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Solar active photocatalyst for effective degradation of RR 120 with dye sensitized mechanism



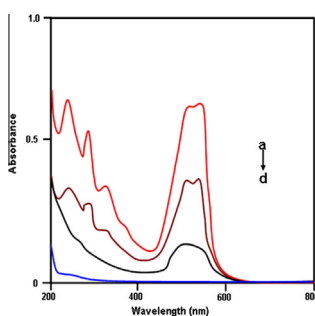
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HIGHLIGHTS

- This catalyst is found to be reusable.
- Treatment of dye effluent under solar light will be more economical and eco-friendly.
- The presence of dye sensitized mechanism also has been proved.
- COD measurements confirm the complete mineralization of the dye molecule.

GRAPHICAL ABSTRACT



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ABSTRACT

Solar active WO₃ loaded Ag–ZnO (WO₃–Ag–ZnO) was successfully synthesized by precipitation–decomposition method. XPS reveals that the presence of metallic silver in the catalyst. The photocatalytic activity of WO₃–Ag–ZnO was investigated for the degradation of Reactive Red 120 (RR 120) in aqueous solution using solar light. WO₃–Ag–ZnO is found to be more efficient than Ag–ZnO, WO₃–ZnO, Ag–WO₃, commercial ZnO, prepared ZnO, Degussa TiO₂–P25, pure WO₃ and TiO₂ (Merck) at pH 7 for the mineralization of RR 120. The effects of operational parameters such as the amount of photocatalyst, dye concentration, initial pH on photo mineralization of RR 120 have been analyzed. The mineralization of RR 120 has been confirmed by COD measurements. A dual mechanism has been proposed for efficient degradation of RR 120 dye with WO₃–Ag–ZnO under solar light at neutral pH. This catalyst is found to be reusable.

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Introduction

In view of the critical problem associated with industrial activities, mainly related to the high environmental impact of their residues and the relatively low efficiency of the current remediation process, many efforts have been dedicated to the study of new and more efficient degradation alternatives. Reactive dyes represent an important portion of the commercial synthetic dyes, mainly because of their excellent binding ability initiated by the formation of a covalent bond between their reactive groups and the surface groups of the textile and cellulose fibers. They are used

widely in textile industries, and their release in the ecosystem represents increasing environmental hazard, because of their toxicity, mutagenicity, and non-biodegradability [1,2]. Also, reactive dyes are, in general, the most problematic among other dyes, as they tend to pass through conventional treatment systems unaffected [2–4]. Among reactive dyes used in textile industry, Reactive Red 120 (RR 120) is one of the frequently used dye in textile industries and is a potential threat to the aquatic environment due to its poor biodegradability [5].

Disposal of these dyes and remediation of associated contaminated sites remains a universal problem. Therefore, foregoing to discharge of wastewaters to water ecosystems, removal of recalcitrant pollutants has become a prerequisite for living Earth. Therefore semiconductor-assisted photochemical process occupies a

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“prominent place”, mainly because of its high degradation capacity towards toxic chemical degradation chemical species through relatively simple and low-cost procedures. Semiconductor (ZnO or TiO₂) mediated photocatalysis is a process that aims at the destruction of pollutants present in water and air in a non-toxic way. Photocatalysis is activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy (E_{bg}) 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 and an electron in the conduction band, then the activated electron is to react with dissolved oxygen to produce superoxide radical anion, while the hole reacts with water to produce hydroxyl radical. Both species are highly reactive towards toxic chemical degradation. In most the cases, TiO₂ has been widely employed for this process under ultraviolet (UV) light circumstance [6–8]. However, UV light sources are generally pricey and not easy to obtain scientifically feasible for applications. The biggest advantage of ZnO is that it absorbs a large fraction of solar spectrum than TiO₂ [9]. Usually, sunlight contains about 4% ultraviolet light [10,11], and TiO₂ can only absorb wavelengths in the near ultraviolet (UV) region ($\lambda < 400$ nm), which is only about 3% of the solar spectrum. Hence it cannot utilize visible light efficiently [12,13]. Utilization of “solar energy” is a very interesting aspect of science. Semiconductor oxides are important for many environmental and energy issues because, they utilize solar energy to eliminate harmful pollutants present in air and water efficiently and detoxify toxic and harmful gases [13,14]. Therefore, it is of great interest to develop new visible or solar light photocatalysts to extend the absorption wavelength range into the entire visible light region [15–19]. ZnO is an important wide band gap semiconductor, which is bio-safe and biocompatible material and can be directly used in heterogeneous photocatalysis [20]. Many problems arise, such as the fast recombination rate of the photoexcited electron–hole pairs, which is the key factor in the process of semiconductor photocatalysis [21]. For that reason, there has been much interest in lowering the recombination rate of electron–hole pairs in order to improve the photocatalytic efficiency of semiconductor photocatalysts [22,23].

The design and modification of ZnO photocatalyst with high sensitivity and reactivity have attracted much attention in recent years. One successful approach is to modify semiconductor photocatalyst with noble metal ions such as Pt, and Ag [24–28]. On the contrary to the coupled semiconductor system with different band gap widths has been demonstrated in many studies as one of the most effective method to improve the photocatalytic activity of semiconductor. In addition to single semiconductor photocatalyst, many coupled semiconductor systems, such as ZnO–Fe₂O₃ [29,30], ZnO–WO₃ [29,30], ZnO–SnO₂ [31], TiO₂–WO₃ [32,33] have been reported earlier. WO₃ is one of the best visible or sunlight responsive photocatalyst and an n-type semiconductor for O₂⁻ generation using sacrificial reagents [34,35], but reports on the degradation of organic substances over WO₃ are limited [36–39]. Additionally,

mesoporous WO₃/TiO₂ films have successfully shown an enhanced activity in the degradation of organic pollutants [40,41]. Degussa P25, a commercially available ZnO and TiO₂ have been reported to have exhibited a good performance under solar light photocatalysis [42,43] but suffer the disadvantage of non-reusability as it does not settle out of the solution, and will require additional separation techniques, which will automatically increase cost. In this present work, the photocatalytic activity of WO₃ loaded Ag–ZnO towards RR 120 dye degradation under solar light is established.

Experimental

Materials

The commercial azo dye Reactive Red 120 (Fig. 1) from Balaji Colour Company, Dyes and Auxiliaries (Chennai) was used as such. Oxalic acid dihydrate (99%) and zinc nitrate hexahydrate (99%) were obtained from Himedia chemicals. AgNO₃ and WO₃ were obtained from sigma Aldrich. ZnO (Himedia), TiO₂ (Merck) were used as received. A gift sample of Degussa TiO₂-P25 was gained from Evonik (Germany). It is a 80:20 mixture of anatase and rutile. It has a particle size of 30 nm and BET surface area 50 m² g⁻¹. K₂Cr₂O₇ (s.d.fine), Ag₂SO₄ (s.d.fine), HgSO₄ and FeSO₄·7H₂O (Qualigens) were used as received. The double distilled water was used to prepare experimental solutions. The pH of the solutions before irradiation was adjusted using H₂SO₄ or NaOH.

Analytical methods

X-ray photoelectron spectra of the catalyst was recorded in an ESCA-3 Mark II spectrometer (VG scientific Ltd., England) using Al K α (1486.6 eV) radiation as the source. The spectra were referenced to the binding energy of C1s (285 eV). UV spectral measurements were done using Hitachi-U-2001 spectrometer.

Irradiation experiments

All photocatalytic experiments were carried out under similar conditions on sunny days between 11 am and 2 pm. An open borosilicate glass tube of 50 mL capacity, 40 cm height and 20 mm diameter was used as the reaction vessel. The suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between dye and WO₃–Ag–ZnO. Irradiation was carried out in the open-air condition. Fifty milliliters of dye solution with WO₃–Ag–ZnO was continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. During the illumination time no volatility of the solvent was observed. After dark adsorption the first sample was taken. At specific time intervals 2–3 mL of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the centrifugate was suitably diluted and its absorbance at 285 nm was measured.

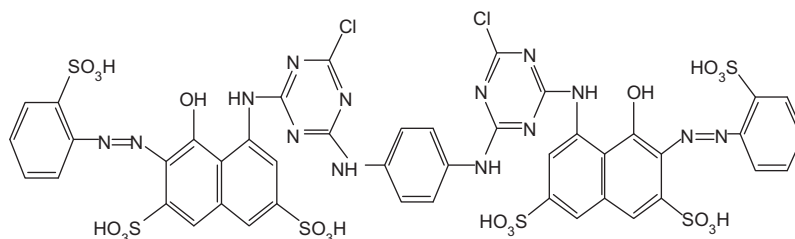


Fig. 1. Chemical structure of RR 120.

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