Studies on Photo Degradation of Indigo Carmine Dye by Mechanochemically Synthesized Nano Zinc Selenite

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Abstract: In the present paper a novel mechanochemical synthesis method was introduced for the synthesis of zinc selenite. The product was obtained at 320 °C by mechanochemical method for a period of 20 h. The structural and micro structural properties of ZnSeO₃ material was characterized by various analytical techniques like FT-IR, UV-DRS, XRD and SEM. The aim of the present work is to see the application of nanocrystalline material ZnSeO₃ for photodegradation of indigo carmine dye with respect to various dye concentrations and amount of catalyst. The XRD analysis confirms orthorhombic structure of ZnSeO₃ and the average particle size was found to be below 10 nm. Further, the effect of pH and dye concentration on photodegradation was studied. The photodegradation reaction was monitored on the UV-visible double beam spectrophotometer. ZnSeO₃ treatment exhibited 93% degradation of indigo carmine dye.

Key words: Mechanochemical method, zinc selenite, indigo carmine, photodegradation.

1. Introduction

A variety of hazardous pollutants are discharged into the aquatic bodies from several industrial streams [1-2]. The dye from textile industries and other commercial dyestuffs have been a focus of environmental remediation in the last few years [2-4]. Conventional methods for the abatement of water pollution from dye and textile industries like adsorption, absorption, incineration and biodegradation were found to be ineffective and expensive. Moreover, they pose secondary disposal problems and associated increase in time and cost of operation [5-11].

Recent development in the real chemical water treatment techniques has lead to the improvement in oxidative degradation by photochemical methods. Photo-catalytic oxidation is cost effective and capable

of degrading any complex organic chemicals when compared to other purification techniques. The formation of transient hydroxyl radicals (OH[•]) during photooxidation are highly reactive than any oxidation agent. The photodegradation are generally classified into two categories such as homogeneous and heterogeneous processes. Homogeneous processes occur in presence of UV light in conjunction with an oxidants such as ozone and hydrogen peroxide. Heterogeneous processes occur in presence of oxidants and solid photocatalyst. Photocatalytic degradations are very sensitive to pH, catalyst dosage, type of effluent, effluent concentration and the charges between the effluent and the catalyst [12].

There are many methods for eliminating water pollutants. Widely used semiconductor photocatalysts such as ZnO, SnO₂ and TiO₂, shows photoactivity. In order to enhance the activity of the TiO₂ catalyst, some researchers have tried to shift the E_g toward the visible

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light region by adding transition metal oxides such as HfO_2 , CdO , ZnO , Ge_2O_3 and In_2O_3 [13-15]. In this way, the beneficial effect of the Zn-doping of TiO_2 catalysts has already been reported in waste water treatment [5, 17]. Semiconductor photocatalysis has attracted a great deal of attention. The strong oxidative power of photogenerated holes on the surface of TiO_2 has made it the most practical photocatalytic material in fields such as environmental remediation [5, 17]. The photodegradation of organic compounds in colloidal and particulate TiO_2 catalyst suspensions has been well studied [18, 19]. ZnO is one of the representatives of the metal oxide class, which is important to the study of electrochemistry and catalysis. Other workers have tried to increase the reactivity of the semiconductors manipulating the morphology of the particle [20, 21]. However, this way is a complex one for obtaining semiconductors doped in small amounts with Zn and well-defined morphology, since there is a strong dependence on the preparation method and conditions [13, 22].

We reported the preparation of ZnSeO_3 powder and its photocatalytic activity in the degradation, a cationic dye usually used as a model to test for photocatalytic activity. In the present work, the scope was extended to cover indigo carmine (IC) which is an anionic dye usually used in the textile, food, and cosmetic industries. Indigo carmine is regarded as a highly toxic dye that may lead to tumours at the site of application, cause skin or eye irritation, and permanent injury to cornea and can be fatal if consumed. The toxicity tests of IC dye revealed long-term toxicity in mice and short-term toxicity in pigs [23-25]. In this report, the degradation of IC dye was investigated by using ZnSeO_3 nanocrystalline particles. The effect of various parameters such as pH, initial concentration of dye and intensity of UV light were studied.

2. Experiment

2.1 Synthesis of ZnSeO_3

The Zinc oxide, selenium dioxide, reagents used

were analytical reagent grade (AR), Indigo carmine ($\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$, Mol. Wt. 466.36 gm/mol) was purchased from research lab Fine Chem. Industries Mumbai, India. ZnSeO_3 Polycrystalline powder was prepared by using stoichiometric mixture of ZnO and SeO_2 and it was subjected to stepwise calcinations until terminal temperature of the reaction mixture occurred by heating in the muffle furnace with increase in temperature at the rate of 10°C per minute from one temperature to the subsequent higher temperature. After heating at higher temperature the material was cooled and grinded with gap of 2 h by using mortar and pestle. Later on, the grinded material was further heated at 100°C to 320°C for 12 h. The material was again grinded with gap of 2 h using mortar and pestle.

2.2 Characterization of ZnSeO_3

The XRD analysis of the sample was carried out by DX-2000 X-ray powder diffractometer with $\text{CuK}\alpha$ monochromatic radiation. The mean particle size of the product was calculated by using Debye Scherrer's equation from the full width at half maximum (FWHM) of the XRD pattern. FT-IR spectra of a powder sample was performed with KBr pellet on Shimadzu fourier transform infrared spectrophotometer 84000 S model. UV-DRS Spectra was carried out using JASCO UV-visible diffuse reflectance spectrophotometer. The structural morphology and association elemental composition is determined by scanning electron microscopy (SEM).

2.3 Photodegradation Study

The concentration of indigo carmine dye solution was 5 ppm. A 50 mL of dye solution was transferred into the reaction cell and then 50 mg of ZnSeO_3 nanocrystalline powder was added. This mixture was irradiated by UV lamp, which induced the photochemical reaction to proceed. Every 15 min the reaction mixture was taken and centrifuged to discard other sediment. These solutions were monitored on spectrophotometer (Shimadzu 1800) before and after

reaction at wavelength 610 nm. Experiments were repeated to get better results. An investigation of the effects of reaction conditions was also done by varying conditions and monitors the activity.

3. Results and Discussion

3.1 UV-DRS

The UV-diffused reflectance spectrum for ZnSeO_3 is depicted in Fig. 1 and show the broad absorption edge cut off in the vicinity of 370 nm. The broad shoulder in nanocrystalline material in the UV-visible range probably shows the formation of nano ZnSeO_3 . The band gap was calculated by using equation $E = h\nu$ and is found to be 3.40 eV.

3.2 XRD

Fig. 2 shows the X-ray powder diffraction pattern of the mechanochemically synthesized nanocrystalline ZnSeO_3 . Observed X-ray diffraction pattern for ZnSeO_3 nanoparticles shows high degree of crystallinity. All the peaks in XRD pattern match well with reported characteristic reflection peaks of ZnSeO_3 (JCPDS Card No.01-0864) and some peak from Card No. 31-1473. The crystallite size has been estimated from the X-ray peak broadening of (h, k, l) diffraction using Scherrer formula.

The average grain size of sample estimated from half width of the XRD (200) peak and found to be about 8.30 nm for ZnSeO_3 . The XRD peaks correspond to the orthorhombic structure of the zinc selenite.

3.3 FT-IR

Fig. 3 shows the FTIR spectra of nanocrystalline ZnSeO_3 . The bands around 887.24 cm^{-1} , 781 cm^{-1} , 522 cm^{-1} , 451 cm^{-1} are possibly caused by the stretching vibration due to the interactions produced between the oxygen and the cation occurring the octahedral and tetrahedral sites. The bands at $1,668\text{ cm}^{-1}$, $3,417\text{ cm}^{-1}$ are due to the stretching vibrational modes of metal-oxygen bond.

Fig. 1 UV-DRS spectra of ZnSeO_3 nanoparticle.

Fig. 2 XRD pattern of ZnSeO_3 nanoparticles.

Fig. 3 IR spectra of ZnSeO_3 nanoparticles.

3.4 SEM

The crystal morphology with elemental detection of milled powder for ZnSeO_3 is depicted in Fig. 4. A careful inspection of Fig.4 shows that some of crystals show tetragonal structure. The surface of the catalyst presents a spongy discrete particle appearance.

Fig. 4 SEM images of ZnSeO₃ nanoparticles.

3.5 Effect of pH

The degradation of dye was carried out at pH = 7 (Natural pH Range), as per the effluents from factories may cover a wide range of pH. To carry the efficiency of degradation by ZnSeO₃ solution of several pH value (3, 5, 7 and 8) were investigated. In general it is known that the metal oxide particles in water exhibit amphoteric behavior and readily reacts with dye.

3.6 Effect of Dye Concentration

The study of initial concentration of indigo carmine dye on the photocatalytic efficiency was investigated with concentration of 5, 10, 15 and 20 ppm solution. It was observed that the increase in dye concentration, decrease in degradation efficiency. Hence, the photo-oxidation process will work faster at a low concentration of pollutants. These results are in good agreement with previous reports [26-28] that photodegradation of textile dye Reactive Red 2, C.I. Acid Yellow 17 and Direct Yellow 12 decreased with increasing concentrations. At high concentrations of dye, the deeper coloured solution would be less transparent to UV light and the dye molecules may absorb a significant amount of UV light causing less light to reach the catalyst and thus reducing the OH• radical formation. Since OH• radicals are of prime importance in the attack of the dye molecules, lowering

the amount of OH• radicals would cause the photodegradation efficiency to decrease [29].

3.7 Effect of Amount of Catalyst

The experiment was carried out with and without catalyst (25 mg, 50 mg, 75 mg and 100 mg) at pH = 7 under the UV lamp. No degradation was found without catalyst loading dosage. Fig. 5 shows the % of untreated indigo carmine with time at pH = 7. The complete degradation of indigo carmine dye was found in the 120 min with catalyst of 50 mg gave a better results than other catalyst dosage when studied under same constant pH condition (Fig. 6). The amount has increased from 25 mg to 100 mg catalyst, this shows

Fig. 5 Effect of amount of dye concentration on dye degradation.

Fig. 6 UV Spectra of Absorbance vs wavelength.

Fig. 7 Effect of amount of photocatalyst on dye degradation.

that increase in catalyst loading decrease the rate of decoloration (Fig. 7). Therefore, 50 mg catalyst loading is considered to be an optimal value. This phenomenon may be explained as, with an increase in catalyst loading the light penetration through the solution becomes difficult. Increase in catalyst concentration decreases photo absorption which in turn reduces the dye adsorption onto the catalyst surface thus reducing the reaction rates [12, 30-32]. Fig. 7 shows the degradation of IC is higher for 50 mg catalyst loading after 120 min exposure to UV irradiation. Optimal concentration of the catalyst depends on working condition and the incident radiation [31, 33, 34].

4. Conclusions

The ZnSeO₃ synthesis was carried out under ecofriendly, easily and cheap solid state mechanochemical method. ZnSeO₃ was successfully employed in the degradation of indigo carmine dye. The optimization studies revealed the dependence of the degradation of indigo carmine on initial dye concentration and amount of the catalyst. This study highlights that the ZnSeO₃ can be used as the heterogeneous photocatalyst.

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