Structural and photocatalytic degradation studies of rice straw based MgO nanocomposite

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Abstract. The present study is focused on the comparison of structural and photocatalytic degradation activities of nanocomposite of MgO formed with rice straw, a biopolymer. For comparison, counter parts were also synthesized. Nanoparticles of magnesium oxide were synthesized through controlled co-precipitation method in presence of citric acid. Structural characterizations of all the synthesized samples were carried out using XRD. Comparison of XRD of metal oxide with JCPDS confirmed that the formed metal oxide was MgO. Photocatalytic degradation of organic dyes Congo Red, an acidic dye and Methylene Blue, a basic dye was done.

1. Introduction
Photocatalysis is a special method that can be used for a variety of purposes such as degradation of different types of organic pollutants in wastewater, hydrogen production, air purification and antibacterial activity [1]. Photocatalysis based research is growing rapidly and gaining researchers more attention due to its advantages like low cost and high quality efficiency when compared to other methods. It is a unique method for rectifying issues related to energy and environment. With the various efficient methods that have come up in the technologies for the treatment of wastewater, low cost and less time consuming methods is the need to access pure water [2]. Natural materials applications as eco-friendly products, for disposing waste is the field gained great attention of the researchers, especially, in the synthesis of composites [3]. The use of farm residues like rice straw, rice husks and corn stover that are cheaper, available, renewable and biodegradable, can make profitable results. Since nature is the huge source of natural/bio-fibers, the utilization of bio-composites is expanding at a brisk pace. Because of the diversity in the optical, electrical and catalytic properties of nanocomposites prepared by incorporating metal nanoparticles into polymer matrix were found very significant applications. These have huge applications in the field of bioengineering, electronics, catalysis, and photonics [3]. Synthesis of nanocomposites is an expanding trend of nanoscience. In order to exploit the full potential of the technological applications of the nanomaterials, the scientists were guided towards the conventional polymers as one component of the nanocomposite. In the present work, we are focussed on the comparison of structural and photocatalytic degradation activity of nanocomposite of MgO formed with rice straw, a biopolymer.
2. Experimental
Merck’s AR grade chemicals were used in the precipitation of rice straw based MgO nanocomposite. Co-precipitation method was applied in order to prepare MgO nanoparticles in presence of capping agent.

Metal oxide of MgO nanoparticles was prepared as follows. Starting materials used were Magnesium nitrate dihydrate and sodium hydroxide with Citric acid as a stabilizer. Aqueous solutions of 25 ml, 0.1 M magnesium nitrate and 50 ml, 0.5 M sodium hydroxide were added drop wise into a beaker containing 25 ml, 0.01 M aqueous solution of citric acid while stirring using a magnetic stirrer. The stabilizer was used to prevent growth and agglomeration of the particles. The particle size was governed by the experimental parameters like concentration of the reactants, rate of mixing, pH, viscosity of the solutions etc. The stabilizers used for controlling the precipitation reaction should be easily and completely removable from the sample so as to avoid any possible contamination of the samples. After two hours of continuous stirring, the precipitate formed was in hydroxide form. The precipitated hydroxide that contains ions and other impurities was washed several times using distilled water to free from it. The wet precipitate was filtered and dried at room temperature and used an agate motor to obtain the hydroxide precursor in the form of fine powder. The powder so obtained was annealed at 600°C for 4 hours in a muffle furnace to obtain the respective metal oxide nanoparticles.

After proper cleaning and drying process rice straw waste was used. For the treatment of rice straw waste, basic NaOH solution and methanol were used. Small pieces of 5g rice straw washed using distilled water. NaOH solution was prepared by measuring NaOH equal to the weight of 10% of rice straw (0.5g) and making it upto 50 ml by dissolving NaOH in distilled water. Liquor to fiber ratio was taken as 10:1, ie, 50g of methanol for 5g of rice straw. Liquor and NaOH solution were added to the rice straw and were cooked on a heater for 20 minutes until the solution reduced to some amount on open air. It cool for some time and the pulps were further applied for acid pulping, where nitric acid (69% concentration) diluted (2.5 ml of acid and making it upto 25 ml using distilled water) was used in the pulp for heating until it reduces. It was cooled for some time. Again 25 ml of concentrated acid was added. After reduction and cooling process another 25 ml of acid was added and heated. The pulp turned to particles. After cooling distilled water was added to it and stirred for 15 minutes on a magnetic stirrer. After some time the powder settled. Water was decanted. The process was repeated thrice and finally washing was done using 50 ml of methanol. The solution was filtered using filter paper and dried at room temperature. Dried rice straw powder was collected and used for analysis. In case of nanocomposite based on rice straw annealed MgO was added at the time of pulp formation.

| Sample | Notations |
|--------|-----------|
| Magnesium oxide nanoparticles annealed at 600°C | MS |
| Rice Straw | RS |
| Rice Straw based Magnesium oxide nanocomposite | RSMS |

3. Results and discussions
Metal oxide prepared using co-precipitation method in present study was obtained in the form of hydroxide. Magnesium hydroxide and after annealing Magnesium oxide both were obtained as white powders. Rice straw and rice straw based nanocomposite was obtained as pale yellow.

3.1. XRD Analysis
XRD studies were done with XPERT-PRO model powder diffractometer (PAN analytical, Netherlands) that employing Cu- Kα radiation (\(λ = 1.54060\text{Å}\)) operating at 40kV, 30mA.
3.1.1. XRD analysis of MS

Figure 1 shows XRD of MS. The interplanar spacing (d_{hkl} values), 2\theta values and relative intensity values of magnesium oxide corresponding to the observed diffraction peaks were compared with the standard values of magnesium oxide as reported by JCPDS-International Centre for Diffraction Data. The data obtained for MgO in case of MS was matched with JCPDS-ICDD pattern number #89-7746. For MS diffraction peaks at 2\theta the values 36.67°, 42.88°, 62.19°, 74.6° and 78.51° corresponding to the crystal planes of (111), (200), (220), (311) and (222) respectively with no characteristic peaks corresponding to the impurities were detected, which further confirms the formation of pure stable MgO phase. JCPDS matching confirmed the cubic structure for MgO with FCC lattice. The average crystallite size of MS calculated from the line broadening of the XRD pattern, using FWHM values of three major peaks in the XRD spectrum making use of Scherrer formula are shown in Tables 2.

Table 2. Crystallite size calculation of MS using Scherrer equation.

| 2\theta | \theta  | \cos\theta | FWHM | D (nm) |
|---------|---------|------------|------|--------|
| 42.88   | 21.44   | 0.9309     | 0.745| 11.45  |
| 62.19   | 31.09   | 0.8565     | 0.779| 11.90  |
| 78.51   | 39.26   | 0.7746     | 0.789| 12.99  |

Average Crystallite size = 12.11 nm
3.1.2. XRD analysis of RS and RSMS

The XRD pattern of RS was found to match well with the XRD patterns in literature [4]. The XRD of rice straw showed the presence of a sharp crystalline peak in the diffraction pattern having 2θ value at 22.03°. The XRD of RS showed a few peaks having 2θ values between 15° and 30° and broad peaks between 30° and 50°. Figure 2 shows the XRD diffraction pattern of RS. The variation of XRD of RSMS when compared with RS confirms the formation of nanocomposite. Since doping level of metal oxide was low no sharp peaks of metal oxide was obtained in case of nanocomposite.

3.2. Photocatalytic Studies

Acidic dye Congo red and basic dye Methylene Blue of 1000 ppm concentration were prepared and the desired concentrations were taken and used as dye samples.

The photocatalytic activity of samples for the degradation of the dyes; Congo red (CR) and Methylene Blue (MB) were studied using the respective photocatalyst under the visible light illumination in a photoreactor. The experiments were performed by suspending the required quantity of photocatalyst into 300 ml of dye solution of needed concentration which was varied from 50 ppm to 75 ppm. The experiment was done isothermally at 300 K. The concentration of remaining dye in the solution after irradiation for 24 hrs was determined by monitoring the absorbance intensity of solution samples at their maximum absorbance wavelength by using UV-Vis spectrophotometer (JASCO V 650 UV/Vis spectrophotometer).

In the present work the factors affecting photocatalytic degradation like effect of contact time, amount of photocatalyst and dye concentration were also investigated.

To study the effect of contact time on the photodegradation of organic dyes, to the respective dye solution of concentration, 50 ppm in 300 ml solution kept at 300 K, 0.1 g of the photocatalyst was added and was kept under visible light. After desired time intervals [1, 2, 3 and 24 hrs], 10 mL of the solution was taken out, centrifuged and UV/Vis absorption spectra was recorded.

In the above experiment, the amount of photocatalyst was varied. 0.1 g and 0.15 g was used to study its effect on photodegradation.

Dye solutions of two different concentrations were selected (50 ppm and 75 ppm) to study the effect of initial dye concentration on photodegradation efficiency.

The photocatalytic degradation efficiency was calculated as follows:

\[
\text{Photocatalytic Degradation Efficiency(\%)} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]
\( C_0 \): initial concentration of dye solution [mgL\(^{-1}\)]

\( C_c \): final concentration of dye solution [mgL\(^{-1}\)]

The photodegradation of Congo red and Methylene Blue using the nanocomposite RSMS as well as its counterparts RS and MS were studied in detail. The results show high rate of photodegradation of the dye with increase in contact time. The photodegradation rate after 24 hrs for all the samples for both Congo Red and Methylene Blue are given in Table 3 and Table 4 respectively. Figure 3 shows the absorbance spectrum obtained for a few samples at various contact time.

In the calculation of degradation efficiency, the amount of loading catalyst is one of the chief parameters. For the efficient dye removal, it is required to find optimal loading in order to avoid the excessive use of the catalyst. The results showed that there was a slight decrease in the degradation percentage when catalyst dosage was increased. The significant decrease was due to the decrease in the formation of hydroxyl radicals. It should mention here that, the number of active sites on photocatalysts and the visible light penetration through the suspension, both affect the catalyst loading [5]. The number of active sites increases with the increase catalyst loading, but the visible light penetration decreases because of the shielding effect [6]. It should also be noted that the optimum value of catalyst loading is strongly dependent on the type and initial concentration of the dye and the operating conditions of the photoreactor [7].

The results imply that the photocatalytic degradation rate decreased according to the increasing of initial dye concentration. The colour of dye solution becomes deeper as the initial dye concentration increase, which reduces the light penetration into the catalyst’s surface and thereby decreasing the excited dye molecule. With the increase of initial dye concentration more and more organic substances get adsorbed on the surface of the photocatalyst. Therefore, the hydroxyl radicals generation is reduced, since there are only fewer active sites in the system [8]. The activity of the nanocomposite was also compared with the counter parts.

![Figure 3](image1.png)

**Figure 3.** Absorbance spectrum showing photodegradation of CR using MS, 50 ppm and RS, 75 ppm.
Figure 4. Absorbance spectrum showing photodegradation of MB using RS, 50 ppm and RS, 75 ppm.

Table 3. % Photodegradation of Congo Red using Synthesized samples.

| Sample   | Weight (g) | Concentration (ppm) | % Photodegradation |
|----------|------------|---------------------|--------------------|
| MS, CR   | 0.1        | 50 ppm              | 85.23              |
|          | 0.15       | 50 ppm              | 80.15              |
|          | 0.1        | 75 ppm              | 82.05              |
|          | 0.15       | 75 ppm              | 78.43              |
| RS, CR   | 0.1        | 50 ppm              | 59.54              |
|          | 0.15       | 50 ppm              | 54.23              |
|          | 0.1        | 75 ppm              | 53.24              |
|          | 0.15       | 75 ppm              | 46.36              |
| RSMS, CR | 0.1        | 50 ppm              | 96.46              |
|          | 0.15       | 50 ppm              | 90.54              |
|          | 0.1        | 75 ppm              | 91.45              |
|          | 0.15       | 75 ppm              | 87.23              |
Table 4. % Photodegradation of Methylene Blue using Synthesized samples.

| Sample     | Weight (g) | Concentration (ppm) | % Photodegradation |
|------------|------------|---------------------|--------------------|
| MS, MB     | 0.1        | 50 ppm              | 73.56              |
|            | 0.15       | 50 ppm              | 68.12              |
|            | 0.1        | 75 ppm              | 70.24              |
|            | 0.15       | 75 ppm              | 64.81              |
| RS, MB     | 0.1        | 50 ppm              | 43.12              |
|            | 0.15       | 50 ppm              | 35.84              |
|            | 0.1        | 75 ppm              | 34.29              |
|            | 0.15       | 75 ppm              | 29.15              |
| RSMS, MB   | 0.1        | 50 ppm              | 82.15              |
|            | 0.15       | 50 ppm              | 75.19              |
|            | 0.1        | 75 ppm              | 76.20              |
|            | 0.15       | 75 ppm              | 68.15              |

4. Conclusions
Structural characterizations of all the three synthesized samples were carried out using XRD. Comparison of XRD of metal oxide with JCPDS confirmed that the formed metal oxide was MgO. Phase purity and crystallinity of the sample was confirmed from XRD. Crystallite size was calculated using Scherrer equation. Photocatalytic degradation of organic dyes Congo Red, an acidic dye and Methylene Blue, a basic dye was done. In the present work the factors affecting photocatalytic degradation like effect of contact time, amount of photocatalyst and dye concentration were also investigated. The results show high rate of photodegradation of the dye with increase in contact time. Also, when catalyst dosage was increased, there was a slight decrease in the degradation percentage. The results also, indicate that the photocatalytic degradation rate decreased with the increasing initial dye concentration. The synthesized nanocomposite is a good photocatalyst for the photodegradation of organic dyes.

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