REMEDIATION OF ENVIRONMENTAL DYE POLLUTANTS USING ECO-FRIENDLY PHOTOCATALYTIC MATERIALS

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Abstract

Malachite green is taken as a model pollutant. Many researchers have reported that ZNO is a suitable alternate to TIO_2, as ZNO has the advantage of absorbing larger fraction of solar spectrum than tio_2 and its low cost. Hence, in the present study, the best semiconductor zno has been selected for the photo catalytic degradation of dye as it has high photosensitivity and large band gap. The high band gap of semiconductors makes them UV light active and hence used as catalyst in AOPS. It is also possible to make them active in the visible region which covers major fraction of solar spectrum by reducing the band gap of semiconductors by surface modification. India is a tropical country, so sunlight is an abundantly available natural energy source, which can be utilized for irradiation. Dyes can be degraded in the presence of photo catalyst upon irradiation with visible light because of their absorption in the visible region. Hence, in the present work, to develop its dual role as adsorbent and photo catalyst, agar-agar has been used for modification of the semiconductor photo catalyst, ZNO. In order to utilize the synergistic effect of both agar-agar and ZNO, the chemical modification has been done in the form of composite to carry out photo catalytic reactions under sunlight irradiation

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Introduction

Interactions between groundwater and surface water are complex. Consequently, groundwater pollution, sometimes referred to as groundwater contamination, is not as easily classified as surface water pollution. By its very nature, groundwater aquifers are susceptible to contamination from sources that may not directly affect surface water bodies, and the distinction of point vs. non-point source may be irrelevant. a spill or on-going releases of chemical or radionuclide contaminants into soil (located away from a surface water body) may not create point source or non-point source pollution, but can contaminate the aquifer below, defined as a toxin plume. The movement of the plume, called a plume front, may be analysed through a hydrological transport model or groundwater model. Analysis of groundwater contamination may focus on the soil characteristics and site geology, hydrogeology, hydrology, and the nature of the contaminants. Advanced Oxidation Processes (AOP) has been reported to be one of the most promising treatments based on total degradation of hazardous organic compounds. AOP's oxidize or mineralize the pollutants into their simpler forms, which are easily biodegradable and so it is facilitating their treatments in conventional processes, which are having an advantage of being cheaper than any other process.

AOP's can be homogeneous and heterogeneous in nature. Homogenous processes include simply the use of some chemicals/oxidation. The applications of homogeneous photo degradation to treat contaminated water, involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. The major oxidants used are hydrogen peroxide (UV/h_2o_2), ozone (UV/o_3), hydrogen peroxide and ozone ($UV/o_3/h_2o_2$), photo-fenton system (fe^{3+}/h_2o_2).

Photo catalysis is mainly applicable to the oxidation of organic compounds and reduction of inorganic species like metal ions. It is a photo induced reaction which is accelerated by the presence of a catalyst. photo catalytic reactions are activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy (e_g) of the catalyst. the absorption leads to a charge separation due to promotion of an electron (e^-) from the valence band of the semiconductor catalyst to the conduction band, thus generating a hole (h^+) in the valence band.

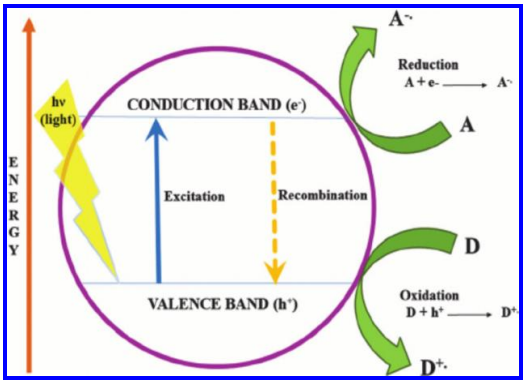

Figure 1 General Mechanistic Pathway of Photo catalytic Oxidation & Reduction

In addition to the usual photo catalytic oxidation mechanism, Nasr et al., and Zhang et al., added ''photosensitizing oxidation'' mechanism to explain their ''visible light'' induced photo-oxidation of dyes. their proposed photosensitizing oxidation mechanism suggests that the electron from the excited dye molecule is injected into the conduction band of the tio_2, and the cation radical formed at the surface quickly undergoes degradation to yield products [reaction (1.1)-(1.3)].

Dye + HγDye * ⟶ (1.1)

Dye * + Tio_2dye $^{\bullet+}$ + Tio_2 (E^-) ⟶ (1.2)

Tio_2 (E^-) $^{\bullet-}$ + O_2 Tio_2+ O2 ⟶ (1.3)

In the photo catalytic oxidation, tio_2 has to be irradiated and excited in near-UV energy. On the other hand, tio_2 is not necessary to be excited, if the excited dye (from visible light) is able to inject an electron on to its conduction band of tio_2, which leads to photosensitized oxidation. It is hard to judge whether the photo catalytic oxidation is superior to the photosensitizing oxidation mechanism, but the photosensitizing mechanism will help to improve the overall efficiency, and make the photo bleaching of dyes using visible light more feasible.

Materials

Agar-Agar

Agar is the Phycocolloid of most ancient origin. in japan, agar is considered to have been discovered by Minoyatarozaemon in 1658 and a monument is Shimizu-mura commemorates the first time it was manufactured. originally, and even in the present times, it was made and sold as an extract in solution (hot) or in gel form (cold), to be used promptly in areas near the factories; the product was then known as tokoroten. Its industrialization as a dry and stable product started at the beginning of the 18th century and it has since been called kanten. The word "Agar-Agar", however, has a Malayan origin and agar is the most commonly accepted term, although in French- and Portuguese-speaking countries it is also called gelosa. Agar is a mixture of the agarose polysaccharide and smaller polysaccharides called agaropectins. It can be extracted from the cell walls of certain seaweeds and is commonly used in the food and pharmaceutical industries as thickeners and in research and development as a substrate for cultivating microorganisms.

Figure 2 Agar and Zinc Oxide

Zincoxide

Zinc oxide (zno) is one of efficient Photo catalyst materials. The photo catalytic activity of zno was tested for the degradation of dye with initial concentration of 10 ppm under irradiation of solar simulator. The rate of decrease in concentration was measured using UV-visible spectrophotometer. Zinc oxide has attracted much attention because of its property of high photosensitivity, which causes degradation of various pollutants. ZNO has potential as photo catalyst material because its property of wide band gap. It is reported that zinc oxide is an n-type semiconductor with a wide band gap of 3.37 ev and a large exciton binding energy of 60 mev.

Malachite Green

Malachite green also is used as a direct dye for silk, wool, jute, and leather and to dye cotton that has been Mordant with tannin. Prepared from Benz aldehyde and dimethyl aniline, the dye occurs as lustrous green crystals soluble in water and in alcohol.

The dye employed for the photo catalytic studies in the present work is malachite green and this dye was obtained from m/s.sreechemidyes (India), Bangalore, and used as such without further purification. The structure of this dye is shown in fig. 2.1 and their properties are given in table 2.1. Stock solution of 1000 mg/l of dye was prepared by dissolving 1.0 g of the dye and was made up to

one litre using doubly distilled water. The required concentration of dye solution was prepared by diluting the stock solution.

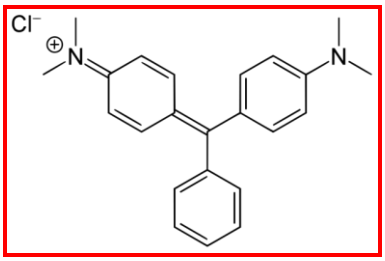

Figure 3 Structure of Malachite Green

Table 1 Properties of Dye Selected

Properties	Malachite Green
C.I. Name	Basic Green 4
Class	Triarylmethane
Color	Green
Molecular Formula	$C_{23}h_{25}n_2$
Molecular Weight	364.91 G/Mol
Synonyms	[4-[[4-(Dimethylamino)Phenyl]-Phenylmethylidene] Cyclohexa-2,5-Dien-1-Ylidene]-Dimethylazanium;Chloride
Λ_{Max}	616 Nm

Fabrication of Zinc Oxide/Agar Composite

Zinc oxide/agar composite was synthesized by a microwave method. About 1 g of the agar-agar was dissolved in 100 ml of distilled water at 95ºc under magnetic stirring. After complete dissolution, 100 ml of 0.1 m zinc chloride solution was added in to the agar-agar solution drop wise. 0.1 m naoh was prepared and added with stirring to zinc chloride-agar mixture solution to the PH of 10. The mixture was kept in a domestic microwave oven at 170 w for 25 minutes. After the reaction, a milky white composite was obtained. The composite was washed with distilled water and the obtained sample was dried at 80ºc in an oven.

Figure 4 Fabrication of Zinc Oxide/Agar Composite

Analytical Instrumental Techniques

The physico-chemical characteristics of the as-synthesized bio polymeric photo catalytic material were carried out using the following techniques.

Fourier Transforms Infrared Spectrometer (FTIR)

FTIR stands for "Fourier Transform Infrared" and it is the most common form of infrared spectroscopy. All Infrared Spectroscopies act on the principle that when Infrared (IR) radiation passes through a sample, some of the radiation is absorbed. The radiation that passes through the sample is recorded. FTIR spectra of the samples were obtained using FTIR spectrometer (jasco-460 plus model) by making a pellet of homogeneous mixture of kbr and solid sample using kbr die set. each sample was carried out with a resolution of 4 cm^{-1} in transmittance mode with 16 scans. The result of FTIR spectra was used to confirm the functional groups present in the as-synthesized bio polymeric photo catalytic material.

Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Analyzer (EDAX)

Energy-dispersive x-ray (EDX or EDS) analysis is a widely employed technique by today's materials scientists and used together with a Scanning Electron Microscope (SEM), an EDX detector can generate more information about a sample than an SEM can alone Using EDX, researchers can quickly generate information about the chemical composition of a sample, including what elements are present as well as their distribution and concentration. But how exactly does EDX work with an SEM, a variety of signals offer up different information about a given sample.

X-Ray Diffraction (XRD)

X-Ray Diffraction, or XRD, is a technique for analysing the atomic or molecular structure of materials. It is non-destructive, and works most effectively with materials that are wholly, or part, crystalline. The technique is often known as x-ray powder diffraction because the material being analysed typically is a finely ground down to a uniform state. Diffraction is when light bends slightly as it passes around the edge of an object or encounters an obstacle or aperture. The degree to which it occurs depends on the relative size of a wavelength compared to the dimensions of the obstacle or aperture it encounters. X-rays are a form of electromagnetic radiation includes wavelengths measurable in nanometers (a nanometer is equivalent to one billionth of a meter).

UV-Vis Diffuse Reflectance Spectra (DRS)

UV-Vis most often refers to absorption spectroscopy, measured by transmission, whereas DRS specifically refer to diffuse reflection spectroscopy. Normally, the former is used for solutions/suspensions or thin films, whereas the latter is used for solids - optically rough films or powder. Differential reflectance spectroscopy (DRS) is a surface analytical technique. It uses Ultraviolet (UV), visible, or Infrared (IR) light as a probing medium.

Photo Catalytic Studies

In order to study the synergistic effect of agar (biopolymer) and zinc oxide (photo catalyst), the respective dye solution were treated with agar, zinc oxide and zinc oxide/ agar composite respectively in the dark as well as in the presence of light.

The photo catalytic experiments were carried out by irradiation of dye with sunlight for a fixed time, the solution was filtered and the concentration of dye was measured by UV-Vis spectrophotometer. Prior to irradiation, solution suspended with photo catalyst was stirred in dark condition for 30 min to ensure that surface of catalyst was saturated with the dye. in the photo catalytic experiments, the extent of dye decolorization in terms of the percentage has been calculated using the following relationship (eq. 2.1).

$$\text{Decolorization}(\%) = \frac{C_O - C_T}{C_O} \text{ X } 100 \qquad (2.1)$$

Where,

C_O = Initial Concentration of dye (mg/l)

C_T = Final Concentration of dye (mg/l)

Analysis of Sample

The analysis of concentration of the dye before and after photo catalytic treatment was measured by UV-Vis spectrophotometer (Spectroquantpharo 300, Merck) at its wavelength.

Results and Discussion

This chapter deals with the characterization of bio polymeric photo catalytic material, zno/agar composite and its efficiency in the removal of malachite green dye by photo degradation. The photo catalytic material was characterized by suitable instrumental techniques like FTIR, SEM with EDAX, XRD and UV-DRS.

Characterization of fabricated Zno/Agar Composite

FTIR

The functional groups present in agar, the synthesized zno/agar composite and dye molecules adsorbed zno/agar composite are shown in fig. 5. the strong and broad peak was observed in the range of 3200–3600 cm^{-1} shows the possibility of overlapping between -nh_2 and -oh stretching vibrations in all the three categories. The sharp peak at 1630 cm^{-1} corresponds to bending vibration of -nh present in the agar, the synthesized zno/agar composite and dye molecules adsorbed zno/agar composite.

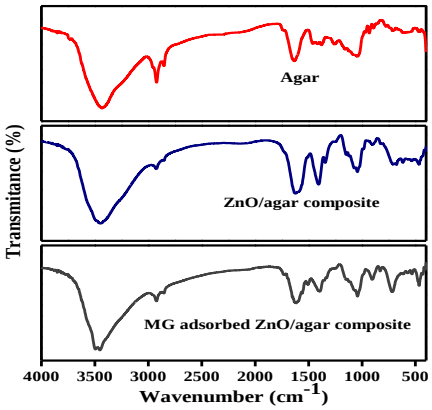

Figure 5 FTIR Spectra of Agar, ZNO/Agar Composite and ZNO/Agar Composite after treatment With mg Dye Under Sun Light

SEM Analysis

The surface morphology of synthesized Zno/agar composite before and after treatment with malachite green is shown in fig. 6. (a) Before treatment, fig. 6. (b) Show the surface is rough and have uneven edges and abundant pores on the Zno/agar composite surface. This kind of heterogeneous structure facilitates the diffusion of dye molecules into the surface and enhances the efficiency during the dye degradation treatment.

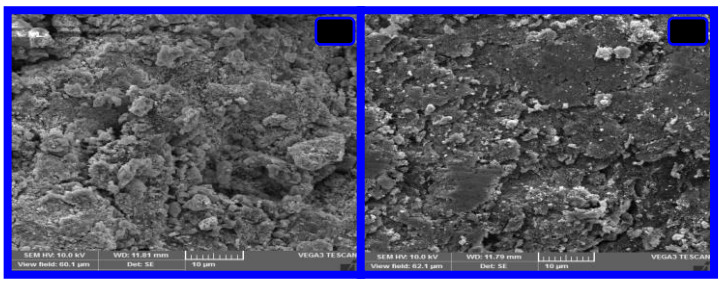

Figure 6 SEM Images of (a) ZNO/Agar Composite and (b) ZNO/Agar Composite After Treatment with mg Dye Under Sun Light

EDAX Analysis

The elemental analyses of zno/agar composite before and after dye degradation are shown in fig. 7. the characteristic peaks of zinc oxide was appeared (1–5 kev) in the EDAX spectra along with other ions such as c, n and o and it was confirmed that the respective ions were successfully embedded in the corresponding synthesized zno/agar composite.

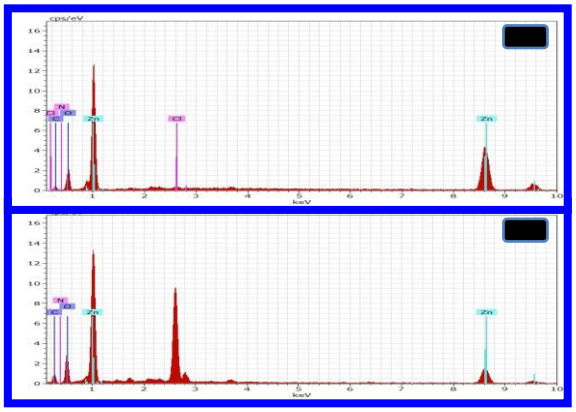

Figure 7 EDAX Spectra of (a) ZNO/Agar Composite and (b) ZNO/Agar Composite After Treatment with mg Dye Under Sun Light

XRD studies

The XRD analysis is a useful tool to describe the crystallographic information about the synthesized materials. The X-Ray diffraction patterns of zno/agar composite and after treatment with malachite green are shown in fig. 8. The presence of peaks at 2θ = 31.82°, 34.58°, 36.33°, 47.71°, 56.61°, 62.87°, 67.98° and 75.35° of zinc oxide clearly confirmed that the respective zinc oxide was successfully incorporated on the synthesized zno/agar composite.

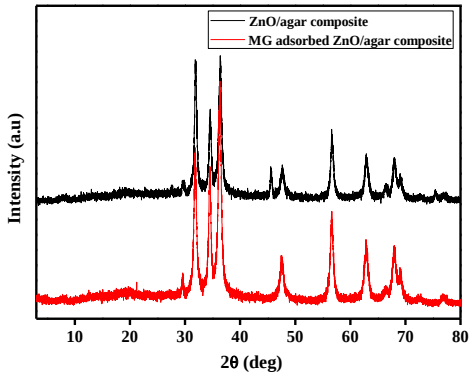

Figure 8 XRD Patterns of (a) ZNO/Agar Composite and (b) ZNO/Agar Composite after Treatment with mg Dye Under Sun Light

UV-VIS DRS Study

The UV-VIS diffuse reflectance spectrum was used to calculate the absorption edges of photo catalytic material and its corresponding band gap energy. ZNO has absorption edge cut off at 368 nm and had no absorption in visible range (> 400 nm).

However, when zno is modified with agar, a significant absorption edge cut off of 551.48 nm was observed for zno/agar composite. Additionally, the energy gap can be calculated from absorption edges which resulted from UV-VIS diffuse reflectance spectrum. The direct band gap of Zno/agar

composite was calculated by analyzing their absorption coefficients by tauc approach using the following equation.

$$\alpha = \frac{C(h\nu - E_g)^{1/2}}{h\nu} \quad (3.1)$$

Where α is the absorption coefficient, c is a constant, $h\nu$ is the photon energy and e_g is the band gap and can be calculated from the following equation.

$$E_g = \frac{hc}{\lambda} \quad (3.2)$$

Where h is plank's constant, c is the velocity of light and λ is the wavelength.

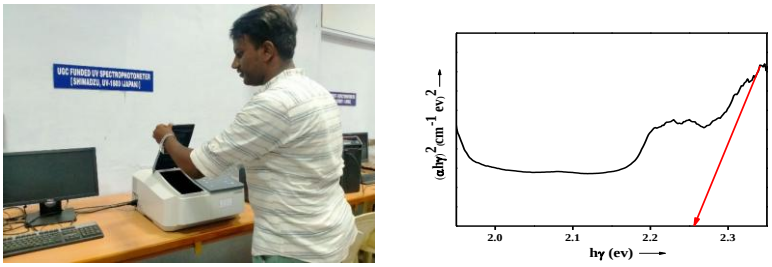

Figure 9 Tauc Plot-Band Gap Energy of ZNO/Agar Composite

Decolorization of Malachite Green Dye

The experiments were carried out for the decolorization of malachite green dye, at a fixed contact time of 120 min, 100 mg of catalytic dosage and 20 mg/l of 50 ml initial dye concentration. the percentage of decolorization of malachite green dye using the respective Agar, ZNO and ZNO/Agar Composite in dark was mainly due to the adsorption of dye over the surface of respective materials.

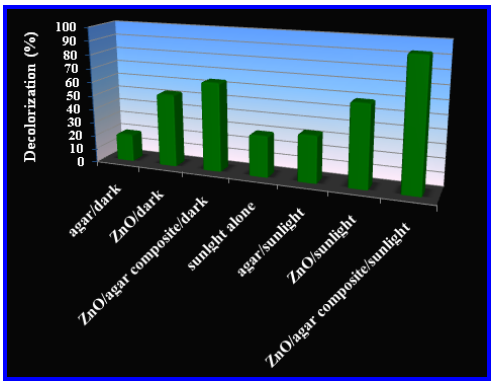

Figure 10 Adsorption, Photolysis, and Photo Catalytic Decolorization of Malachite Green Dyeunder Sunlight Irradiation

Photo Catalytic Degradation of Malachite Green Dye

The photo degradation of malachite green dye (50 ml) was carried out using zinc oxide/Agar Composite at various initial concentrations of dye ranging from 20 to 100 mg/l with constant

irradiation time of 120 min and 100 mg as fixed dosage of zinc oxide/Agar composite under sunlight irradiation.

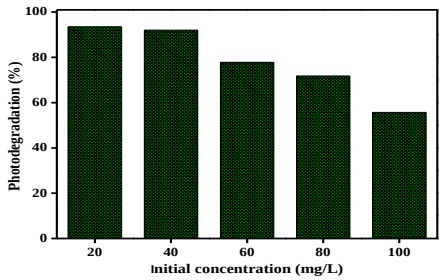

Figure 11 Effect of Initial Dye Concentration on Photo Degradation of Malachite Green Dye Using ZNO/Agar Composite

Conclusion

The bio polymeric photo catalytic material, zno/agar composite fabricated by micro-wave method exhibits simple operation and high photo catalytic activity. Sunlight was materialized as a light source because of its availability and non-hazardous nature. Therefore, to develop the technology, zno is modified with biopolymer such as agar which is cost-effective. From the FTIR spectra, it is clear that after treatment with malachite green dye molecules, most of the peak intensity was significantly decreased and this may be due to the dye molecules having the network with synthesized ZNO/Agar Composite. It is evident from the XRD pattern of ZNO/Agar Composite, the presence of peaks at $2\theta = 29.62°$ and 45.51° belong to agar present in the as-synthesized zno/agar composite. ZNO/Agar Composite could absorb more photons and eventually improve the photo response of ZNO to visible light region which is evident from UV-VIS, DRS that the band gap of the as-synthesized composite is 2.25 ev. The photo degradation of malachite green was found to be 93.5% with the irradiation time of 120 min and 100 mg as fixed dosage of zinc oxide/Agar composite under sunlight irradiation. The results of the present study will be useful in designing the cost effective and efficient treatment plant for the economic removal of malachite green from industrial waste water and textile effluents.

References

1. J.C. Henniker, Reviews Of Modern Physics 21 (1949) 322.
2. P.H. Gleick, Ed. (1993). Water In Crisis: A Guide To The World's Freshwater Resources. Oxford University Press. Pp. 13, Table 2.1 "Water Reserves On The Earth".
3. S.N. Kulshreshtha, Water Resources Management 12(1998)167.
4. "Charting Our Water Future: Economic Frameworks To Inform Decision Making", Retrieved 2010-07-25.
5. L. Baroni, L. Cenci, M. Tettamanti, M. Berati, Eur. J. Clin. Nutr. 61 (2007) 279.
6. L. Braun, Charles, N. Sergei, J. Chem. Edu. 70 (1993) 612.

7. C. Michael Hogan (2010), National Council on Science and the Environment, Washington, Dc.
8. H. Zolinger, Colour Chemistry- Synthesis, Properties of Organic Dyes and Pigments, Vch Publishers, New York, (1987) Pp 92.
9. E.J. Weber, R.L. Adams, Environ. Sci. Technol. 29 (1995) 1163.
10. C. Wang, A. Yediler, D. Linert, Z. Wang, A. Kettrup, Chemosphere, 46 (2002) 339.
11. E. Rindle, W.J. Troll, J. National Cancer Inst. 55 (1975) 181.
12. C.N. Sivaramakrishnan, Colorage, 9 (2004) 27.