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Fast and quick degradation properties of doped and capped ZnO nanoparticles under UV–Visible light radiations

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Abstract

Undoped and Manganese (Mn) doped zinc oxide (ZnO) ($Zn_{1-x}Mn_xO$, $x = 0.005$, 0.01, 0.015 and 0.02) nanoparticles (NPs) capped with (1.0%) Thioglycerol (TG) has been successfully synthesized by co-precipitation method. Optical and morphological studies have been done for photophysical and structural analysis of synthesized materials. The photocatalytic activity of undoped and Mn doped ZnO NPs were investigated by degradation of crystal violet (CV) dye under UV–Visible light radiations. It has been found that Mn (1.0%) doping concentration is optimal for photophysical and photocatalytic properties. When the pH of as synthesized optimum doped ZnO NPs varied from natural pH i.e. from 6.7 to 8.0 and 10.0, the degradation of CV dye increases from 92% to 95% and 98% in 180 min respectively. Further on increasing the pH of optimum doped synthesized NPs to 12.0, almost 100% degradation has been achieved in 150 min. Optimum doped photocatalyst synthesized at pH-12.0 has also effectively degraded the CV dye solution in acidic and basic medium thus showed its utility in various industries. However, it has been found that 100% of CV dye quickly degraded in 30 min when only 1.0% of hydrogen peroxide (H_2O_2) was introduced along with optimized NPs synthesized at pH-12. Kinetic studies show that the degradation of CV dye follows pseudo first and second-order kinetic law. Further an industrial anionic polyazo Sirius red F3B (SRF3B) dye has been degraded to 100% with optimized NPs synthesized at pH-12.0 in 15 min only.

Keywords: ZnO; Photocatalytic degradation; Nanoparticles; Doping; pH

1. Introduction

With increasing diversity in industrial products environmental problems related to industrial effluents are becoming more and more complex. The residual dyes from different sources like textile industries, pharmaceutical industries, bleaching industries, dyeing, paper and pulp industries etc. introduces a variety of organic pollutants into natural resources of water. Such dye effluents pose a major threat to the surrounding ecosystem owning to their toxicity, non-biodegradability and even may cause cancer or mutagenic to life (Lima et al., 2015). These dyes remain in water for long time without adequate treatment. Various processes such as flocculation, adsorption, ultra-filtration, precipitation and reverse osmosis are applied to remove toxic substances generated from dyes in wastewater. However, using these processes highly concentrated pollutant phases are generated (Akyol and Bayramoglu, 2005). Recently, semiconductor based photocatalytic degradation

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of dyes has attracted more attention because it is able to oxidize low concentration of organic pollutants into non toxic products (Kislov et al., 2009). It is generally accepted that, when semiconductor absorbs a photon with energy greater than or equal to band gap energy of semiconductor, an electron is excited from filled valence band to empty conduction band, leaving a hole in the valence band. If suitable trap states created by defects or by dopant are available to trap these photo-generated electrons and holes, recombination is prevented and thus they can be used to perform redox reactions. Hole lying in the valence band react with the surface bound H_2O or OH^- to produce powerful oxidizing agent such as hydroxyl radical. On the other hand, the electron in the conduction band reacts with dissolved oxygen species to generate superoxide anion radicals, which are again highly reactive for oxidizing organic compounds (Akpan and Hameed, 2009). Till now, many kinds of semiconductors have been studied as photocatalysts such as TiO_2, ZnO, ZnS, WO_3, and CdS (Rehman et al., 2009; Sharma et al., 2012; Bhosale et al., 2014; Chandran et al., 2014). TiO_2 is the most widely used effective photocatalyst for its high efficiency, non-toxic nature, low cost and photochemical stability. To significantly improve the photocatalytic efficiency of TiO_2, it has been doped with Au, Fe (III), Co, Al^{3+}, V etc. (Kamat, 2002; Martin et al., 2004; Chio et al., 1994; Klosek and Raftery, 2001). It has been found that on doping with Au and Fe (III) in TiO_2 increases the photocatalytic efficiency by small amount but doping Co and Al^{3+} has inverse effect on photo-reactivity of TiO_2. However, V^- doped TiO_2 showed better photo-reactivity but the by-products were carbon monoxide and formic acid which are also toxic in nature. On the other hand ZnO has been found to be better alternative to TiO_2 because of its higher reaction and mineralization rates and also it generates oxidizing agents more efficiently (Behnajady et al., 2006; Poulios et al., 1999). Biggest advantage of ZnO over TiO_2 is that it absorbs larger fraction of UV spectrum and its corresponding threshold is 425 nm. Since the contaminant molecules need to be adsorbed on the surface of photocatalyst before the photocatalytic reaction takes place, the surface area and crystal defects play a significant role in the photocatalytic activity. Doping of metal oxide with transition metal ions improve the photocatalytic activity by increasing the crystal defects and tailoring the band gap energies to shift the optical absorption toward visible region (Wang et al., 2013). Mn doped ZnO shows better degradation in visible region as Mn doping creates defect states which act as the intermediate steps for the electrons to excite from valence band to the conduction band (Wang et al., 2013; Mahmood et al., 2011). To the best of our knowledge, in most of the studies pH of the dye has been varied with the addition of acids or bases to make it cationic or anionic without varying the pH of as synthesized semiconductor photocatalyst (Ji et al., 2009; Kong et al., 2010). We have already reported the effect of pH of as synthesized Cu doped ZnO NPs on photocatalytic activity (Mittal et al., 2014). Till date, no study has been done on the effect of pH of as synthesized Mn doped ZnO NPs on photocatalytic degradation studies. In the present work, nanosized undoped and manganese (Mn) doped with TG capped ZnO NPs were prepared by co-precipitation route at different pH. These synthesized NPs were used as a photocatalyst to study the photocatalytic degradation of CV dye as a model of organic compound under UV–Visible irradiations. The effect of doping concentration and pH has been studied in detail. The results confirm that Mn doped ZnO NPs synthesized at higher pH values show enhanced UV–Visible light induced degradation of CV dye. Further the addition of 1.0% H_2O_2 to optimum doping concentration of as synthesized Mn doped ZnO NPs at pH-8.0, 10.0 and 12.0, fast and quick degradation of CV dye has been observed. The photocatalytic results so obtained are contradictory to others who reported that Cu and Mn doped ZnO NPs show nearly same or lesser photocatalytic activity than undoped ZnO NPs (Milenova et al., 2013; Donkova et al., 2010).

2. Experimental section

For these studies chemicals of analytical grade were purchased from Sigma Aldrich. ZnO NPs were synthesized by chemical co-precipitation method (Mittal et al., 2014). In the first step 40 mL homogeneous solution of 0.5 M zinc acetate, (1.0%) (at. wt.) TG and 0.5 M sodium hydroxide were prepared in distilled water separately by stirring them for half an hour. For the synthesis of undoped and capped ZnO NPs, 1.0% TG solution was added to the 40 mL solution of 0.5 M zinc acetate in aqueous medium. After half an hour 0.5 M sodium hydroxide was added dropwise to the above solution. Soon after the addition of sodium hydroxide the precipitation phenomenon occurs and the concentration of precipitates increases as the addition was increased. Sodium hydroxide was added into the solution till the pH of the solution reaches to 8.0. The stirring was allowed for another half an hour. For synthesis of Mn (0.5%) doped and TG (1.0%) capped ZnO NPs at pH-8.0, 40 mL homogeneous solution of 0.5 M zinc acetate and 40 mL solution of 0.5 M sodium hydroxide was prepared. 40 mL homogeneous solution of 0.5 M manganese acetate and TG solution of 1.0% (at. wt.) each were prepared in distilled water separately with constant stirring for half an hour. Firstly (0.5%) manganese acetate solution was added dropwise to 40 mL zinc acetate solution and then TG (1.0%) was added to same solution. After stirring of about half an hour sodium hydroxide solution was added dropwise till the pH of the solution reaches to 8.0. The stirring was allowed for another half an hour. For synthesis of Mn (1.0%, 1.5% & 2.0%) doped and TG (1.0%) capped ZnO NPs at pH-8.0 and Mn (1.0%) doped and TG (1.0%) capped ZnO NPs at pH-10.0 and 12.0, similar procedure was adopted. The capping agent was used for avoiding agglomeration. Different solutions containing TG (1.0%) capped undoped and Mn (0.5%, 1.0%, 1.5% and