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Sol-gel Derived Films of Nano-crystals of TiO₂ for Photocatalytic Degradation of Azorubine Dye

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Abstract: Immobilized films of nano-crystals of TiO_2 were prepared using sol-gel technique. The films were then characterized using SEM (Scanning Electron Microscopy), XRD (X-ray Diffraction) and UV-spectroscopy to evaluate the nanocrystalline nature. The photocatalytic performance of the prepared films in degradation of Azorubine dye was studied in detail. The results of the study confirmed that the photocatalytic degradation of Azorubine using sol-gel derived films is an efficient degradation process and it follows Langmuir –Hinshelwood (L-H) kinetics of heterogeneous reactions.

Keywords: Sol-gel technique, titanium dioxide, photocatalysis, Azorubine..

Introduction and Experimental

The presence of organic dyes in textile wastewaters may result in poor water quality. They need to be removed from waste water by different methods. Conventional methods such as biological, physical and chemical processes are having several drawbacks and they are not effective for complete degradation of recalcitrant organic compounds [1]. The development of alternative methods able to degrade toxic organic compounds is necessary. In this regard advanced oxidation processes (AOP) have attracted a great attention. Heterogeneous photocatalysis mediated by TiO₂ is of considerable interest for the waste water treatment. Photocatalysis by TiO₂ under UV light excitation involves generation of e^- and h^+ in conduction and valence band respectively. These species undergoes charge transfer reactions across the interface with the oxygen, water or organic pollutant adsorbed on TiO_2 surface. The reaction of h^+ with $OH^$ or H₂O leads to the generation of reactive OH 'radicals which are powerful oxidants attacking the recalcitrant organic compound of interest [2].

Most of the studies related to photodegradation have been carried out using the suspension of powder TiO_2

in aqueous solutions. The use of TiO_2 slurries in wastewater treatment has some disadvantages: the separation of the fine particles is difficult for reuse and penetration of light is limited. These problems can be minimized by supporting TiO_2 on various materials. Many techniques have been developed to obtain immobilized films of nano-crystals of TiO_2 [3]. The production of nanostructured films is nowadays an established method and TiO_2 nanoparticles are routinely produced through the sol-gel process. Porous TiO_2 thin films with large specific area have attracted more and more attention. The sol-gel process is generally recognized to be an efficient route for fabricating homogeneous porous films [4-6].

In the present work, nanosized TiO₂ films have been prepared on microscope glass slides using sol-gel process. The films are characterized using XRD (X-ray Diffraction), SEM (Scanning Electron Microscopy) and UV-spectroscopy. The photocatalytic performance and kinetics of the prepared films in the degradation of Azorubine dye have also been studied.

Materials

The chemicals used in this study were used as purchased. Azorubine $(C_{20}H_{11}N_2O_{10}S_3Na_3)$ dye powder, Nitric Acid (HNO₃) LR and Ethyl alcohol (C₂H₅OH) AR were obtained from s d Fine-Chem Ltd, Mumbai. Titanium (IV) isopropoxide (TIPO) was obtained from Acros, USA and Cetyltrimethyl-ammonium bromide (CTAB) AR was purchased from HiMedia Laboratories Pvt. Ltd. Mumbai.

Preparation of films

The sol-gel solution was prepared according to procedure explained by Valtierra et al., 2006 [7]. The sol-gel films on the microscope glass slides (75 mm \times 25 mm \times 1mm) were deposited by dipping and coating them in the sol-gel solution followed by heat treatment. The glass substrates were dipped in the sol-gel solution for 60 seconds and withdrawn slowly. One side of the microscope slides was covered with removable tape in order to avoid the deposit on it. The coated samples were dried at room temperature and then heated in a muffle furnace at 500 °C for 2 hours. The dipping, coating and heating process was repeated three times in order to get the uniform and thick films.

Characterization of prepared films

The SEM analysis of the nanostructure of the films, after being coated with gold, was done with the help of scanning electron microscope JSM 6100 (JEOL) operated at 25 kV. The phase composition of the films was studied by plate XRD technique [8]. The X-ray diffraction pattern were obtained on a Phillips PW-1710 X-ray diffractometer using Cu Kα radiation as X-ray source at an angle of 2θ ranging from 20-80°. The measurement was carried out at a scanning rate of 0.034 (2 θ)/second. The strongest peak of TiO₂ corresponding to anatase (1 0 1) were selected to evaluate the crystallinity of the samples. The mean crystallite size, L was determined from the broadening, β (the peak width of half maximum) of the most intense line in the X-ray diffraction pattern based on the Scherrer equation [9]

$$L = \frac{k \lambda}{(\beta \cos \theta)}$$

where k = 0.9 is the Scherrer constant; $\lambda = 1.5406 \text{ A}^{\circ}$ is wavelength of Cu K α radiation; $\beta = 0.5018$ is the full width at half maximum (FWHM); θ is the Braggs diffraction angle and L is the crystalline size.

UV-spectroscopy was used to record the transmittance spectra of films on HP 8453 UV-Vis spectrophotometer in the wavelength range of 300-550 nm. A microscope glass slide without any film was used as a blank.

Photocatalytic performance test

Photocatalytic degradation experiments were carried out in a photocatalytic chamber containing two 15W lamps as source of UV light to evaluate the photocatalytic performance of the sol-gel derived films. A dye solution of 50ml with concentration of 10ppm was poured into a beaker having cross sectional area of 86.6 cm². The slides carrying films of TiO_2 were placed in the beaker in such a manner that the total available surface of photocatalyst was 50 mm \times 75 mm. The beaker was then placed onto the working area of the photocatalytic reactor. A magnetic stirrer was used to provide mixing. Two UV light sources were then switched on and the solution was irradiated with the ultraviolet light The concentration of the dye at different reaction times were determined by measuring the absorbance intensity at $\lambda_{max} = 520$ nm with the help of the UV-Vis spectrophotometer. The decrease in concentration of the Azorubine was plotted with respect to time for analysis.

Kinetic Modeling

It has been agreed that the expression for the rate of degradation of dyes with irradiated TiO_2 follows the Langmuir –Hinshelwood (L-H) law of heterogeneous photocatalytic reactions [10]. According to L-H model, when initial concentration C_o is very small the following pseudo-first order rate equation is followed.

$$\ln \frac{C}{Co} = -kt$$

where k is pseudo- first order rate constant and t is time. A plot of ln (C/Co) versus time represents a straight line, the slope of which upon linear regression equals the pseudo-first order rate constant k.



Figure 1: SEM image of the sol-gel derived film supported on glass slide



Figure 2: XRD Patterns of sol-gel derived film supported on glass slide



Figure 3: Transmittance spectra of sol-gel derived film



Figure 4: Time effect on degradation of Azorubine



Figure 5: Kinetics of Azorubine degradation by sol-gel derived film

Results and Discussion

The SEM image of the surface of the sol-gel derived film at x3000 magnification was taken and is shown in Figure 1. It demonstrates the nanostructure of the film. Nano-sized particles are well known to exhibit different physical and chemical properties than larger particles. When nano-sized particles are used as catalyst, catalytic activity is expected to be enhanced due to the increased surface area.

Figure 2 depicts the XRD patterns of the sol-gel derived films with one major peak at $2\theta = 25.32^{\circ}$ which corresponds to (1 0 1) reflections of the anatase phase of TiO₂. The anatase phase is supposed to be the most active one for photocatalytic reactions. Films were calcined at a temperature of 500 °C which was high enough for the formation of the active anatase phase. The use of surfactant also contributed to the formation of anatase phase. The crystallite size was determined from the (1 0 1) peak of anatase phase using the Scherrer equation and calculated to be 16 nm (nanosized).

The UV-vis transmittance spectrum of sol-gel derived film was measured and is represented in Figure 3. It is obvious from the figure that the film absorbs UV radiations for activation of catalytic characteristics while almost all the visible radiations are transmitted.

The data for photocatalytic degradation of Azorubine solution by prepared films was recorded. The decrease in concentration of amaranth was plotted with respect to time and is depicted in Figure 4 It is obvious from the figure that the dye concentration decreased effectively with time. There was 67.5% decrease in Azorubine concentration after 5 hours of UV light

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illumination. The concentration versus time data was best fitted by an exponential equation with regression coefficient as high as 0.9996. The value of half-life time $(t_{1/2})$ for the degradation of Azorubine was calculated to be 3.11 hour. The sol-gel derived films showed a good performance in degradation of Azorubine.

The kinetics of degradation of Azorubine by sol-gel derived films supported on glass slides were also studied and are presented in Figure 5. The obtained data when plotted as ln(C/Co) versus time showed a straight line fit indicating that the degradation followed pseudo-first order kinetics according to the Langmuir – Hinshelwood (L-H) law. The pseudo-first order reaction rate constant calculated was 0.22 hr⁻¹

Conclusion

A detailed study for preparation and characterization of titanium dioxide films, and degradation of Azorubine dye was carried out. The results of SEM and XRD analysis showed that the sol-gel technique is an efficient process for the preparation of films of nanocrystalline TiO₂. UV-spectroscopy of the prepared films indicated that the nanoparticles of TiO₂ absorb UV-radiations for activation of its photocatalytic characteristics. The results of the photocatalytic degradation of Azorubine showed that sol-gel derived films are effective in removing the dye from water with a half-life time $(t_{1/2})$ of 3.11 hour. The degradation kinetics followed the Langmuir Hinshelwood (L-H) law of heterogeneous reactions. The pseudo-first order reaction rate constant recorded was 0.22 hr⁻¹

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