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Sm–ZnO–Ag: An efficient photo degradation of Congo Red dye with Light Emitting Diodes illumination

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Abstract : The Sm-ZnO-Ag photocatalyst was successfully synthesized by precipitation-decomposition method. The photocatalytic activity of Sm-ZnO-Ag was investigated for the degradation of Congo Red (CR) in aqueous solution using Light emitting diodes. Sm-ZnO-Ag is found to be more efficient than doped and undoped ZnO Nps at pH 9 for the mineralization of Congo red under LEDs. The influence of operational parameters such as the amount of photocatalyst, dye concentration, initial pH on photo mineralization of congo red has been analyzed. The catalyst is found to be reusable and the mechanism of degradation by Sm-ZnO-Ag is proposed.

1. Introduction

The recent rapid development of the industrial sector has contributed to environmental problems and to high levels of water pollution globally. Additionally, there is an increase in demand for water in the industrial, agricultural, and domestic sectors, which generate large amounts of contaminated wastewater. The general classes of compounds that occur in contaminated water are solvents, dyes, dioxins, pesticides, asbestos, arsenic, and heavy metals [1,2]. Dyes are often difficult to decompose in water; a considerable amount of dye-containing wastewater is generated in industries such as fabrics, leather, paper, food, cosmetics, agricultural research, pharmaceuticals, electroplating, and distillation. This causes damage to the environment as dyes are toxic to aquatic life [3]. The principal methods of water treatment such as coagulation, flocculation, filtration, electro-flocculation, reverse osmosis, and adsorption does not degrade pollutants, but instead decrease their levels by winning over the pollutants from one phase to another, thereby creating secondary pollution [4]. An alternative method used to degrade dyes in wastewater is oxidation. The oxidation process uses oxidants such as molecular oxygen, ozone, or peroxide. However, a limitation of this process is the poor oxidation potentials of the oxidants and thus long treatment time is required. Thus, there is a need to identify new materials with higher oxidation potentials to treat dye wastewater. The advanced oxidation process can also be used in which hydroxyl radical species are generated to degrade the dyes in wastewater . This technique requires a high energy light irradiation source and an oxidant to generate hydroxyl radicals [5,6]. These photocatalytic degradations have been carried out in the presence of natural sunlight or a mercury vapor lamp [7]. However, energy-efficient light emitting diodes (LEDs) have recently been used as an alternative light source for the photocatalytic degradation of various pollutants present in water and air [8]. LEDs are emerging as a new irradiation source and many researchers are studying the photocatalytic activity of synthesized photocatalysts under LED irradiation and exploring photocatalytic reactor designs [9,10]. We repot the Sm-Zno-Ag nps demonstrate the photocatalytic activity and its stability for photodegratation of congo dye with LEDs illumination; Among this a possible mechanisms of photodegratation have been described.

2. Experimental

2.1 Materials and Methods

All the reagents taken in this work were of AR grade and used as it is. The commercial Congo Red dye, Zinc nitrate, Oxalic acid, Silver nitrate and Samarium chloride were obtained from Sigma-Aldrich and Merck. Distilled water is taken to prepare experimental (alkaline $KmnO_4$) solutions. Proper pH is maintained by adding acid or base before irradiation of the solution.

2.2 Analytical Methods

Powder X-ray diffraction pattern was obtained using an X'Pert PRO diffractometer equipped with Cu-Ka radiation (wavelength = 1.5406 A˚) at 2.2 kW (max). The morphology of the samples was examined using a JEOL JSM-6701F Field Emission Scanning Electron Microscope (FE-SEM). Before FE-SEM measurements with gold coating and equipped with OXFORD, energy dispersive X-ray microanalysis (EDS). UV-Visible Absorbance and diffuse reflectance spectra were recorded in Shimadzu, (UV 2450) double-beam spectrophotometer. Photodegradation of dye using LEDs illuminations experiments were early discussed [11].

3. Results and Discussion

3.1. Characterization of catalyst

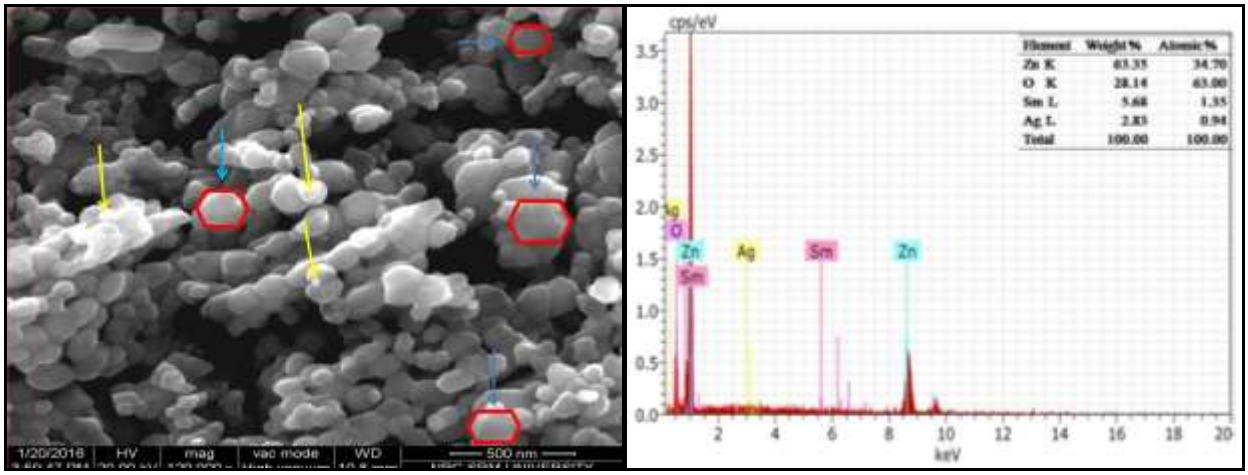
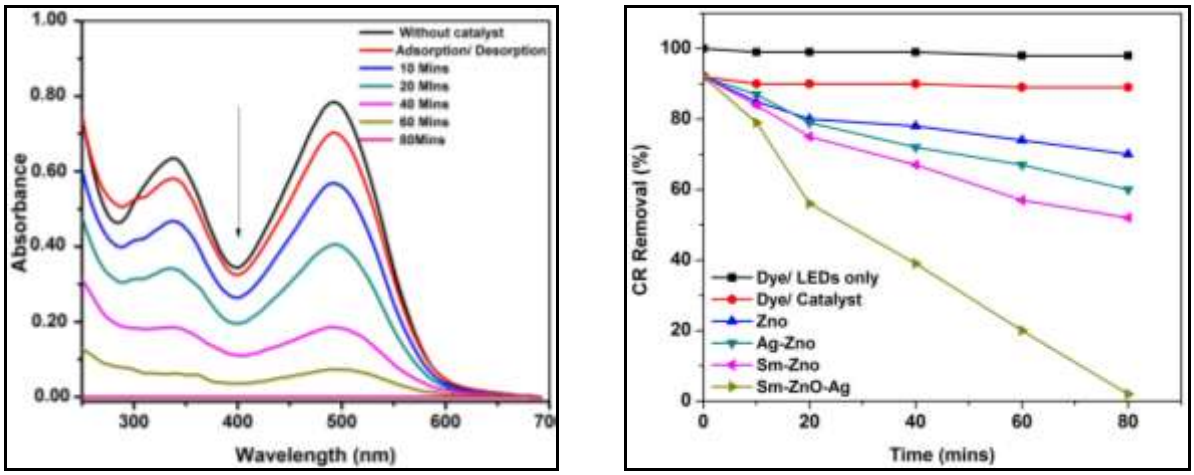


Fig. 1 FE SEM Image and EDX data of Sm-ZnO-Ag Nps.

Synthesis, characterization and its photocatalytic activity of 4 wt% Sm-ZnO-Ag for the degradation of MB solar light/LEDs were reported earlier [11]. XRD analysis of Sm-ZnO-Ag, four major peaks obtained at wurtzite ZnO structure 36.18, 34.36, 36.18, and 56.56. The hexagonal structure of ZnO is clearly seen from HR-SEM images at higher magnification. The hexagonal structure of ZnO particles is clearly seen (Fig. 1). Sm/Ag particles are well dispersed on the surface of ZnO (indicated by arrow marks).



Fig, 2 UV-vis spectra of CR on irradiation with LEDs light in the presence Sm-ZnO-Ag: [CR] 2 x 10^{-4} M; pH - 9; catalyst suspended 3g L^{-1} and the same conduction with different catalyst to degradation of CR Dye.

3.2 Photodegradability of CONGO RED

Fig. 5 shows the percentage of CR on irradiation of an aqueous solution of CR (2x 10^{-4}M) in the absence and the presence of photocatalysts under LEDs. It has been observed that almost complete degradation of the dye takes place at the time of 80 min with Sm-ZnO-Ag under LEDs. This was contrasted with 11.3% decrease in dye concentration occurred for the same experiment performed with Sm-ZnO-Ag in the absence of LEDs. This decrease may be due to adsorption of the dye on the surface of the catalyst. Negligible degradation (0.4%) was observed when the reaction was allowed to occur in the presence of LEDs without any catalyst (Fig. 2). These observations reveal that LEDs and photocatalyst are needed for effective destruction of CR. When Sm/ZnO, Ag/ZnO, and bare ZnO were used under same conditions only 63.6%, 49.6% and 44.5% degradations occurred, respectively. This shows that UV/Sm-ZnO-Ag process is more efficient in CR degradation than other processes. Since the degradation was effective with Sm-ZnO-Ag, the influence of operational parameters had been investigated for this process to find out the optimum conditions[12,13].

3.3 Effect of Operational Parameters

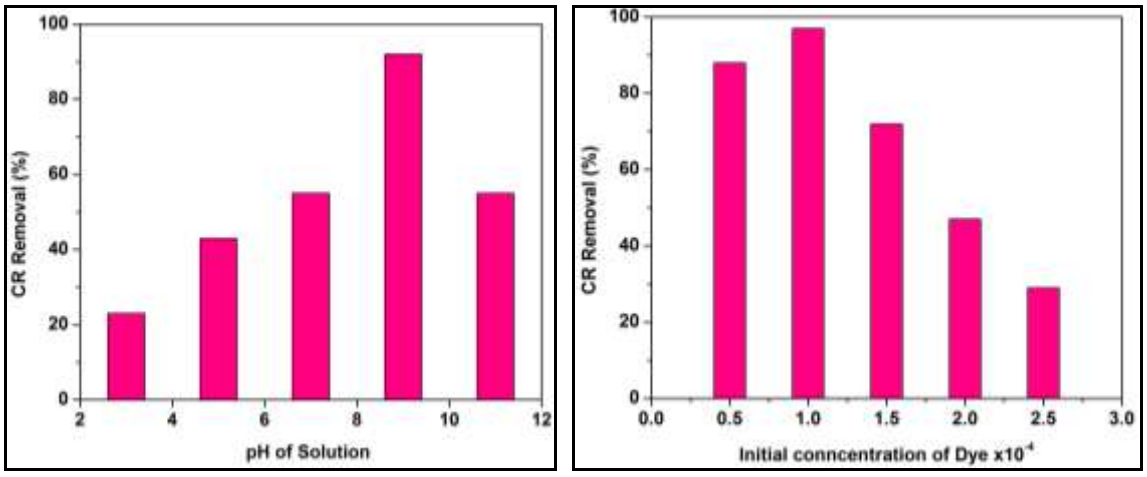


Fig. 3 Effect of solution pH and initial dye concentration of CR on irradiation with LEDs light in the presence 4% Sm-ZnO-Ag: catalyst suspended 2g L^{-1}

3.3.1 Effect of solution pH

The solution pH plays an important role in the photocatalytic degradation process of various pollutants [14,15]. The effect of pH on the photodegradation of CR was studied in the pH range 3–11. The pH of the

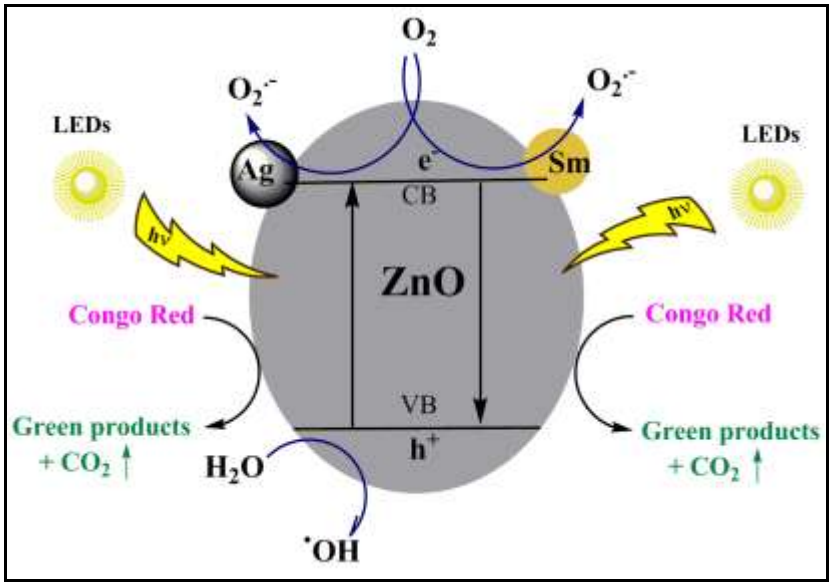
solution was adjusted before irradiation and it was not controlled during the course of the reaction. The degradation percentage for Sm-ZnO-Ag at pH 3, 5, 7, 9 and 11 are 29, 43, 78, 92and 55, respectively (Fig. 3). It is observed that increase in pH from 5 to 9 increases the removal efficiency of CR and then decreases.

3.3.2 Effect of Catalyst loading

A series of experiments were carried out to assess the optimum catalyst loading by varying the amount of catalyst from 1 to 5 gL^{-1}. The increase of catalyst concentration decreases the rate constant of degradation. Enhancement of removal rate is due to the increase in the amount of catalyst which increases the number of dye molecules adsorbed, and the increase in the density of catalyst particles in the area of illumination. The decrease in the removal efficiency of CR at higher concentrations is due to the light reflectance by catalyst particles. Similar results have been reported for the photodegradation of dyes by TiO2 and ZnO [11].

3.3.3 Effect of initial dye concentration

The effect of various initial dye concentrations on the degradation of CR on Sm-ZnO-Ag surface has been investigated. Increase of dye concentration from 1 to $4x10^{-4}$M decreases the rate of degradation (Fig. 3). The rate of degradation relates to the $^{\cdot}OH$ radical formation on catalyst surface and probability of $^{\cdot}OH$ radical reacting with dye molecule. At high initial dye concentrations, the path length of photon entering into the solution also decreases.



Scheme 1. Mechanism of degradation of CR by Sm-ZnO-Ag Nps.

3.3.4 Mechanism of degradation

The catalyst exhibited 95% activity even at fourth successive cycle under the LEDs irradiation. These results indicated that Sm-ZnO-Ag catalyst remained effective and reusable under LEDs light. Since photo catalyst is found to stable, reusable and more active when compared to bare and doped ZnO catalysts, a mechanism based on the energy levels of Sm-ZnO-Ag is proposed for the degradation of dye. Band energy levels for Sm-ZnO-Ag discussed (Scheme 1) Electrons generated by LED light are transferred from CB of Ag/Sm to CB of ZnO whereas holes are transferred from VB of ZnO to VB of Ag/Sm. It was earlier reported that, even though the CB level of electron donor (Ag/Sm) is lower than that of electron acceptor (ZnO), electron transfer may also happen from Ag/Sm to ZnO [11,14]. This electron–hole transfer process is faster than its recombination in Ag/Sm. The electrons in CB of ZnO produce $O_2^{\cdot-}$ which degrades the dyes. The holes in the Ag/Sm and the holes produced in ZnO by photoexcitation react with H_2O and $^{\cdot}OH$ to produce $^{\cdot}OH$ radicals for the degradation of the dye molecule.

4. Conclusions

A new Sm-ZnO-Ag was synthesized by precipitation–decomposition method. The catalyst was cheresterised XRD, HR-SEM, EDS, Optical spectral analysis. The PL spectra reveal the suppression of recombination of the photogenerated electron–hole pairs by catalyst. Sm-ZnO-Ag is found to be more efficient than pure and doped ZnO for degradation of CR under LEDs light. The optimum pH and catalyst concentration for efficient removal of dye are found to be 7 and 3 g L^{-1}, respectively. The catalyst was found to be reusable and mechanism also discussed.

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