrous, hydrophilic and highly porous nature, paper is easily subjected to microbial attack, ultraviolet degradation and higher water vapour transmission rate. In addition, the sizing agents like starch that are applied to the surface of paper make the condition still worse. To circumvent these problems new mineral fillers are being tried as paper coating to meet the improved quality standards of high-grade papers. The demand for high quality print papers has been becoming always higher in particular for home use with the rapid spread and advancement of digital cameras. Use of nano pigments with an appropriate binder in the coating formulation will help to fill the micro-voids and offer better barrier properties. Since the first half of 2006, colloidal titania is exploited commercially by Nippon® and Ahlstrom® paper manufacturers in Japan to produce photocatalytic papers. Here, apart from improvement in opacity and whiteness, colloidal titania imparts deodorizing and antimicrobial properties by photocatalysis. However, its cost and UV-dependent photocatalysis limits its usage to printing papers on a commercial scale. As an alternative, nano-ZnO is a low cost material exhibiting excellent optical and chemical properties with broad range of applications for antimicrobial and UV-protecting properties [6].

Recently, coating of nano- ZnO on paper surface without the aid of binders is reported. Though this nano coated paper showed antibacterial activity against the bacterium Escherichia coli, commercial application is not attainable as the coating is ultrasound assisted deposition process [7]. From the previous discussion, this work focuses on studying the physical properties of nanoparticle coated papers and illustrates the interactions between the nanoparticles and cellulose fibers as well as both antibacterial and UV- protecting properties. This work also describes our attempt to use nano-ZnO as pigment to coat pre-formed paper to impart the above mentioned functional properties without affecting its innate parameters.

2-Material and methods

Materials: - Paper of Rakta Company 60, 70 and 80 gm were used in this study. All chemicals used are chemical reagent grades.

2.1-Synthesis of nano ZnO

All the reagents are of analytical grade and used without further purification. Zinc acetate ($Zn(CH_3COO)_2.2H_2O$) and oxalic acid ($H_2C_2O_4.2H_2O$) were used as raw materials to prepare nano zinc oxide by using a method reported by K. G. Kanade [8] where 300 ml of 0.15 M oxalic acid solution was added slowly, (drop by drop), to 300 ml of 0.1 m zinc acetate solution under stirring for 18 hour. A white precipitate of zinc oxalate was obtained, which was filtered and washed with water several times. The powder was then dried at 120°C for 30 minutes and finally heated for 30 minutes at 450°C to form ZnO.

$$\mathbf{Zn(CH_3COO)_2.2H_2O+H_2C_2O_4.2H_2O \rightarrow ZnC_2O_4.2H_2O+2CH_3COOH+2H_2O}$$

$$\mathbf{ZnC_2O_4.2H_2O+1/2O_2 \rightarrow ZnO+2CO_2+2H_2O}$$

2.2-Coating of paper with ZnO

The paper (60, 70 and 80 gm) were coated by pure bulk and nano ZnO as well as (50: 50 wt %) ZnO. Oxidized starch filler (78.0 g) was dissolved in 100 ml distilled water and processed under continuous agitation at temperature 90-95 °C, for 15 min., to make it fully gelatinized. Then the pigment slurry was prepared, by dispersing 0.67 gm of dispersant in to 29.8 ml distilled water and stirring to get homogeneous solution in this solution 57.73 g ZnO nano plus 28.87 g china clay were added under constant stirring to the formulation became a uniform thick paste. Then freshly prepared oxidized starch solution and styrene butadiene latex were added to the pigment pasta. [9] The same method was used to prepare paper coated with 50 wt. % bulk ZnO.

Abbreviations: The paper, paper coated with 50% bulk ZnO, paper coated with 50% nano ZnO, paper coated with pure bulk ZnO and paper coated with pure nano ZnO will be donated as P, P_{bZ5}, P_{nZ5}, P_{bZ} and P_{nZ}.

2.3- Characterization of coated paper by bulk and nano ZnO.

The crystalline phases for all investigated samples were identified by X-ray diffraction (XRD) using a Philips X'Pert Pro Super diffractometer with Cu Kα radiation (λ = 1.54 Å). The sample was scanned from 20 to 70° (2θ) with a scanning rate of $0.1° s^{-1}$.

Scanning electron microscopy (SEM), JEOL JEM-100CXII was taken to examine the morphology and dimension of the investigated samples using conductive carbon paint.

Thermogravemetric analysis was carried out with the aid of Thermoanalyzer (D-50) shimadzu, Japan. Samples were heated at a rate of 10 °C/min in a steam of dry nitrogen. The experiments were carried out in the temperature range between room temperature and 800 °C.

Infrared reflection measurement of the investigated samples was carried out on a BRUKER FTIR (vector 22), made in Germany, in rang of 400 – 4000 cm^{-1}.

Fluorescence spectra were recorded in Perkin Elmer LS55 spectrofluorimeter with the help of solid sample holder having quartz window. The entire scanning was done at the speed of (100 nm/min). The data were analyzed using the FL Winlab software.

Resistance of paper to absorption of paraffin oil was tested using the following method:- drop of paraffin oil is placed on treated and untreated papers. The time required for the oil to spread is taken in a definite area as an indication of the rate of penetration in to the papers**.**

The effect of heat on the properties of paper were studied by heating the samples in an electric oven, equipped with circulating hot air, at different temperatures namely 100, 120, 140 and 160 ^{o}C and different periods. Samples were allowed to cool in desiccators. The breaking length and brightness of these samples were measured.

Tensile breaking and brightness of the studied samples were analyzed using standard methods reported in table 1.

Table1:- Standard methods followed for paper analysis

Properties	***Standard methods***
Tensile breaking strength	TAPPI-404 OS-1974 [10]
% Brightness	TAPPI- 525 su-72 [11].

Antibacterial and Antifungal Activity of the Synthesized Samples were studied using **t**he well-plate methods (diffusion methods) was followed with some modification [12]. The spore suspension of the test organisms (gram negative bacteria) such as Escherichia coli, Serratia marcescens and Agrobacterium species, and (gram positive bacteria) such as Bacillus megath-erium, yeast (Candida albicans), and fungi, (Aspergillus niger) was prepared in previously sterile and checked inoculating flasks, each contained 50 ml of previously and checked medium of the following composition for the target test organisms:-

For bacteria;-

1. Nutrient broth medium: (Beef extract 3.0 g, Peptone 10.0 g, H_2O 1000 ml). For yeast and fungi, used Czapeks Dox broth medium: (Sucrose 30.0 g, $MgSO_4$ 0.5 g, KCl 0.5 g, $FeSO_4$ 0.01 g, $NaNO_3$ 3.0 g, K_2HPO_4 1.0 g, H_2O 1000 ml).

2. A solid medium containing the following ingredients for bacteria (g/l) (Beef extract 3.0 g, Peptone 10.0 g, Agar 20.0 g, H_2O 1000 ml), and for yeast and fungi (Sucrose 30.0 g, $MgSO_4$ 0.5 g, KCl 0.5 g, $FeSO_4$ 0.01 g, $NaNO_3$ 3.0 g, K_2HPO_4 1.0 g, Agar 20.0 g, H_2O 1000 ml), was sterilized and divided while warm (50 :55 °C) in 15 ml portions among sterile Petri-dishes of 9 cm diameters.

3.0.2 ml of the spore suspension was surface placed on the surface of the solid medium in the Petri dished and spread all over the surface.

4. 0.1 gm of the test substances was weighted.

5. In Petri dishes containing the culture of one of the chosen, one well of 10 mm diameter was made in the centre of the dish. It was marked on the bottom of the dish, and filled with the 0.1 gm of the test substances.

6. The Petri dishes were incubated at 5 °C for 2 hrs to permit good diffusion and then transferred to an incubator at 37 °C for 48 hrs for bacterial test organisms, and at 30 °C for 72 hrs for yeast and fungi test organisms.

7. Antimicrobial activities were observed after 48 hrs of incubation time for bacteria at 37 °C, and after 72 hrs of incubation time for yeast and fungi at 30 °C. The zones of inhibitions were measured in mm**.**

3- Results and discussion

3.1-XRD of uncoated and coated paper by Nano ZnO

Figures (1-2) show the X-ray diffraction pattern of nano ZnO, base paper and the coated papers with each of nano ZnO as well as bulk-ZnO to determine the crystalline phases and further confirm the presence of ZnO on the paper . The XRD pattern of the prepared ZnO sample formation in Fig (1); shows typical peak patterns characterized to high crystallinity ZnO with the hexagonal wurtzite structured (P63mc) as indexed in the standard data (JCPDS Card No. 36- 1451, a=3.249 Å and c=5.206 Å) [13]. No characteristic peaks for impurities were detected indicating the formation of pure ZnO.

The composition of the satisfied paper in general is very complex. However the major composition of paper includes cellulose, $CaCO_3$, silicates, thickeners, and binders. For simplicity, we have focused on tracing major components like cellulose and $CaCO_3$ in the XRD spectra. The XRD spectra of blank paper, Fig. (2-a) show peaks corresponding to amorphous and crystalline regions cellulose as well as $CaCO_3$. [14]

The XRD pattern recorded for paper coated with bulk ZnO (P_{bZ}) is shown in Fig. (2-b). It shows characteristic peaks of ZnO hexagonal phase at 2θ values of (31.8, 34.4, 36.2, 47.5, 56.5 and 62.9^{o}). The rather narrow diffraction maxima indicate the high crystallinity of ZnO. The remaining peaks in the spectra are attributed to cellulose and $CaCO_3$. The bulk- ZnO as a coating pigment reduced the intensity of cellulose peaks to~60%.

The XRD pattern recorded for paper coated with nano – ZnO (P_{nZ}), Fig. (2-c) shows peaks at 2θ value of (31.8, 34.4, 36.2, 56.6, 62.9 and 67.95^{o}) characteristic for crystalline ZnO nano particles [15]. The peaks assigned to diffractions from various planes corresponding to hexagonal close packed structure of zinc oxide. The broading of peaks observed is mainly due to the nano size effect and its low crystallinitty. The remaining peaks in the spectra are attributed to cellulose, $CaCO_3$ and $Al_2Si_2O_5(OH)_4$ which is a monoclinic phase and appear at 2θ value of (12.4, 19.8 and 24.9^{o}) [14]. The peaks at different crystal planes of nano ZnO matches exactly with that of bulk ZnO. Nano- ZnO reduced the intensity peaks of the cellulose by about ~20%. This refer to the transparent nature of nano ZnO coating and thick opaque nature of bulk- ZnO coating on the paper.

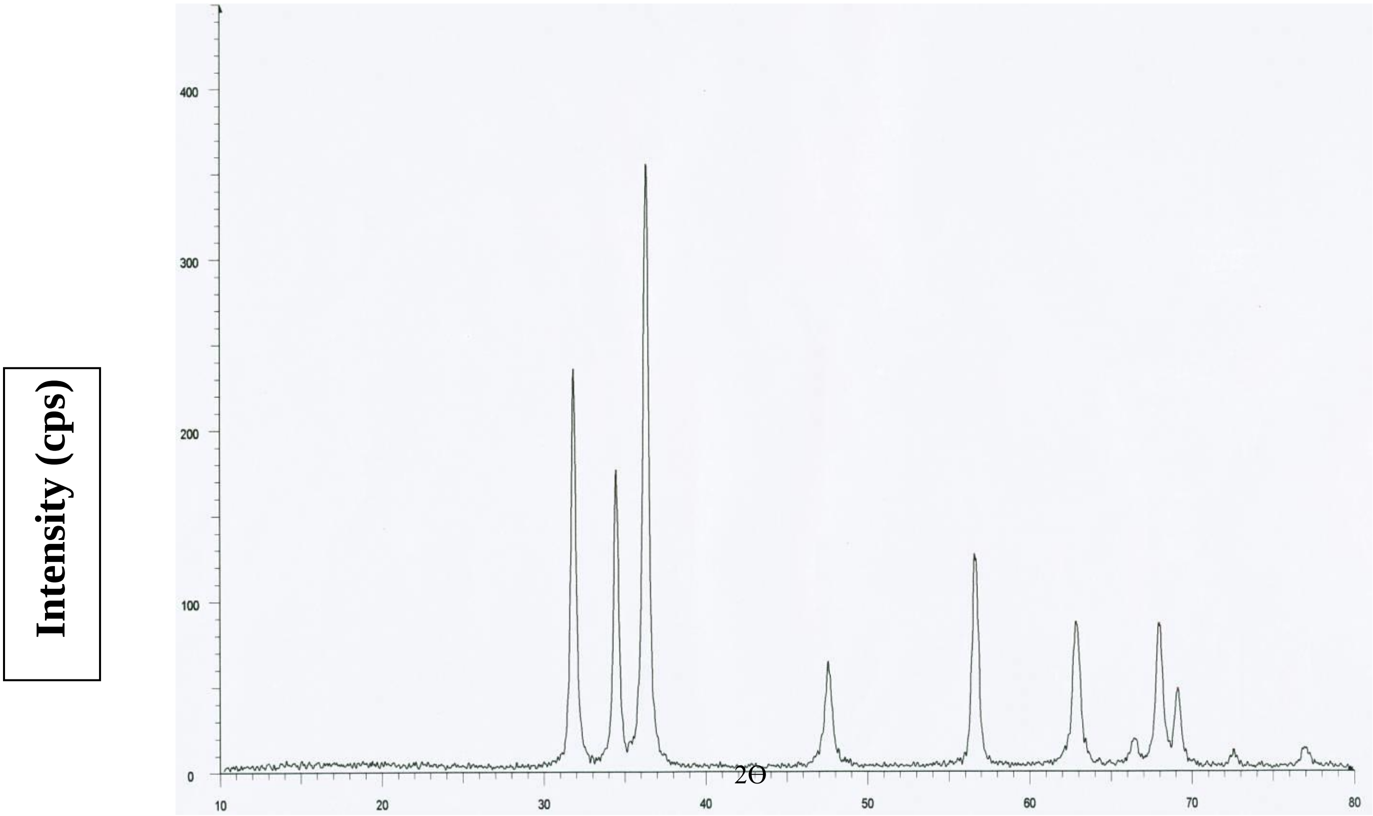

Fig. (1). X-ray diffraction spectra of nano – ZnO.

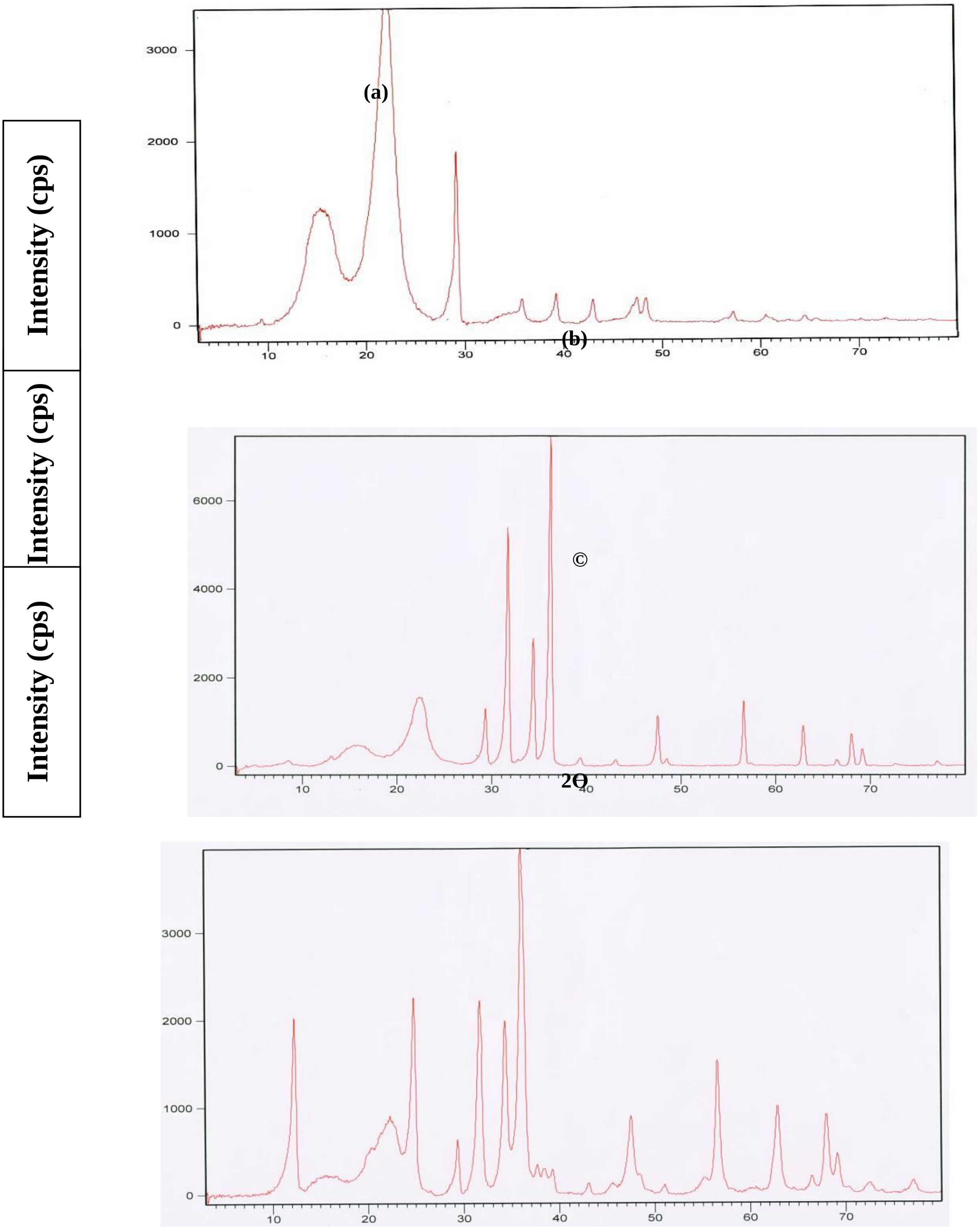

Fig. (2) XRD spectra of base paper (a), paper coated by bulk- ZnO (b) and paper coated by nano- ZnO (c).

3-2- Scanning electron microscope (SEM):-

The SEM morphology of the nano crystalline ZnO sample is shown in Fig. (3). The image of nano ZnO sample shows deformed spherical particles with cotton like structure.

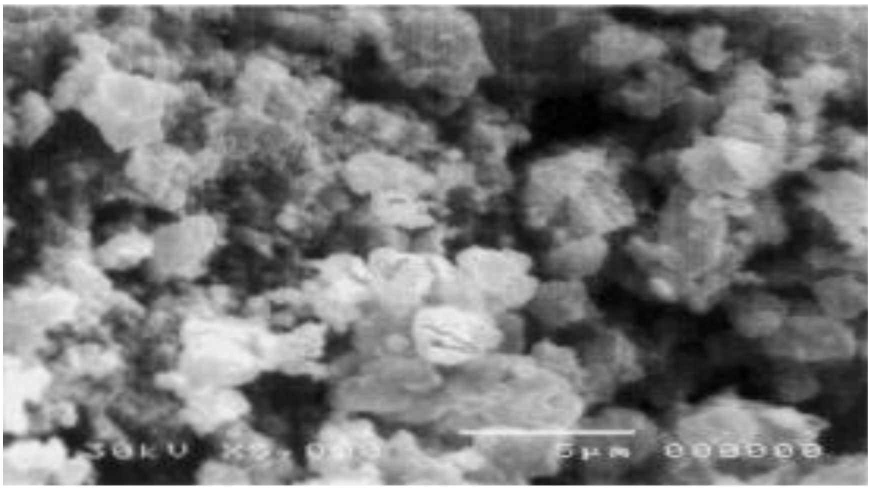

Fig. (3):- Scanning electron micrographs of nano ZnO.

The morphology of both uncoated and coated papers with ZnO is shown in Fig. (4.a-c).The uncoated base paper shows cellulose fibre bundles and accumulated fillers such as calcium carbonates Fig. (4-a), it also shows the extensive interwoven cellulosic fibrils. The complete absence of visible cellulose fibrils in the SEM images of coated papers Fig. 4(b-c) confirms the uniform distribution and coverage of ZnO. Fig. (4-c) shows different morphologies of nano zinc. The absence of cellulose fiber in the image indicates that nano particles of ZnO effectively cover the fibrous substrate of paper and flatten the microporosity of the fibrous substrate. This behaviour means that nano ZnO crystals effectively completely covering the fibers and/or pigments and smooth the surface irregularities, also nano ZnO particles adhere into pores and have lower tendency to migrate and fill surface irregularities. The coverage coating of paper surface with nano ZnO is found to be more efficient than that with bulk ZnO. The entrapment of ZnO nano particles inside the starch globules also cancels out the possibility of its release into the environment. [14]

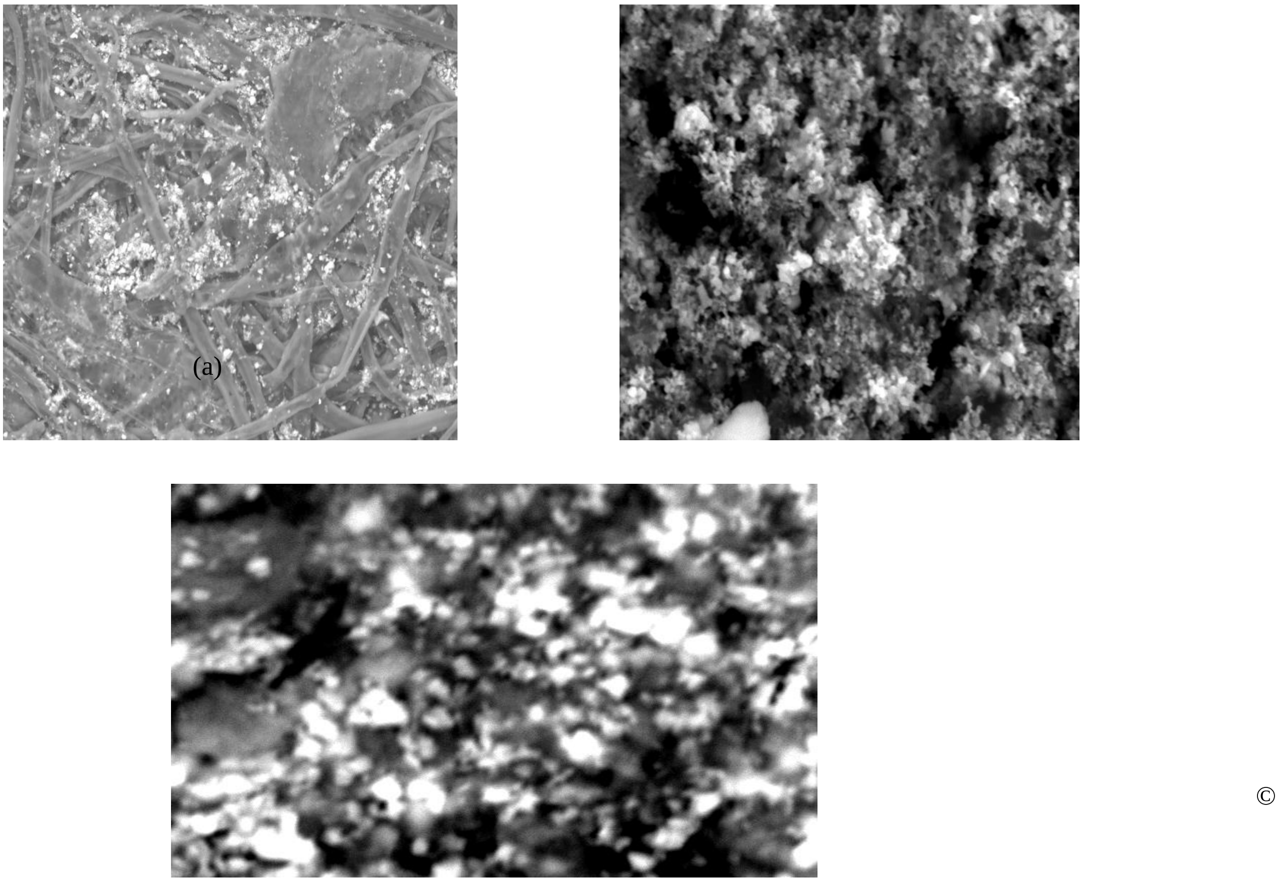

Fig. (4). Scanning electron micrographs of (a) base paper, (b) bulk- ZnO coated paper © nano- ZnO coated paper.

3.3- Thermal analysis

The thermal stability that accompanied by the addition of ZnO to the base paper was studied using thermogravimetry analysis (TGA). Figure (5) illustrates a comparison of the thermogravimetry analysis (TGA) carried out from room temperature to 800 °C each of uncoated and coated paper with ZnO. The results show that:-

(i) TGA thermogram of blank paper exhibits several weighting loss steps. The first weight loss below 100 °C is due to desorption of moisture and the two consecutive weight losses around 253, 372, 491 extending to 680 °C are attributed to the decomposition steps of cellulose. The residual weight remaining 12.5 % is attributed to binder and pigments used during the paper fabrication process.

(ii) TGA thermogram obtained for the paper coated with bulk ZnO shows firstly weight loss at around 100 °C due to desorption of moisture and three consecutive weight losses around (235, 365, 531 extending to 650 °C) as a result of decomposition of cellulose. Total weight loss is (64.20 %). The difference in weight loss compared to base paper (23.31 %) corresponds to the amount of bulk ZnO deposited on the paper surface.

(iii)TGA thermogram obtained from the paper coated with nano - ZnO shows firstly weight loss around 95 °C due to desorption of moisture and four consecutive weight losses around (219, 354.4, 484, 580 extending to 650 °C) as a result also of decomposition of cellulose. Total weight loss was (61.16 %), the difference in weight loss (26.35 %) compared to blank paper corresponds to the amount of nano ZnO deposited on the paper surface.

The results obtained reveal to that ZnO nano particles increase the thermal stability of paper. One of possible mechanisms of enhancing thermal stabilization is the interaction occurring between the surfaces of nano particles ZnO and OH functional groups of cellulose which reduces segmental mobility. The stabilization effect is enhanced by increasing the interaction.

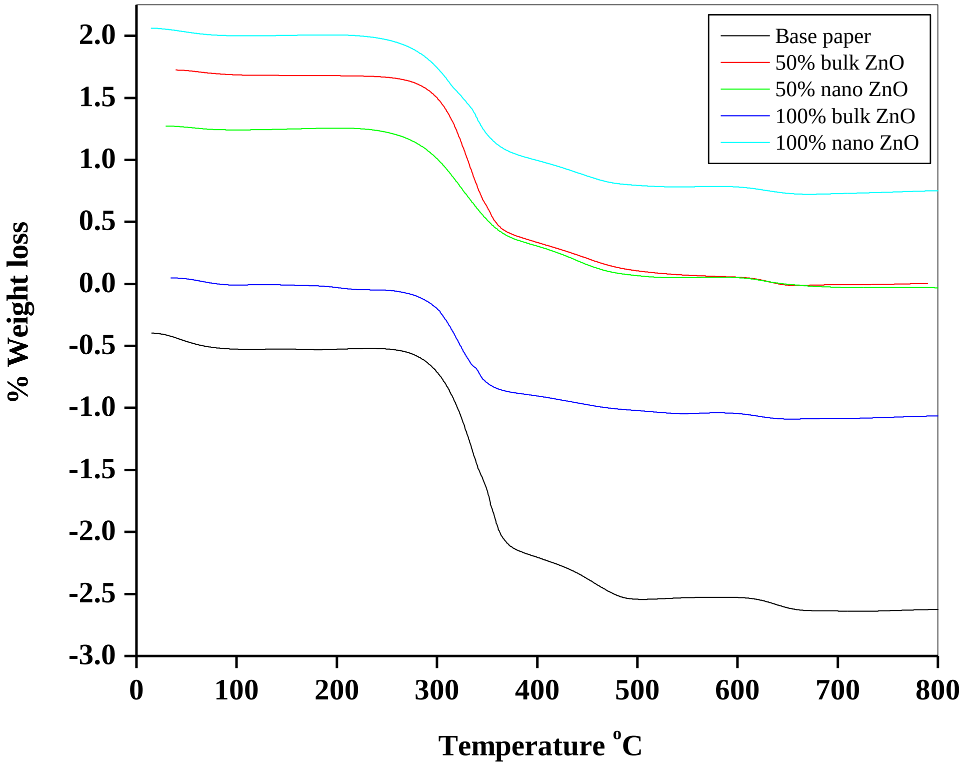

Fig. (5):- Thermogravemetric analysis for uncoated and coated paper by bulk and nano ZnO.

3.4- FTIR-Analysis

To further support the coating mechanism, FTIR spectra were recorded for the blank paper coated with ZnO particle coated paper Fig. (7). The spectra recorded for blank paper (Fig. (6)) shows a weak band, possibly arising from $CaCO_3$, CaO, MgO or silicates usually used during paper making process. A weak broad band at 732 cm^{-1} might be due to the overlap of the bands at 710 and 750 cm^{-1}, which are characteristic of I_β and $I\alpha$ phases of cellulose. [16] This possibly indicates their presence as a mixture in the composition of paper. The bands in the range from 900-1300 cm^{-1} and 1300-1500 cm^{-1} are associated with C-O and C-H vibration of cellulose.[17] Band at 1509 cm^{-1} origin from phenyl ring vibration of lignin present in the sample. The band at 1640 cm^{-1} can be attributed to the absorbed water in the cellulose fibers as confirmed by TGA data. The band at 1735 cm^{-1} is characteristic of hemicelluloses and the band at 2909 cm^{-1} can be attributed to the C-H stretching vibrations of cellulose. A broad band (3100-3700 cm^{-1}) centred around 3367 cm^{-1} characteristic of O-H functional group (free H-bonded) is also observed.[14] Similarly, FTIR spectra for each of paper coated with bulk and ZnO nano particle, Fig. (8), showed that:-

(1) A broad band at 560 cm^{-1} due to overlap of bands at 460 cm^{-1} characteristic of M-O vibrational band.

(2) The decrease in the intensities of the bands of free OH - group at (950, 1110, 1179, 1274 and 3590 cm^{-1}) suggests that the hydroxyl functional groups are associated or occupied with the ZnO nano particles. The bands of OH group seems to be disappeared, suggesting also that almost all the –OH functional groups are occupied.

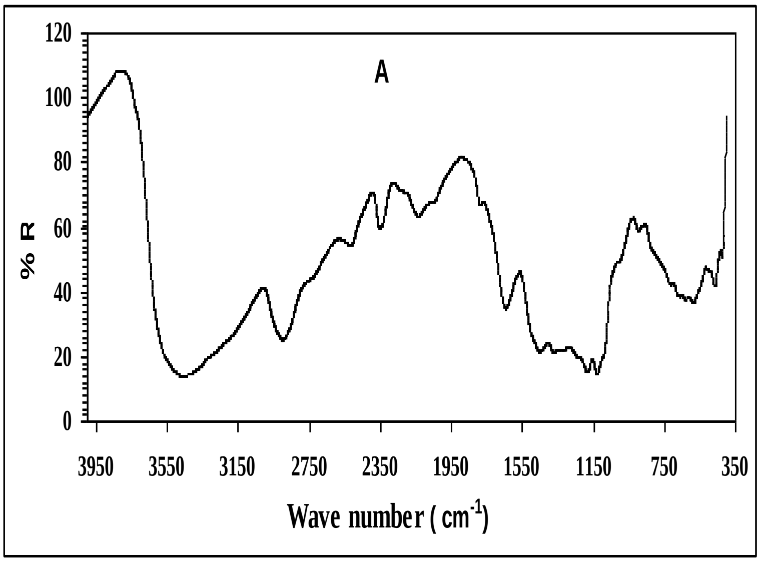

Fig. (6) FTIR spectra obtained from base paper (70gm).

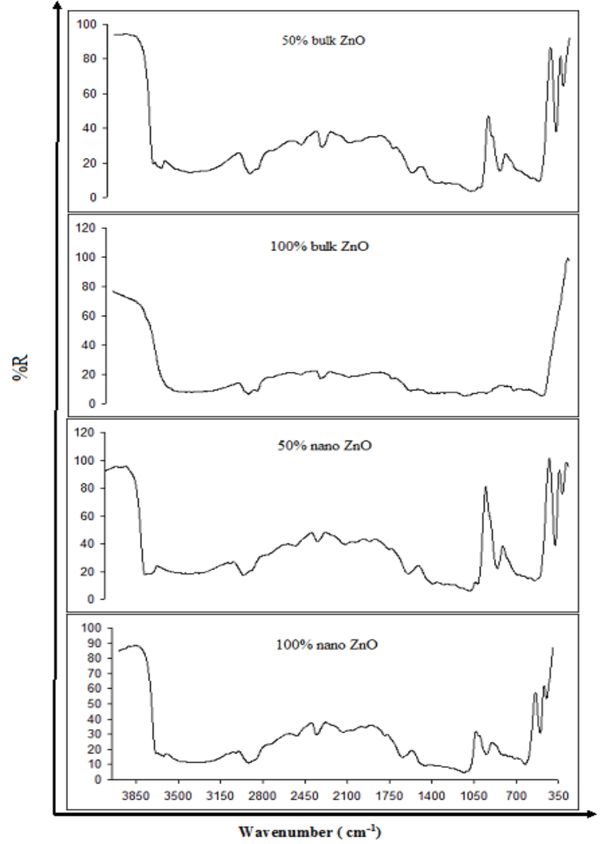

Fig. (7) FTIR spectra obtained from paper coated by bulk and nano ZnO.

3.5-Photoluminescence:-

Photoluminescence spectra (PL) were recorded to study the luminescence properties of coated paper with bulk and nano zinc oxide, using alamp with an excitation wave length of 330 nm. Fig. (8) shows the fluorescence behavior of coated papers. The paper coated with nano- ZnO exhibited strong visible fluorescence at **390** nm. Similar fluorescence was observed for the paper coated with bulk zinc oxide but with less intensity. The band edge emission is generally attributed to the free excitations emission at the near band edge (band gab fluorescence caused by a transition from the lower edge of the conduction band to the upper edge of the valence band) recombination [19]. All samples which coated by bulk and nano zinc oxide also show strong green emission band at nearly **491** nm, which is attributed to the recombination of a delocalized electron close to the conduction band with the density of a single charged state of surface oxygen vacancy [18].

The PL intensity of both peaks appearing at near band edge **390** nm and at **491** nm for paper coated by nano zinc oxide is much stronger than that of the peak for paper coated by bulk zinc oxide. This indicates that the paper treated by nano zinc oxide have an excellent luminescence properties than that the paper treated by bulk ZnO.

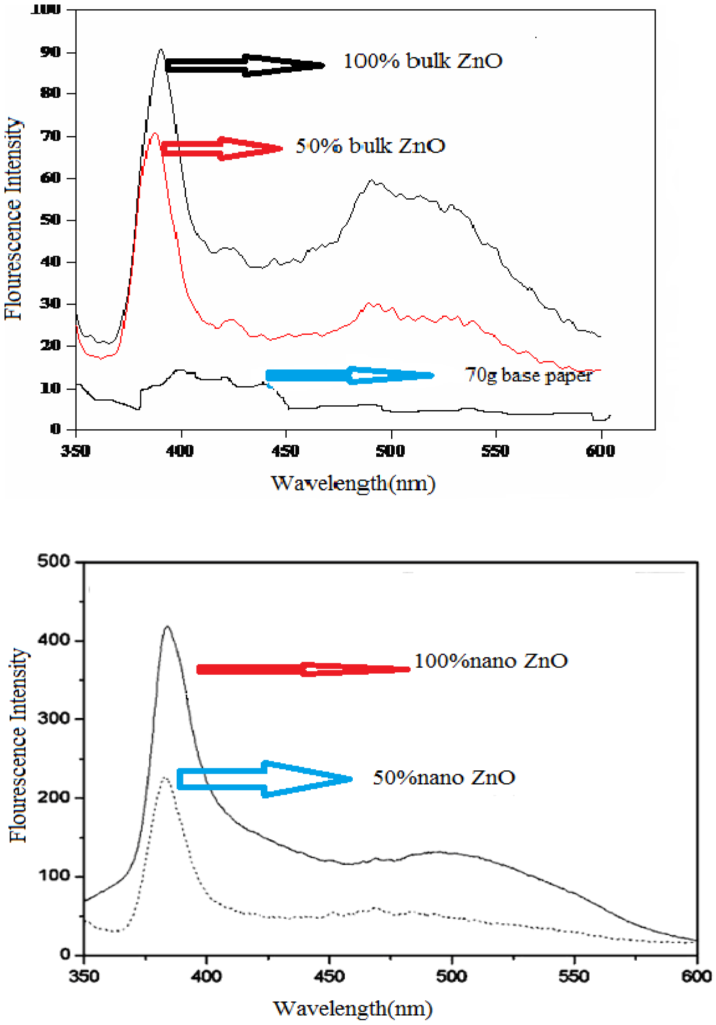

Fig. (8). Fluorescence spectra of coated paper.

3.6-Biological activity:-

At present, antimicrobial packaging materials are being developed to solve many problems associated with food distribution and safety [20-25]. In fact, antimicrobial packaging is considered as active packaging that can be defined as a mode of packaging in which the package, the product and the environment interact to prolong shelf life or enhance safety or sensory properties, while maintaining the quality of the product [26]. The demand for safer and more natural food has been increasing since consumers have become more concerned with chemical residues in food, so natural compounds such as spices and herbal oils are alternatives to be used as food preservatives since they have antimicrobial or antifungal properties. Furthermore, they do not have any significant medical or environmental impact [20-31].

The inhibitory effects of nano ZnO, base paper and coated paper with bulk and nano Zno against four type of common pathogens and food spoilage bacteria and fungai were investigated including a Gram-negative bacterium (*Escherichia coli), a Gram-positive organism (Staphylococcus aureus) and the others two fungus are (Aspergillus Flavus and Candida Albicans)* using the agar well diffusion method. The results obtained are shown in Fig. (9-10) and summarized in table (3).

The results showed that nano ZnO in dimethylsulphoxide (DMSO) was the most effective antimicrobial coating solution against both (Gram positive and Gram negative) bacteria. The inhibitor zone diameter for Escherichia coli is found to be 15 mm/mg sample while the inhibitor diameter zone for the other bacteria Staphylococcus aurous is 20 mm/mg sample. Nano ZnO did not resist growth of Aspergillus flavus as fungi but resisted growth of Candida albicans by inhibitor zone diameter equal 10 mm/mg sample.

From the results obtained we can say that the nano ZnO showed excellent antibacterial activity against two representative bacteria Escherichia coli (Gram negative) and Staphylococcus aurous (Gram positive). The antibacterial activity for all the investigated samples increases according to the following order:
paper coated by 100% nanoZnO (P_{nz}) › paper coated by 100% bulk ZnO (P_{bz}) › paper coated by 50% nano ZnO (P_{bz5})› paper coated by 50% bulk ZnO (P_{nz5}) › paper it self (P).

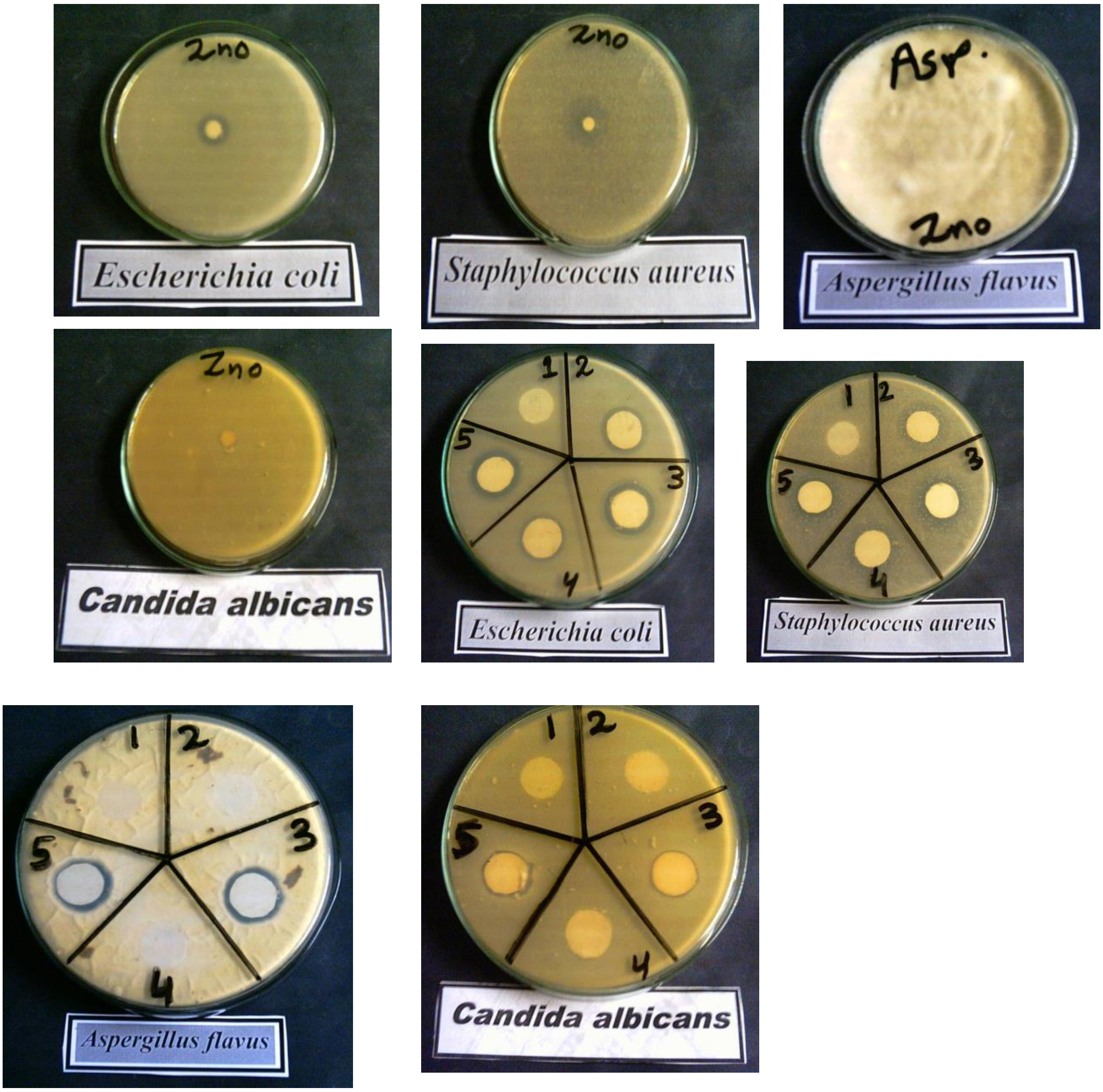

Fig. (9). Inhibitory zones of nano ZnO against (Escherichia coli, Staphylococcus aureus, Aspergillus flavus and candida albicans).

Sample		**Inhibition zone diameter (mm / mg sample)**			
		Escherichia coli **(G^-)**	***Staphylococcus aureus*** **(G^+)**	***Aspergillus flavus*** **(Fungus)**	***Candida albicans*** **(Fungus)**
Standard	**Tetracycline Antibacterial agent**	31	29	--	--
	Amphotericin B Antifungal agent	--	--	18	21
Control: DMSO		0.0	0.0	0.0	0.0
ZnO		15	20	0.0	10

Fig. (10). Inhibitory zones of base paper and coated paper against (Escherichia coli, Staphylococcus aureus, Aspergillus flavus and candida albicans).

(1) Base paper (P) (2) Paper coated by 50%bulk ZnO (P_{bz5}) (3) Paper coated by 100%bulk ZnO (P_{bz}) (4) Paper coated by 50% nano ZnO (P_{nz5}) (5) Paper coated by 100% nano ZnO (P_{nz}).

Table (2):- Inhibitor zone diameters (mm/mg sample).

Table (3):- Inhibitor zone diameter (mm/ 1cm sample) for base paper (70gm) and coated papers.

Sample	**Inhibition zone diameter (mm / 1 cm^2 sample)**			
	Escherichia coli **(G^-)**	***Staphylococcus aureus*** **(G^+)**	***Aspergillus flavus*** **(Fungus)**	***Candida albicans*** **(Fungus)**
P	0.0	0.0	0.0	0.0
P_{bz5}	17	15	0.0	0.0
P_{bz}	22	16	18	12
P_{nz5}	14	16	0.0	0.0
P_{nz}	22	18	19	14

The size of ZnO greatly affects anti-fungal properties due to its quantum size effect and tremendously high surface area. The interesting fact here is that nano ZnO, in spite of the presence of starch stabilizer showed excellent antifungal property. Antifungal activity in the absence of light supports the fact that hydrogen peroxide generated from ZnO is the major contributor of antifungal activity. Under this environment, nano ZnO coated paper could perform better antifungal property even in the absence of light .[21]

3.7-Resistance of paper to absorb paraffin oil:-

The effect of ZnO coating on the resistivity of the papers to absorb paraffin oil was also studied. The results obtained are illustrated in Figures (11, 12). Figure (11) shows the resistance of base paper (80 gm rakta) which coated by (100% nano ZnO) to absorb paraffin oil. The figure shows two images, one on opaque surface and the other when exposed to sun light. The image illustrates the paraffin oil diffuse in regular way.

Figure (12) shows the resistance of bases papers and that treated by bulk and nano ZnO to absorb paraffin oil. The oil penetration and absorption into the paper depend on the homogeneity and internal structure of the coating. The coating formulation is not yet optimized for complete barrier protection and may contain further binding agents.

Table (4) represents resistance of different weight of paper coated by bulk and nano ZnO to absorb paraffin oil. The oil absorption and penetration to the paper depend on the weight of the paper, as the weight of the paper increases the strength of the paper to absorb paraffin oil decreases. This is due to the presence of greater binding energy between the bundles of fibers. Not only the weight of paper but also the thickness of the coating materials affect on the absorption and penetration of water and oil.

The results also illustrated that the addition of ZnO, especially in nano size, increases the resistance of paraffin oil diffusion. This is attributed to the increase in the interaction occurring between ZnO and OH groups in the base paper.

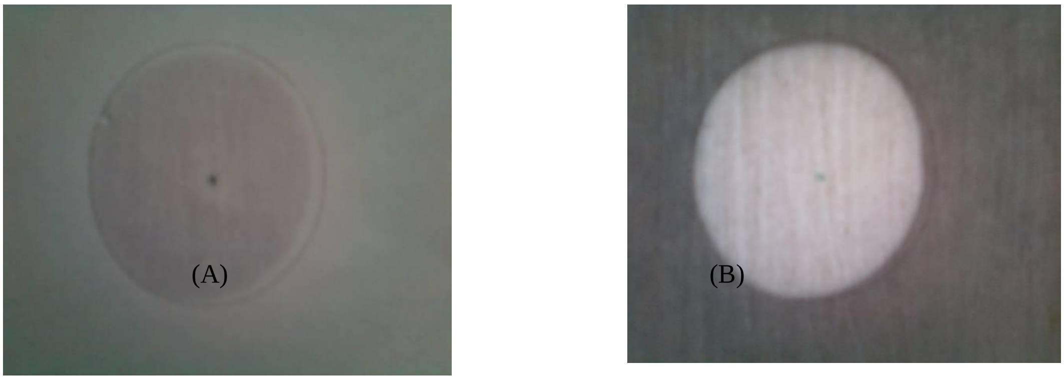

Fig. (11): Resistance of coated paper (80gm) with nano ZnO to absorbance paraffin oil (P_{nz}).
(A) Paper in opaque surface, (B) paper when exposed to light.

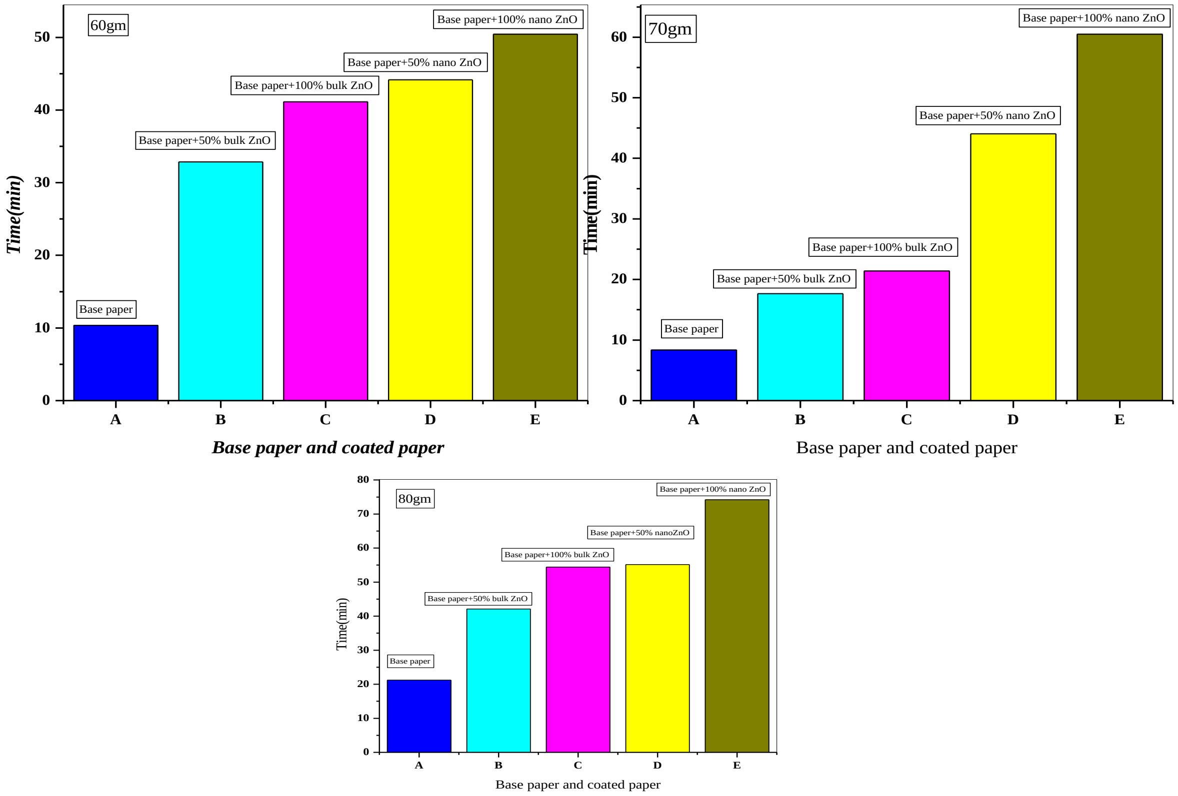

Fig. (12): Resistance of different weight of paper and this paper which coated by bulk and nano ZnO to absorbance of paraffin oil

Table (4):- Resistance of different weight of paper which coated by bulk and nano Zno to absorb paraffin oil.

Sample name	***Symbol***	***Time (min)***		
		60gm	***70gm***	***80gm***
Base paper	***P***	*10.35*	*8.34*	*21.19*
Paper coated by 50% bulk - ZnO	P_{bZ5}	*32.85*	*21.40*	*42.09*
Paper coated by 100% bulk - ZnO	P_{bZ}	*41.12*	*17.65*	*54.43*
Paper coated by 50% nano - ZnO	P_{nZ5}	*44.17*	*44.06*	*55.15*
Paper coated by 100% nano - ZnO	P_{nZ}	*50.44*	*60.35*	*74.21*

3.8-Mechanical testing:-

The mechanical and strength properties of paper reflect the intrinsic chemistry, morphology, and structure of the individual fibbers as well as the network structure of the paper. These properties also reflect those chemical changes that cause the paper to lose its permanence with time. Strength properties can thereby serve as indicators of the permanence of paper, even when the nature of the chemical changes responsible for the deterioration remains unknown.

Effect of temperature upon tensile properties for uncoated and coated paper is shown in table (5). For uncoated paper, the tensile strength along machine direction (MD) is higher compared to the cross-direction (CD) due to anisotropy of the paper web. For coated papers, only tensile tests in the direction of highest strength (MD) are represented and tensile strength of the coated papers is significantly higher than the uncoated paper. The somewhat higher tensile strength for coated paper is due to each of the interaction between OH-groups of cellulose and ZnO particles, and the increase in weight of the papers due to the coating. As the thickness of coated paper increases the tensile strength increases, it means that nano particle adsorption at the paper surface significantly increases the intrinsic paper strength. The change in tensile properties might indicate that the nano particles partly penetrate in to the cellulose web and enhance the fiber to fiber bonding because of better adhesive interactions (higher strength), while the cellulose fibbers gain some flexibility because of swelling by solvent penetration. The good adhesion between the coating and cellulose and strengthening of the paper was confirmed by optical and scanning electron microscopy.

Table (5):-Effect of different temperature at constant time 50 min. upon tensile of paper (80 gm).

Samples name	***Symbol***	**Temperature**			
		80°C	***100°C***	***140°C***	***160°C***
Base Paper	P	5.4	5	4.6	3.9
Paper coated by 50 % bulk- ZnO	P_{bZ5}	2.8	2.7	2.6	2.6
Paper coated by 100 % bulk ZnO	P_{bZ}	3.4	3.4	2.8	2.4
Paper coated by 50% nano- ZnO	P_{nZ5}	4.7	4.3	4.1	3.7
Paper coated by 100% nano-ZnO	P_{nZ}	5.5	5	4.9	4.6

Table (6):-Effect of different temperature at constant time 50 min. upon brightness of paper (80 gm).

Samples name	***Symbol***	**Temperature**			
		80°C	***100°C***	***140°C***	***160°C***
Base Paper	P	90.1	88.4	83.7	79.4
Paper coated by 50 % bulk- ZnO	P_{bZ5}	94.7	94.1	91.5	85.2
Paper coated by 100 % bulk ZnO	P_{bZ}	96	96	93.6	78.9
Paper coated by 50% nano- ZnO	P_{nZ5}	90.5	90.2	88.5	84.7
Paper coated by 100% nano-ZnO	P_{nZ}	89.1	87.7	85.7	77.1

Table (7):-Effect of different temperature at constant time 50 min. upon tensile of paper (70 gm).

Samples name	***Symbol***	**Temperature**			
		80°C	***100°C***	***140°C***	***160°C***
Base Paper	P	5.6	5.2	4.9	4.3
Paper coated by 50 % bulk- ZnO	P_{bZ5}	4.3	4.2	4.2	4.1
Paper coated by 100 % bulk ZnO	P_{bZ}	4.8	4.6	4.5	4.3
Paper coated by 50% nano- ZnO	P_{nZ5}	5.7	5.4	4.8	4.5
Paper coated by 100% nano-ZnO	P_{nZ}	6	5.6	5.5	5.2

Table (8):-Effect of different temperature at constant time 50 min. upon brightness of paper (70 gm).

Samples name	***Symbol***	**Temperature**			
		80°C	***100°C***	***140°C***	***160°C***
Base Paper	P	90.7	89.7	85.4	84.2
Paper coated by 50 % bulk- ZnO	P_{bZ5}	90.9	90.7	88.3	83.7
Paper coated by 100 % bulk ZnO	P_{bZ}	94.9	94.8	92.6	84.2
Paper coated by 50% nano- ZnO	P_{nZ5}	90.5	86.5	83.3	80.7
Paper coated by 100% nano-ZnO	P_{nZ}	87.2	85.7	83.5	78.5

Table (9):-Effect of different time at constant temperature 120 ^{o}C upon tensile of paper (70 gm).

Samples name	Symbol	Time (min)				
		20	30	40	50	60
Base Paper	P	5.6	5.4	5.2	4.8	4.5
Paper coated by 50 % bulk- ZnO	P_{bZ5}	4.8	4.3	4	3.8	3.6
Paper coated by 100 % bulk ZnO	P_{bZ}	4.5	4	3.8	3.1	3
Paper coated by 50% nano- ZnO	P_{nZ5}	5.9	5.4	4.7	4.6	4.2
Paper coated by 100% nano-ZnO	P_{nZ}	6.3	6.2	6.1	5.7	5.6

Table (10):-Effect of different time at constant temperature 120 ^{o}C upon brightness of paper (70 gm).

Samples name	Symbol	Time (min)				
		20	30	40	50	60
Base Paper	P	90.7	90.4	90.2	88.9	87.9
Paper coated by 50 % bulk- ZnO	P_{bZ5}	88.6	87.8	87.6	87.4	87.2
Paper coated by 100 % bulk ZnO	P_{bZ}	91.9	91.8	91.4	90.9	90.7
Paper coated by 50% nano- ZnO	P_{nZ5}	85.7	85.4	84.9	83.9	83.9
Paper coated by 100% nano-ZnO	P_{nZ}	82.4	82.1	81.5	81.2	80

Table (11):-Effect of different time at constant temperature 120 ^{o}C upon tensile of paper (60 gm).

Samples name	Symbol	Time (min)				
		20	30	40	50	60
Base Paper	P	5.4	5.2	5	5	4.8
Paper coated by 50 % bulk- ZnO	P_{bZ5}	4.8	4.7	4.7	4.2	3.6
Paper coated by 100 % bulk ZnO	P_{bZ}	2.8	2.7	2.5	2.3	2.3
Paper coated by 50% nano- ZnO	P_{nZ5}	4.9	4.7	4.3	3.8	3.7
Paper coated by 100% nano-ZnO	P_{nZ}	5.4	5.3	5.2	5.1	5.1

Table (12):-Effect of different time at constant temperature 120 °C upon brightness of paper (60 gm).

Samples name	***Symbol***	**Time (min)**				
		20	***30***	***40***	***50***	***60***
Base Paper	P	91.8	91.5	91.2	89.7	89.4
Paper coated by 50 % bulk- ZnO	P_{bZ5}	89.7	89.6	89.2	89.1	89
Paper coated by 100 % bulk ZnO	P_{bZ}	91.2	89.3	87.1	86.4	86.1
Paper coated by 50% nano- ZnO	P_{nZ5}	83.4	82.9	80.5	79.8	78.3
Paper coated by 100% nano-ZnO	P_{nZ}	77.4	75.8	74.6	74.1	71.8

Conclusion:-

Zinc oxide with wide range of applications in various fields is considered as workhorse of technological development. With an ever increasing demand for a high quality of printing papers, there is an urgent need to focus on nano-coating to improve the functional properties of paper. Nano ZnO reduced the optical intensity of cellulose by about 20% but bulk ZnO reduced the intensity of cellulose by about 60% this is due to the transparent nature of nano ZnO and thick opaque nature of bulk ZnO. ZnO nano particles increase the thermal stability of paper. This is due to the interaction occurring between the surfaces of nano particles ZnO and OH functional groups of cellulose which reduces segmental mobility and the observed the changes in IR spectra referred to some interactions occurring between OH of cellulose and bulk or nano ZnO. Nano ZnO showed excellent antibacterial activity against two representative bacteria Escherichia coli (Gram negative) and Staphylococcus aurous (Gram positive). The addition of ZnO, especially in nano size, increases the resistance of the paper for paraffin oil diffusion. This is attributed to the interaction occurring between ZnO and OH groups in the base paper. The oil absorption and penetration to the paper depend on the weight of the paper; when the weight of the paper increases the strength of the paper to absorb paraffin oil decreases. This is due to the presence of greater binding energy between the bundles of fibers. Not only the weight of paper but also the thickness of the coating materials affect on the absorption and penetration of water and oil. Mechanical testing of paper was affected by treatment of the paper by each of bulk and nano ZnO.

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