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GREEN SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF COBALT AND ZINC OXIDE NANOPARTICLES FUNCTIONALISED STARCH NANOCOMPOSITE

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ABSTRACT:

Cobalt Oxide and Zinc Oxide nanoparticles were synthesized using extract of Annona muricata (sour soup), leaves as a stabilizing and reducing agents. Cobalt Nitrate and Zinc Nitrate as a precursor. Green method was applicable because low cast, sustainable and ozone friendly. Synthesis of polymer metal Nanocomposites of Cobalt Oxide fictionalized in starch and Zinc Oxide functionalized in starch by using solution casting method. The percentage of Cobalt Oxide and Zinc Oxide Nanoparticles were varied from different concentrations (0. 01, 0. 02, 0. 03,0. 04 with the starch (0. 3,0. 4, 0. 5,0. 6). Structural and Composition of these nanocomposites were characterized using UV-Visible, FT-IR,SEM, and XRD. The biological studies of the above composites were evaluated in vitro by using surface inoculation and disc diffusion method. Photocatalytic property of the nanocomposites have investigated by methylene Blue as a dye.

Keywords: Green method,Annona muricata,ZnO and Co_3O_4 nanoparticles,
Starch nanocomposite

1.Introduction:

Nanotechnology is one of the fast developing fields of research in recent years which studiesmaterials and it lies within the nano meter range[1]. Cobalt Oxide and Zinc Oxide Nanoparticles are most important for potential applications like medicine, Industrial, Antimicrobial, Sensor, Supercapasitor, Catalysts, dye degradation etc. In this present work preparation of Cobalt Oxide ,Zinc Oxide nanoparticles are carried out through some chemical and physical methods. However these methods required toxic materials and producing environmental polluted chemicals. Instead of chemical and physical method innovative, non toxic, cost effective, ozone-friendly, easy available green synthesis was introduced. Green parts contain bioactive compound like flavonoids, Terpenoids etc. This bioactive compounds can reduce metal to metal nanoparticles[2-5]. Starch was used to prepare film because of available condition and biodegradable. Starch based biodegradable films contain poor mechanical and high relative humidity. Native starch is naturally found as semi-crystalline and water-insoluble granules, constituted by two glucose polymer amylose and amylopectin[7]. Nanoparticles are incorporated into starch polymer matrix improvement of thermal stability and mechanical strength. Nano composite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nano meters. The mechanical electrical thermal, optical, electrochemical properties of the Nano composite will differ from that of the component materials. The area of the interface between the matrix and reinforcement phases is typically an order of magnitude greater than for conventional composite materials[8-11]. Polymer nanocomposites consist of a polymer or Copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. The transition from micro to nano particles lead to change in its physical as well as chemical properties. Two of the major factors in this are the increase in the ratio of the surface area to volume and the size of the particle. The increase in surface area to volume ratio, which increases as the particles get smaller, leads to an increasing as the particles get smaller leads to an increasing dominance of the behaviour of atoms on the surface area of particle over that of those interiorof the particle. This affects the properties of the other particles when they are reacting with other particles[12-16]. Annona Muricata commonly known as soursop, graviola and sirsak, is a member of the Annona family, native to the warmest tropical areas in south and North America and is now widely distributed throughout tropical areas.All portions of the plant Annona are extensively used as traditional medicines against of human ailments and diseases,especially cancer and parasitic infections [17]. The characteristics of the synthesized nanoparticles differ depending on the source of a plant because of the presence of different concentration and chemical substances in various plant extracts. Plant extract mediated synthesis of cobalt oxide and zinc oxide nanoparticles has been investigated in the following research works. Begun et. al [18], Dhandapani et. al [19], Kumar et. al [20] reported the synthesis of Zinc oxide nanoparticles using the leaf extract of Delonox regia, Melia azedarach and typhus latifolia respectively. Sea et. al [21] discussed review on biosynthesis of cobalt metal nanoparticles. Akhlaghi et. al [22] and Khalil et. al [23] reported the synthesis of cobalt oxide nanoparticle using the leaf extract of Trigonella foenumgraceum and Sageretiathea respectively.

2. Materials and methods

2. 1 Materials

Cobalt nitrate, Zinc nitrate, Sodium hydroxide, Double distilled water were purchased from S A CHEMICALS, Tirunelveli. Fresh Annona muricata leaves were collected from kanyakumari District.

2. 2 Preparation of Annona muricata leaf extract

The fresh Annona muricata leaves were washed with tap water followed by distilled water. These leaves are allowed to shade dry at room temperature for 20 days, then grinded to get a fine powder. Take 10g of leaf powder in a 250 ml Round bottom flask. The flask was kept at 60^0 C on magnetic stirrer for 40 minutes. Finally the extract was filtered using whatman filter paper and stored in refrigerator.

2. 3 Green synthesis of cobalt oxide and Zinc oxide nanoparticles (Co_3O_4 and ZnONps)

Synthesis of Cobalt oxide and Zinc oxide nanoparticles was carried out using Cobalt nitrate and Zinc nitrate as a precursor respectively. 100 ml of Cobalt nitrate and Zinc nitrate are taken in a Erlenmeyer flask separately. Add 20 ml of 0.1M NaOH to the flask. Take 25 ml of freshly prepared Annona muricata leaf extract in burette and added dropwise to the Erlenmeyer flask, then the mixture was stirred at 80 ^oC on heating mantle for 2 hours. The solution allowed to cool and centrifuged 10, 000 rpm, formed nanoparticles are washed with deionized water. The prepared nanoparticles are allowed to dry air oven at 200 ^0C for 3 hours.

2.4 Preparation of starch-zinc oxide (SZn) and starch cobalt oxide (SCo)nanoparticle composite

The ZnO andCo_3O_4nanoparticle composite were synthesized by solution casting method. The prepared ZnO nanoparticle used to synthesize zinc incorporated starch nanocomposites and Co_3O_4 nanoparticle used to synthesize cobalt nanoparticles incorporated starch nanocomposite by solution casting method. In this method, first granular starch was dispersed in Milli Q water which was gelatinized by stirring and heated upto 75^0c. A clear viscous solution was obtained. To this solution, ZnOnanoparticles with different % weight (0.01 ,0.02 ,0.03 ,0.04) and Co_3O_4 nanoparticles with different % weight (0.01 ,0.02 ,0.03 ,0.04) has been separately dispersed. The system was homogenized with the use of sonicator for 10-20 min. Then the solution were casted into the petri dish coated with petroleum jelly to obtain zinc and cobalt incorporated starch nanocomposites films with different % of ZnO and Co_3O_4 nanoparticle. The system was kept aside for two days at room temperature. Nanocomposites films where cured in hot air oven for 3 hours and temperature were maintained at 65^0c.

3.Characterization of the prepared nano composites

Cobalt oxide and Zinc oxide Nano Composite were characterized by the following techniques. Maximum obsorbance weremeasured using UV-Visible Spectrophotometry in the range of 200-800 nm. Optical absorbance was recorded using Agilent cary 100/300 series UV-Vis Spectroscopy.

(FT-IR) spectroscopy was used to identify the functional groups present in the prepared nanoparticles and Nano composite. In this present work Agilent cary 630 FT-IR spectrophotometer was used with a frequency range of 600-4000cm^{-1}. Pellets were prepared by using KBr.

Crystallinity of the nanoparticles was determined by X-Ray difraction (XRD) analysis and Scanning Electron Microscope (SEM) was used to characterize the shape and external morphology of the nanoparticles and Nano composite. XRD was taken in Bruker D8 Advance Slow Scan Range 0.5 to 120 θ and Fast Scan Range 1-120 θ. The SEM can produce very high-

resolution images of a sample surface, revealing details about 1 to 5 in size. SEM images were taken in a JEOL JSM-6360 SEM.

ZnO incorporated starch nanocomposite and Co_3O_4 incorporated starch nanocomposite film were screened in *vitro* for their antibacterial activity against the bacterial strains, Staphylococcus Aureus, by surface inoculation method. The Photo degradation of Methylene Blue (MB) dye solution under UV irradiation was performed to estimate the photocatalytic activity of metal oxide nanocomposites.

4.Result and discussion

The synthesised nanocomposites were characterised using UV-Vis spectrophotometer, FT-IR, X-ray Powder Diffraction and Scanning Electron Microscope.

4.1 UV-Visible spectroscopy

The absorption spectra of SZn (starch incorporated to zinc oxide) and SCo (starch incorporated to cobalt oxide) nanocomposites are shown in figures(2and 3). It was observed that the amount of light absorbed by polymer nanocomposites increased as the wavelength was reduced. The absorbance level was observed to peak between the wavelength range of 330-350nm.This indicates that the polymer SZn NCs (nanocomposites) and SCo nanocomposites exhibit Blue shift phenomenon and also improved the UV shielding property of the polymer.[8]

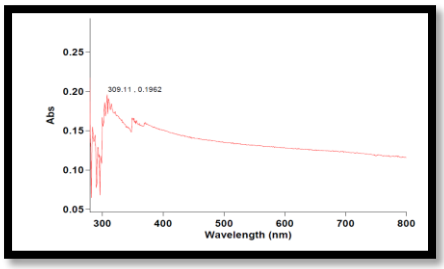

Figure 1 :UV –Visible Spectroscopy of starch

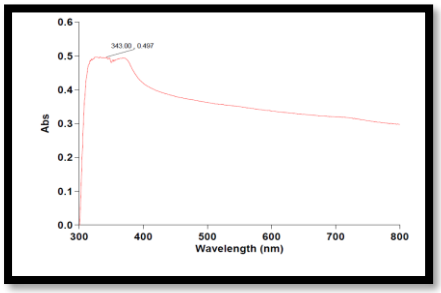

Figure 2: UV-Visible Spectroscopy of SZn nanocomposite

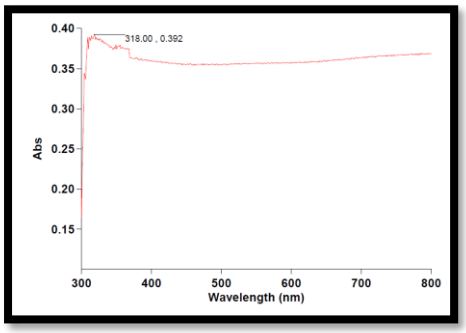

Figure 3: UV-Visible Spectroscopy of SCo nanocomposite

4. 2 FT-IR Spectroscopy

FTIR spectra of SZn and SCo nanocomposites were recorded using KBr pellet, with a resolution of 4 cm^{-1}. IR spectra of all the polymer nanocomposites were examined in detail shown in Figures (4,5). The spectra (Figure 4) clearly showed a broad band at 3179 cm^{-1} due to OH stretching for polymeric hydroxyl compounds. A peak at 2051 cm^{-1} corresponding to the C-H asymmetric stretching vibration. The appearance of peak at 1654 cm^{-1} and 991cm^{-1} observed due to the incorporation of metal in starch.[9,20] A stretching frequency at 3457 cm^{-1} and a weak asymmetric band at 1633cm^{-1} support the presence of OH group due to the absorption of water by nanoparticles during sample preparation. The spectra (Figure 5) clearly showed a broad band at 3267 cm^{-1}due to OH stretching for polymeric hydroxyl compounds. A peak at 2920 cm^{-1}corresponding to the C-H asymmetric stretching vibration .The appearance of peak at 1515 cm^{-1} and 991cm^{-1} observed due to the incorporation of metal in starch.

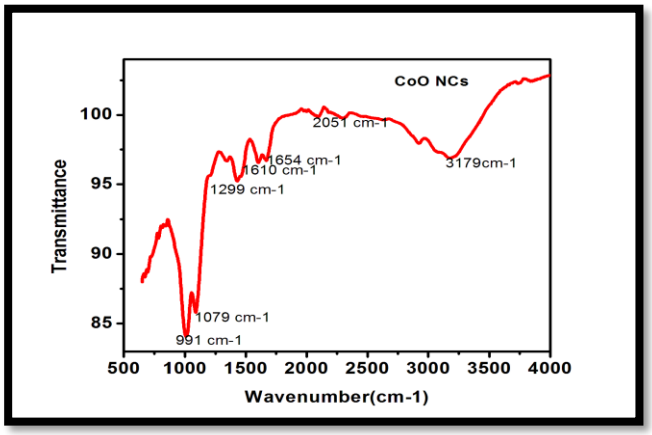

Figure 4 : FTIR spectrum of SConanocomposite

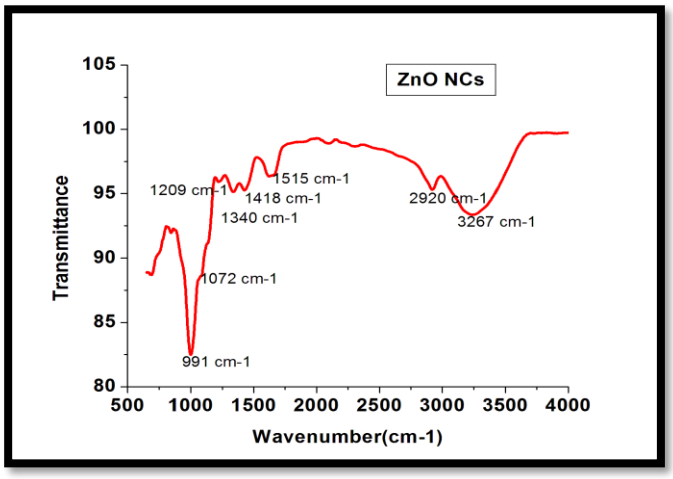

Figure 5:FTIR spectrum of SZn nanocomposite

4.3 X-ray powder diffraction studies

The XRD pattern of ZnO nanoparticles and its composite, Co_3O_4 nanoparticles and its composite are shown in Fig. 6 and 7. According to ZnO pattern (JCPDS: 96-230-0113) the diffraction peaks can be indexed to Crystalline phase. The hkl value of ZnO are (101), (100),(002),(110),(013) planes. These characteristic peaks observed in ZnO Starch nanocomposite confirms incorporation of nanoparticles in to the polymer matrix.[12] The crystalline size of ZnO NPs and SZn composite are 26nm and 29 nm. According to Co_3O_4 pattern (JCPDS: 96-153-6060), the diffraction peaks can be indexed to hexagonal structure. The hkl value of Co_3O_4 are (311), (344), (121), (202), (400) planes. These characteristic peaks observed in Co_3O_4 confirms incorporation of nanoparticles in to the polymer matrix. The crystalline size of Co_3O_4 nanoparticles and SCo composite are 27 nm and 31 nm.

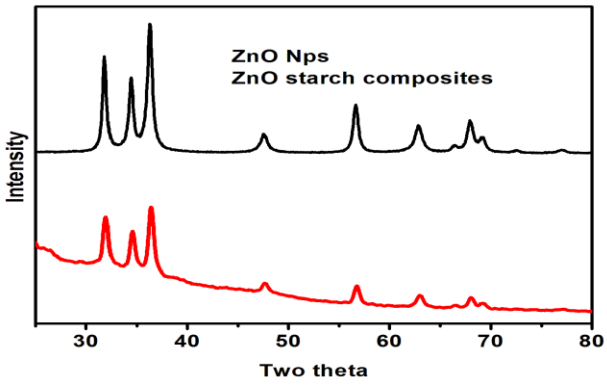

Figure 6: XRD of ZnNPs and SZn nanocomposite

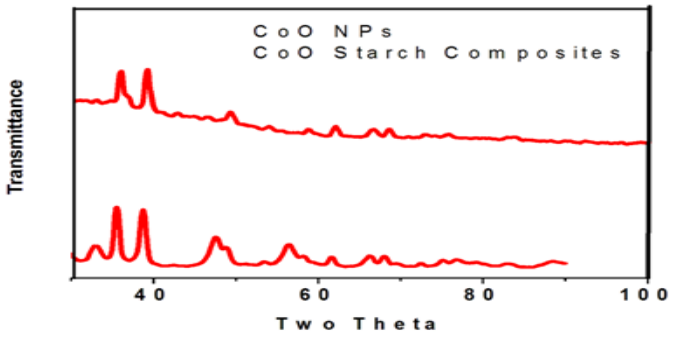

Figure7: XRD of Co_3O_4NPs and SCo nanocomposite

4.4 Scanning ElectronMicroscope

Fig.8 and 9 Shows the SEM images of SZn and SConanocomposites**.** From this image it is observed that nanocomposites are crystalline in nature and agglomeration has taken place. The grains formed are interconnected with each other, which indicate that they have enough binding energy to combine with neighbour grain, [22]. The grains are irregular in structure, some of them are elongate and some are spherical in shape. The grains have low porosity. The several pores formed on the surface are due to rapid evaporation of the solvent.

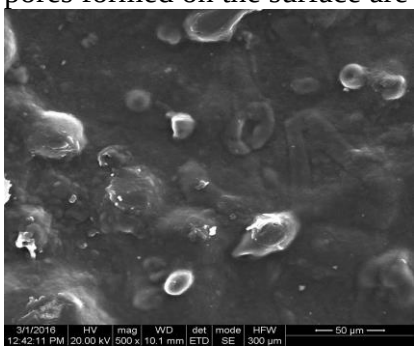

Figure 8: SEM image of SZnnanocomposite

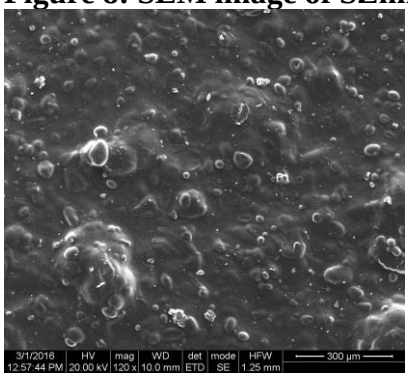

Figure 9: SEM image of SConanocomposites

4.5 Antibacterial Studies

Antibacterial activity of the selected composite films was screened against bacterial strains (*Staphylococcus aureus*). Synthesised compounds either exhibited no or varying degree of inhibitory effects on the growth of test bacterial strains. The nanocomposites SZn 1(50µl), SZn 2(100 µl), SCo1(50µl) and SCo 2(100 µl) were screened against *Staphylococcus aureus*.

ZnO incorporated starch nanocomposite and Co_3O_4 incorporated starch nanocomposite film were screened in *vitro* for their antibacterial activity against the bacterial strains, Staphylococcus Aureus, by surface inoculation method.Stock culture of bacteria was purchased from Science house. A sub-culture was prepared from the stock culture.

4.5.1 Procedure for the preparation of sub-culture from stock culture

7.6g of Muller- Hinton agar was added to a 250ml conical flask and 100 ml distilled water was added to the flask. The medium was sterilized by autoclaving at 151bs pressure (121^0c) for 15 minutes. The medium was poured into pre sterilized Petri dishes in 20-25 ml amount. In order to solidify, the medium was left undisturbed for one hour at room temperature. Suspension of test organisms were made in nutrient broth and adjusted by matching the turbidity with Mc farland standard.

A sterile cotton swab, dipped into the test bacterial suspension was used to evenly inoculate the entire surface of a Mueller-Hinton agar plate. After the agar surface has dried for about 5 minutes, the composite films were placed on the surface with a spatula .The plate was immediately placed in an incubator at 37^0C. After 24 hours of incubation, the culture plates were examined and the diameter of zone of inhibition was measured using a ruler.[3,4]

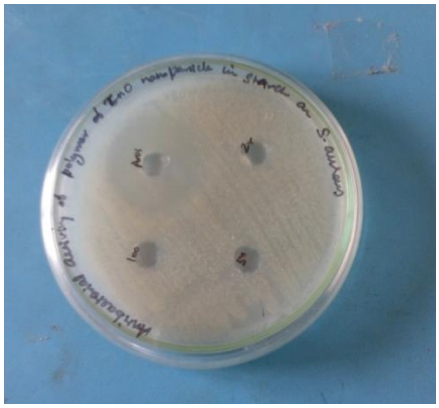

Figure 10 : Sensitivity against *S.aureus*

Figure 11 : Sensitivity against *S.aureus*

The nanocomposites SZn 1and SZn 2 in *S.aureus* and it was found SZn 1and SZn 2 slight inhibition in the growth of bacteria. The nanocomposites SCo 1 and SCo 2 in *S.aureus* and it was found SCo 1 and SCo 2inhibited the growth of bacteria (4 mm) (12 mm) respectively.

4.6 Photo Catalytic studies

In order to evaluate the photo catalytic activity, photo degradation of Methylene Blue dye under UV light irradiation was carried out at room temperature. The catalytic reaction was carried out in a photo reactor, which contain 5ml of MB dye (20mg/ml) solution and 1mg of catalyst. Before, the irradiation was carried out using halogen lamp as light source. The samples were collected at every 30min and stored in glass bottles. The sample solutions were taken in 1cm Quartz curve and their absorbance measured using spectrophotometer.

Semiconducting oxides are used as photo catalyst for degradation purpose is mainly due to their activity and stability ,[20].The photo catalytic activity of the photo catalyst depends on the band gap of the semiconductor and wavelength of the semiconductor to be expanded. The Photo catalytic degradation of Methylene blue follows Pseudo first order kinetics.Fig. 12,13,14and 15 shows photocatalytic degradation of ZnO, Co_3O_4 and SZn, SCo NCs using MB. The degradation was analyzed UV-Vis absorption band.

The photo catalytic study of MB was carried out by the presence of semiconducting ZnO, Co_3O_4 and SZn, SCo NCs. The degradation was observed spectrophotometrically. The photo catalytic activities of synthesised nanoparticles were evaluated by the degradation of organic dye Methylene blue in aqueous solution under light irradiation. The ZnO NPs and Co_3O_4NPs were used as a photo catalysts for the decomposition of Methylene blue by the super oxides and /or hydroxyl radicals formed at their interface. The higher degradation observed in ZnO NPs than the Co_3O_4NPs. In the case of SZn and SCotbe Photocatalytic property becomes lower.

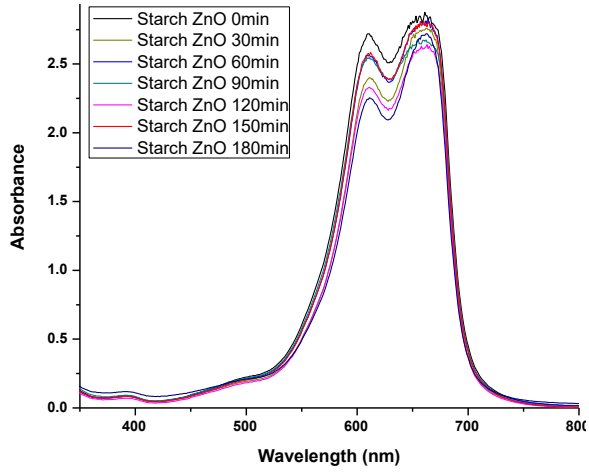

Figure 12 Photo degradation of MB using SZn nanocomposites

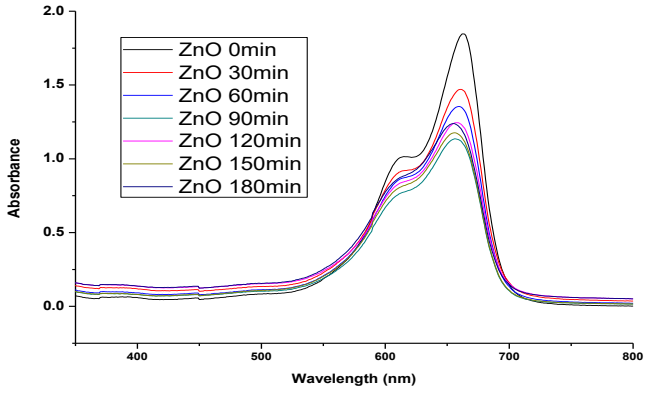

Figure 13: Photo degradation of MB using ZnO nanoparticles

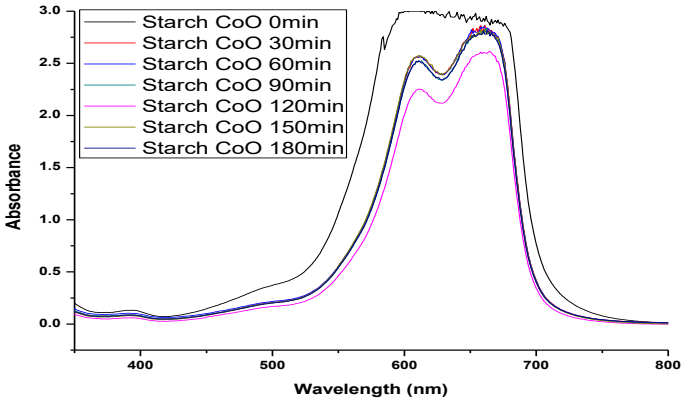

Figure 14: Photodegradation of MB using SCo nanocomposites

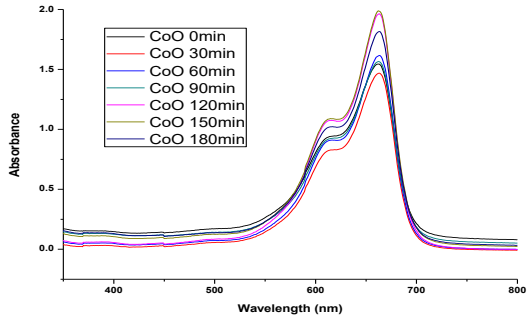

Figure 15: Photo degradation of MB using Co_3O_4 nanoparticles

5.Summary and conclusion

ZnO functionalized starch nanocomposite and Co_3O_4fuctionalised starch nanocomposite of different concentrations were prepared by solution casting method. The absorption spectra and interaction between the metal and polymer nanocomposites were studied UV-Vis Spectroscopy and FT-IR respectively. Chemical modification and surface morphology were studied using XRD and SEM respectively. From XRD data it has shown that the prepared nanocomposites were crystalline in nature. SEM images of prepared nanocomposites revealed that the granulation of the starch was retained partly and crystalline domains were seen.

The antibacterial study of the prepared nanocomposites were evaluated in *vitro* by using surface inoculation method. ZnO functionalized starch nanocomposites and Co_3O_4 functionalised starch nanocomposites shows that there was an inhibition at higher concentration in the growth of bacteria in *S.aureus*.

Our attention was mainly focused on the absorption and photocatalytic activities of synthesized two kinds of catalyst ZnO, Co_3O_4 nanoparticles and SZn, SCo nanocomposites were evaluated by the degradation of organic dye such as Methylene blue in aqueous solution under light irradiation. The absorbance of MB decreases with increase in time of irradiation by using ZnO and Co_3O_4 nanoparticles .

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