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Polyindole Based NiO-MgO Nanocomposite

Photocatalytic and Antimicrobial studies

[Dedhila Devadathan and R. Raveendran]

Abstract—**The aim of the present work was to synthesize polyindole based NiO-MgO nanocomposite, to study the factors affecting photocatalytic process and also to find out the optimal conditions that could be used in this process. The synthesized material was characterized using SEM, EDAX and XRD. The study also investigates the applicability of the nanocomposite as an antimicrobial agent.**

***Keywords*—Nanocomposite, conducting polymer, photocatalyst, photocatalysis, antimicrobial agent**

I. Introduction

Water contamination becomes a serious issue due to the fact that 2% of dyes produced in various industries are discharged directly as aqueous effluent [1]. So it was necessary to find a new way to remove coloured dyes [2, 3] before discharging them into the environment. The various conventional technologies currently employed in the removal of effluents in industrial water are classical and do not lead to complete destruction of pollutants. The conventional methods do not work efficiently due to high solubility of dyes as well as their resistance to chemical and biological degradation; also they just transfer the contaminants from one phase to another [4]. Therefore, there is a need to develop a novel treatment method that is more effective. Due to the economic constraints, development of a cost effective and clean process is essential. Photocatalysis is a promising technology in the field of green technology for the removal of dyes. Presently nanotechnology is widely applied for purification and treatment of waste water. The novel properties of nanomaterials such as large surface area, potential for self assembly, high specificity, high reactivity and catalytic potential make them an excellent candidate for this application [5]. An expanding trend for the nanomaterials is the fabrication of composite structures and devices with materials capable of enhancing the properties of the composite material. This can be achieved by utilizing the size advantage through templating on the nanomaterials and enhancing the properties to drive new synergetic properties of two combined materials [6]. In the present study polyindole based NiO-MgO nanocomposite was prepared, analyzed and used as photocatalyst and as an antimicrobial agent.

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II. Materials and Methods

AR grade chemicals obtained from Merck were used for the preparation of NiO-MgO (NMF) and the polyindole based NiO-MgO nanocomposite (PINM). NMF was prepared by the co-precipitation method in presence of capping agent and the PINM was prepared using chemical oxidation method. For the preparation of the nanocomposite NiO-MgO annealed at 500^0c was used. The surface morphology of the powdered sample was obtained by scanning electron microscope (SEM) [JEOL/EO JSM-6390] and the energy dispersive analysis (EDAX) of X-rays was carried out by the same to ascertain the composition. XRD study was carried out using XPERT-PRO model powder diffractometer (PAN analytical, Netherlands) employing Cu-K_α radiation (λ = $1.54060A^o$) operating at 40kV, 30mA.

III. Results and Discussion

The SEM and EDAX analysis of NMF and PINM are shown in Figures 1 and 2. NMF showed non uniform distribution of tiny particles of nanodimensions and PINM showed entirely different morphology. The EDAX of NMF have 68.92% of nickel, 11.78% of magnesium and 19.3% of oxygen. The mole ration of Ni to Mg is approximately 1:6. The EDAX for PINM was taken only to confirm the presence of metal oxides within the polymer structure. The energy dispersive spectra of PINM showed that chlorine was present as dopant in the nanocomposite. PINM was found to have 83.93% of carbon, 0.7% of oxygen, 13.6 % of chlorine, 1.13% of nickel and 0.63% of magnesium respectively.

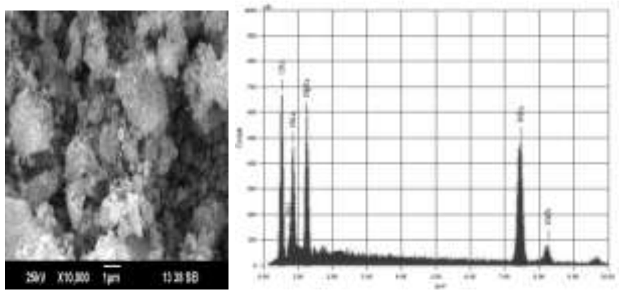


Figure 1. SEM and EDAX of NMF

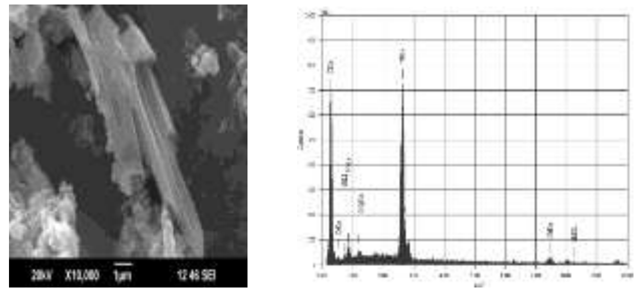


Figure 2. SEM and EDAX of PINM

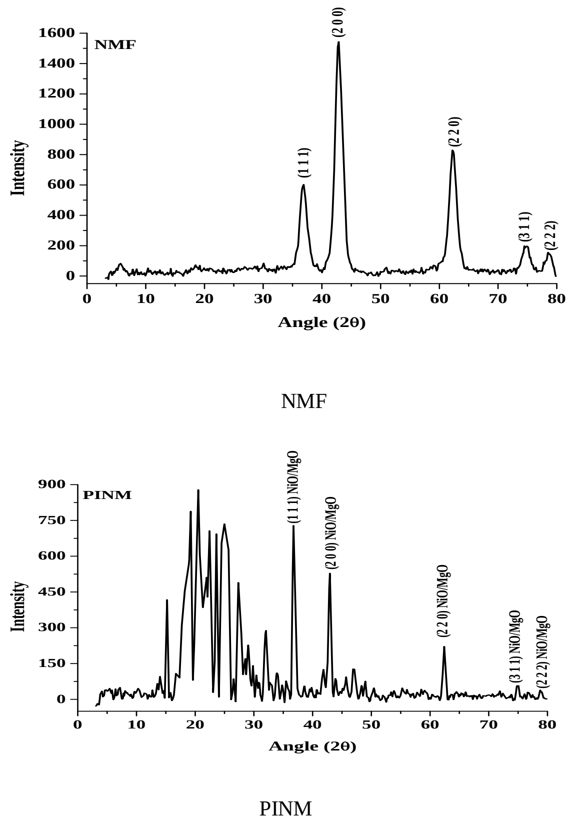


Figure 3. XRD spectrum

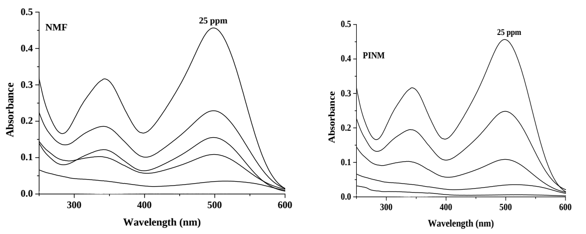
XRD of NMF and PINM are shown in Figures 3. The well defined X-ray diffraction peaks in the case of NMF indicate that it is crystalline. Also, the diffraction peaks are notably broadened indicating the small crystallite size. In order to confirm the phase purity of the sample prepared, the interplanar spacing (d_{hkl} values), 2θ values and relative intensity values corresponding to the observed diffraction peaks were compared with the standard values of reported by JCPDS-International Centre for Diffraction Data. NMF was compared with JCPDS-ICDD pattern number #78-0423 of NiO and JCPDS-ICDD pattern number #89-7746 of MgO. Both NiO and MgO form a cubic system with FCC lattice. Hence it is concluded that the nanocomposite formed is a cubic system with FCC lattice. From the XRD's of the polyindole based nanocomposite it is clear that the metal oxide particles are well distributed in the polymer matrix. The well defined peaks of the metal oxides were found to be incorporated into the XRD peaks of polyindole. From the XRD spectra, the particle size was calculated using Scherrer equation,

$$D = k\lambda / (\beta_{hkl})_{measured} * \cos\theta_{hkl} \qquad (1)$$

Here, D is the average crystallite size normal to the reflecting planes, k is the shape factor which lies between 0.95 and 1.15 depending on the shape of the grains (k =1 for spherical crystallites), λ is the wavelength of x-ray used and $(\beta_{hkl})_{measured}$ is the FWHM of the diffraction line in radians and θ_{hkl} is the Bragg angle corresponding to the diffraction line arising from the planes designated by Miller indices (hkl). The particle size for the NMF was found to be 6.59 ± 0.2 nm.

A. *Photocatalytic Studies*

A set of photocatalytic degradation of Congo red was carried out to measure the photocatalytic activity of PINM as a photocatalyst in presence of UV illumination. The experiments were performed by suspending photocatalyst into reactor with Congo red dye solution. The reaction was carried out isothermally at 30^0C. The concentration of residual Congo red in the solution after irradiation was determined by monitoring the absorbance intensity of solution samples at their maximum absorbance wavelength by using UV-Vis spectrophotometer which was recorded on a JASCO V 650 with a spectrometric quartz cuvette at room temperature. Figure 5 shows the UV spectrum analysis for four different time intervals. The variations in different experimental conditions affecting on photocatalytic oxidation of Congo red using catalyst PINM such as, illumination time (at different periods of time), different dye concentration and amount of catalyst loaded (ranging from 0.05 to 0.15 gm) were taken into account to reach to integrated model for the photocatalytic degradation of Congo red. The photocatalytic activity increased with increase of the illumination time and reaches to 100% after 120 min illumination time. The data reveals the relative high activity of the prepared catalysts which enables the complete degradation of the Congo red in such short illumination time and the catalyst has active sites for carrying out the reaction. The increment of catalyst loading from 0.05 to 0.1 gm increased the photodegradation efficiency of Congo red from 95 to 100% and after that any further increase in catalyst loading did not affect the photodegradation efficiency. This is attributed to the increase in the catalyst loading dose which increased the number of active sites available on the catalyst surface for the reaction, which in turn increased the number of holes and hydroxyl radicals. With increasing catalyst loading the number of active sites increases, but the penetration of UV light decreases due to shielding effect [7]. The rate of photocatalytic degradation decreased with the increasing initial dye concentration. As the initial concentration of a dye increases, the colour of dye solution becomes deeper which results in less penetration of light to the surface of the catalyst, decreasing the number of excited dye molecules. With increase in initial concentration of dye more and more organic substances are adsorbed on the surface of the photocatalyst. Therefore, the generation of hydroxyl radicals is reduced, since there are only fewer active sites in the system. Similar results have been reported by other researchers for the photocatalytic oxidation of pollutants [8, 9, 10].



NMF PINM

Figure 4. Absorbance spectrums at four different time intervals.

(e) V. cholera (f) S. epidermis

B. *Antimicrobial Studies*

PINM showed significant antibacterial effects for the gram positive bacteria: Staphylococcus epidermidis (S. epidermidis) and Clostridium perfringens (C. perfringens), gram negative bacteria: Escherichia coli (E. coli) and Vibrio cholera (V. cholera). Also, they showed antifungal properties against fungi: Penicillium chrysogenum (P. chrysogenum) and Aspergillus flavus (A. flavus). To study the enhancement obtained in composite formation NiO-MgO the test organisms were collected from Institute of Microbial Technology, Microbial Type Culture Collection Centre (IMTECH), Chandigarh. The strains were maintained on their respective medium in slants at 2-8^{0}C. The antibacterial activities of the prepared samples were evaluated by modified Kirby-Bauer disc diffusion method. The pure cultures of organisms were subcultured in Müller-Hinton broth at 35°C ± 2°C on an orbital shaking incubator at 160 rpm. For microbial growth, a lawn of culture was prepared by spreading the 100 µL fresh culture having 106 colony-forming units (CFU)/mL of each test organism on nutrient agar plates with the help of a sterile glass-rod spreader. Plates were left standing for 10 minutes to let the culture get absorbed. Then 8 mm wells were punched into the nutrient agar plates for testing nanomaterial antimicrobial activity. Wells were sealed with one drop of molten agar (0.8% agar) to prevent leakage of nanomaterials from the bottom of the wells. Using a micropipette, 100 µL (50 µg) of the sample of nanoparticle suspension was poured onto each of wells on all plates. After overnight incubation at 35°C ± 2°C, the different levels of zone of inhibition were measured around the disc in units of millimeter. Solvent blank was used as negative control. Antibiotic tetracycline was used as a positive control.

In the case of metal oxides the activity was found to be annealing temperature dependent. The activity of NMF was found to higher than those of NMS. This decrease in activity of samples annealed at higher temperature can be attributed to decrease in surface to volume ratio due to increase in particle size. The antimicrobial activity of the nanoparticles is generally known to be a function of the surface area which is in contact with the microorganisms. Reactions take place at the surface of a chemical or material. Hence, the smaller size and the higher surface to volume ratio *i.e.*, larger surface area of the NMF when compared to NMS has enhanced its interaction with the microbes.

In the case of NMF the inhibition of microbial growth can be attributed to the combined effect of NiO and MgO. The mechanism of the antibacterial activity of the MgO nanoparticles are mainly attributed to the presence of defects or oxygen vacancies at the surface of the nanoparticles which lead to the lipid peroxidation and reactive oxygen species generation. These materials also being good photocatalysts, their antibacterial mechanism can also be attributed to the destruction of the outer membrane of bacteria by the generated superoxide anion radicals ($\bullet O^{2-}$) as the reactive species. The reactive species such as •OH and $\bullet O^{2-}$ are generated at the catalyst's surface, hence the high surface area is very beneficial for degradation of bacteria.

Polyindole was found to have significant antimicrobial activity. Like polyailine, polyindole also contains quarternary ammonium salts (QAS) and halamines. Hence the antibacterial activity of PI can be attributed to the activity of QAS and halamines which are present in the polymer chain due to the presence of charged nitrogen as well as due to chloride ions. Nitrogen is present in the PI structure itself and the EDAX analysis of PI had confirmed the presence of chloride ions in the polymer chain as dopant. The presence of these two combined with the polycationic nature of polymer and the presence of polyfunctional groups is supposed to be a perfect recipe for making an antibacterial agent.

PINM have higher activities when compared to its counter parts. All the factors of PI combined with the activity of metal oxides was found to enhance the activity of the respective nanocomposite.

Among the microbes the activity of these samples were highest for S. epidermis and then for C. perfringens. Both these are gram positive bacteria. For all the samples, the activity was highest for gram positive than for gram negative bacteria. Among gram negative bacteria the activity was higher for E. coli than for V. cholerae. The variation in the sensitivity or resistance to both gram positive and gram negative bacteria populations could be due to the differences in the cell structure, physiology, metabolism or degree of contact of organisms with nanoparticles. Gram negative bacteria have a special cell membrane structure which possesses an important ability to resist antimicrobial agents; it has a relatively impermeable lipid based bacterial outer membrane. Greater sensitivity among gram positive bacteria can also be attributed to the greater abundance of amines and carboxyl groups on their cell surface than gram negative bacteria and the greater affinity of the antimicrobials used in the present work towards these groups.

The activity on the fungus A. flavus was found to be very low when compared with P. chrysogenum. The antibacterial activities of all the samples were higher than antifungal activity.

The polyindole metal oxide nanocomposite prepared in the present work showed comparable antibacterial activity with other polymer based nanocomposites. From the present work it is concluded that proper tuning of PINM nanocomposite can make it a good photocatalyst for photodegradation of organic dyes. Also, proper tuning of the nanocomposite is expected to improve its antimicrobial activity too.

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