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Research Article

Photo-Catalytic Degradation of Acid Blue 113 using Doped Zinc oxide (ZnO) Nano-Particles

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Abstract

Textile dyes in the wastewater let-out by industries has been a growing concern for many years. Literature survey reveals that ~15% of dye used in the staining process viz, leather industry, textile processing industry etc., is released in the effluent. Dye pollutants can have drastic effects on the environment. Textile dyes in wastewater are a concern not only because they are displeasing aesthetically but are linked to health hazards as well. It is therefore crucial to investigate techniques to remove these harmful pollutants safely. Treatment of textile dye house effluent by conventional method is an arduous task due to high level of non-degradable chemicals in the dye. Hence advanced oxidation process – photo catalytic reaction using metal oxide is suggested to treat textile dye house effluent. The (Ni^{2+}, Ag^{2+}) co-doped zinc oxide (ZnO) nanocatalyst can be synthesized by chemical co-precipitation method. These co-doped nanoparticles can be used to determine the photo catalytic activity of acid blue 113 dye solution in the presence of sunlight. The degradation of dye solution is monitored by measuring its concentration for the particle size of about 50-100 nm. The Photo catalytic activity is influenced by three important parameters such as initial pH, initial dye concentration and catalyst loading. The effect of these parameters on photo catalytic degradation can be studied and optimized. The photo-catalytic degradation potential of co-doped (Ni^{2+}, Ag^{2+}) ZnO nanoparticles is to be compared with that of un-doped ZnO in acid blue 113 in the presence of sunlight.

Keywords: Photo catalysis; Doping; Nanosynthesis; Acid blue113; C-dopant.

Introduction

The treatment of water contaminated with traces of toxic compounds is a serious environmental threat throughout the world, due to improper disposal of untreated wastewater from industries which lead to serious health risks in humans. Major pollution source in textile industries is from dyeing and finishing processes [1]. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. Because all of them are not contained in the final product, became waste and cause disposal problems. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, colour, acidity, and other soluble substances. In addition, only 47% of 87 of dyestuff are biodegradable [2]. It has been documented that residual colour is usually due to insoluble dyes which have low biodegradability as reactive blue 21, direct blue 80 and vat violet with COD/BOD ratio of 59.0, 17.7, and 10.8, respectively [2]. To meet the specific standards set, there is need for new treatment methods, which address questions at both local and global level in terms of related research and development of treatment technologies [1,3].

In developing country like India, there is a need to implement these treatment methods which are technically feasible and economically viable to make development sustainable. One such economically viable technology is Advanced Oxidation Processes (AOPs) which uses hydroxyl radical as an oxidant for the degradation of wastewater. Among different AOPs, semiconductor based photocatalyst has been widely used in waste water treatment and air purification. Metal oxides such as TiO_2, ZnO, Fe_2O_3, and MgO were used as potential photocatalyst material for the degradation of organic pollutants presents in the environment [3-6]. Among them, ZnO a versatile oxide material, with a wide band gap of 3.27 eV has

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attracted considerable interest due to its wide range of applications including dye Sensitized Solar Cell, gas sensors, photocatalyst [5-8] and antibacterial agent.

The photocatalytic properties of ZnO were greatly enhanced when modified with the incorporation of dopant ions [3-10]. The doping of metal ions in ZnO nanostructures can lead to effects such as enhancement/decrease in fluorescence and controlling concentration of surface defects. The doping of Ni^{2+}, Ag^{2+} in ZnO is expected to modify absorption, and other physical or chemical properties of ZnO because of the different structure of the electronic shell and the similar size. Ni^{2+} and Ag^{2+} can enter the ZnO lattice substitutionally as deep acceptors in combination with a neighbouring O vacancy [11]. Introducing defects into ZnO structure will narrow the band gap to increase the solar light harvesting capability, and also bring many split energy gaps to set up a possible catalytic system, which sense and shoot environmental contaminants.

Environmental contaminants generally vary with nature of source, and the most serious amongst them is the textile dyes which pollute the river, ground water and as well as land. Many researchers have reported the degradation of textile dyes and the removal of colour is comparatively easier than reducing the organic contamination in dyeing wastewater. Sajjad and Hosakere [4] investigated the photocatalytic degradation of acid yellow in presence of ZnO. Increase in photocatalytic activity of ZnO was reported by Benjamin et al. [12] where some natural pigments are used as coating materials. Egzar et al. [13] carried out the photocatalytic degradation of aniline blue dye using different semiconductors such as ZnO, ZnS and SnO_2. Ahmad et al. [14] synthesized Al-doped ZnO photocatalyst with different Al concentrations and results showed that this photocatalyst doped with 4.0 mol% Al exhibited five times enhanced photocatalytic activity compared to pure ZnO. In the present study, photocatalytic degradation of textile dye acid blue 113 was carried out by nickel and silver doped ZnO nanopowders in the presence of solar light. India being a tropical country has abundant solar energy which could be harnessed for enhancing the photocatalytic activity at the reduced cost. The co-doped ZnO nanopowders have been prepared, characterized, optimized the process parameters such as pH, initial dye concentration and catalyst loading for the degradation of the acid blue 113 dye present in the wastewater.

Materials and Methods

The azo dye acid blue 113 used here has the molecular formula $C_{32}H_{21}N_5O_6Na_2S_2$ (mol.wt 68.64). It was a commercial sample obtained from one of the tanning industries located at Chennai India. All chemicals and reagents were of analytical grade, manufactured and procured from M/s. SD Fine Chemicals, Bangalore, India.

Synthesis of Ni^{2+}, Ag^{2+} doped ZnO nanocatalyst

Un-doped ZnO nanoparticles was synthesized by adding potassium hydroxide solution drop-wise in zinc acetate dihydrate solution in a molar ratio of 1:1 under vigorous stirring, and the stirring was continued for 8 hr. The precipitate obtained was filtered and washed thoroughly with deionized water. The precipitate was dried in an oven at 100°C and ground to fine powder, calcined at 500°C for 1 hr. Then the synthesized particles were characterized for their structure and morphology.

Codoped ZnO nanopowder was synthesized by co-precipitation method. Zinc acetate and potassium hydroxide were used as precursors, were mixed in 1:1 ratio in a stirrer. Then 5 mol % of nickel chloride and 10 mol % of silver nitrate was added under a constant stirring for 8 hr. After filtering, the precipitate is washed repeatedly with double distilled water to remove unreacted chemical species. Finally, the product is dried at 70 ºC for 2 hr, and then grounded and annealed in the furnace at 500 °C for 1 hr.

Photo degradation experimental procedure

The experiments were carried out in an annular reactor made up of plexi glass trays exposed to light source. Prior to illumination, the catalyst and dye solution were thoroughly stirred in the dark to ensure the establishment of absorption equilibrium. Aliquot samples were taken every 30 min for 2 hr, filtered and absorbance was recorded at λ_{max} 561 nm using UV-Vis Spectrophotometer. Further the photo degradation of the dye was monitored by measuring its COD using open reflux method. The percentage of degradation (X) was calculated using Eq. 1:

$$X = \frac{(C_o - C_t)}{C_o} \times 100 \qquad (1)$$

where C_o is the initial dye concentration, ppm and C_t is the dye concentration at time, t.

Results and discussion

Photo degradation Studies

In order to examine the visible light-catalytic efficiency of the ZnO samples, 150 ml of 50 ppm dye solution was first taken in reactor and 0.3 g of ZnO based catalyst was added to it. Photocatalytic degradation was carried out using un-doped ZnO and co-doped ZnO (Ni^{2+}, Ag^{2+}). The mixture was then transferred to the photo-reactor and air was supplied continuously and irradiated. However, samples were collected at zero and sixty minutes for comparison. During reaction, samples were taken at regular intervals, and then centrifuged. The supernatant was analyzed for dye concentration.

Concentration decay curves of dye solutions are shown in Fig. 1. Prior to visible light irradiation there was a drop in the dye concentration due to adsorption of dye onto the catalysts powders which was not appreciable, however, immediately after irradiation, concentration of dye decreased rapidly. This confirmed that the catalysts used in this study oxidized dye effectively in the presence of visible light. About 80% of dye was degraded in 60 minutes by co-doped ZnO, in the same 60 minutes only about 20% of dye was degraded in undoped ZnO. Thus, the photocatalytic degradation of co-doped ZnO is efficient than un-doped ZnO.

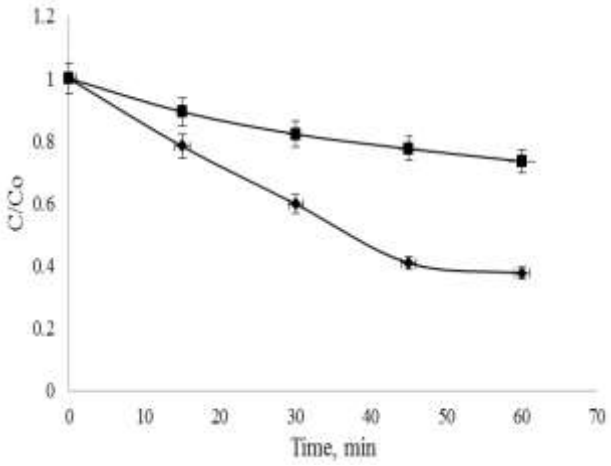

Fig. 1. Effect of dye degradation for co-dopped (♦) and undoped ZnO(■) catalyst

Effect of pH

The effect of pH on the degradation of acid blue 113, shown in Fig. 2, was studied in the pH range from 6 to10 with 50 ppm dye concentration and 0.2 g/l catalyst loading. The pH of the aqueous phase was adjusted using 0.1 N HCl and 0.1 N NaOH. For co-doped photocatalyst, the photocatalytic degradation efficiency increases from a pH 6 to 8 and then decreases for further increase in pH. The maximum degradation efficiency was found to be at pH 8. Thus for further photocatalytic degradation experiments pH 8 was kept constant. For un-doped ZnO, the photocatalytic degradation efficiency increases from pH 6 to 7 and then decreases from pH 7 to 10. The degradation efficiency was found to be optimum at a pH of 7. Effect of pH on photocatalytic efficiency of the samples was investigated at pH 6, 7, 8, 9 and 10. Highest percentage color removal was achieved at pH 8 for these samples in the presence of co-doped ZnO.

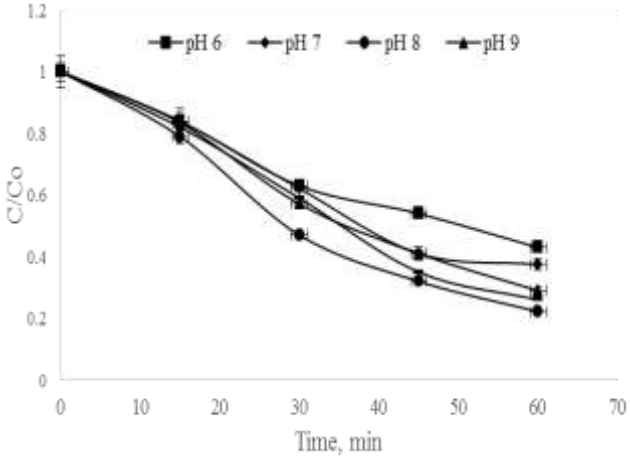

Fig. 2. Effect of pH on dye degradation using co-doped ZnO

Effect of Initial Dye Concentration

The degradation of acid blue 113 at different concentrations, shown in Fig. 3, for a catalyst loading of co-doped ZnO was investigated. The degradation efficiency was to be inversely proportional to the increase in concentration. The optimum degradation was found to be at 20 ppm for co-doped ZnO particles. Also the graph shows that even at 100 ppm the degradation efficiency was 71% which means that co-doped ZnO at lower concentrations is much more efficient than un-doped ZnO. The highest efficiency in un-doped is about only 50% which is much lesser than the

co-doped photocatalytic degradation efficiency even at 100 ppm of initial dye concentration. The high concentration of dye would have acted as a filter for the incident light, which ultimately reduce degradation efficiency.

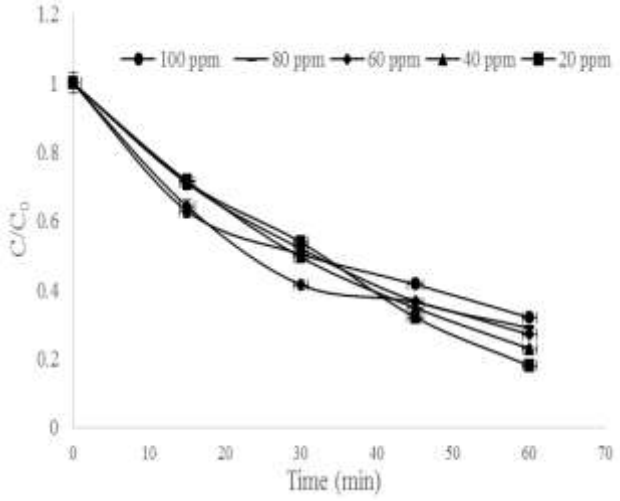

Fig. 3. Effect of initial dye concentration of doped ZnO

Effect of Catalyst loading

Experiments were carried out with different quantities un-doped and co-doped nano-crystalline ZnO for 60 ppm dye concentration of 150 ml dye solution in solar radiation to assess the efficiency of degradation as a function of the amount of catalyst. The degradation efficiency increases until 0.4 g/l of co-doped photocatalyst shown in Fig. 4. For undoped the optimum catalyst is found to be 0.6 g/l. Further, as the opacity of the dye solution penetration of light becomes difficult and fewer nanoparticles are activated and hence the degradation decreases.

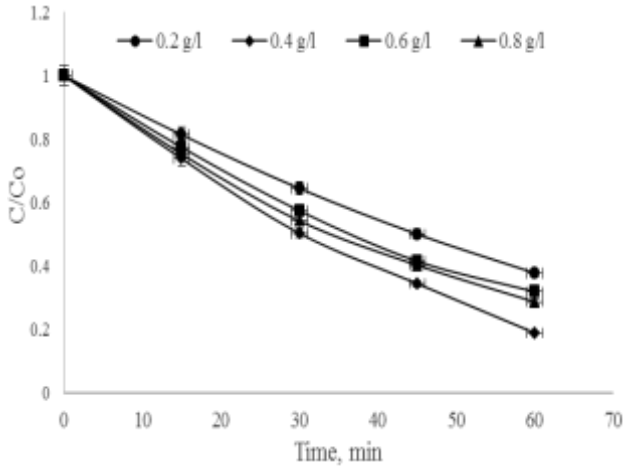

Fig. 4. Effect of catalyst loading on dye degradation of doped ZnO

Conclusions

ZnO nanoparticles can be synthesized by various methods, though co-precipitation method is unique because of its low cost of production, ease of handling, reliability and environmental friendliness. Literature reveals, that the efficiency of ZnO nanoparticles depend upon the control of physical and chemical properties such as size, size dispersity, shape, topographical properties, crystal structure and dispensability. In the present study, nickel ion and silver ion were successfully doped on ZnO nanoparticles, this was confirmed by FTIR, XRD and SEM-EDAX. The synthesized co-doped ZnO was found to be more efficient with reduced band gap than un-doped ZnO in degrading acid blue 113, in the presence of visible light source, at optimum conditions. Co-doped ZnO largely reduced the concentration of the dye pollutant within 45 min when compared to un-doped ZnO. The co-doped ZnO nanoparticles show twice as potent in degrading acid blue 113 in the presence of sunlight compared to un-doped ZnO, because the synthesized photocatalyst was a rich source of oxygen which results in the production of more hydroxyl radicals. Dye solution of lower concentrations also completely mineralized by co-doped ZnO under solar radiation. Thus the degradation efficiency was twice to that of un-doped ZnO particles. Hence the present research shows that the silver and nickel doped ZnO particles could treat acid blue 113 in a much better way in a suitably designed solar photocatalytic reactor.

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Conflicts of Interest

Authors declare no conflict of interest.

References

[1] Mukherjee S, Ray A. Major challenges in the design of a large-scale photocatalytic reactor for water treatment. Chem Eng Technol. 1999;22(3):253-260

[2] Al-Kdasi A, Idris A, Saed K, Guan C. Treatment of textile wastewater by advanced oxidation processes – a review. the Int. J. 2004;6(3):222-230.

[3] Thennarasu G, Sivasamy A, Kavithaa S. Synthesis, characterization and catalytic

activity of nano size semiconductor metal oxide in a visible light batch slurry photo reactor. Journal of Molecular Liquids. 2013;179:18-26.

[4] Khezrianjoo S, Revanasiddappa H. Photocatalytic Degradation of Acid Yellow 36 Using Zinc Oxide Photocatalyst in Aqueous Media. Journal of Catalysts 2013; 2013. doi:10.1155/2013/582058

[5] Thennarasu G, Sivasamy A, Kavithaa S. Photocatalytic degradation of Orange G dye under solar light using nanocrystalline semiconductor metal oxide. Environ Sci Pollut Res. 2012;19:2755-2765.

[6] Joshi KM, Shrivastava VS. Degradation of Alizarine Red-S (A Textiles Dye) by Photocatalysis using ZnO and TiO2 as Photocatalyst. International Journal of Environmental Sciences, 2011;2(1):8-21.

[7] Mehta P, Mehta R, Menkasurana, Kabra BV. Influence of operational parameters on degradation of commercial textile azo dye acid blue 113 (cyanine 5r) by advanced oxidation technology. J Curr Chem Pharm Sci. 2011;1(1):28-36.

[8] Shanthi M, Kuzhalosai V. Photocatalytic degradation of an Azo dye, Acid Red 27 in aqueous solution using nano ZnO, Indian journal of Chemistry, 2012;51A:428-434.

[9] Ravi Krishna R, Swaminathan T. Studies on Photocatalytic Degradation of Monocrotophos in an Annular Slurry Reactor Using Factorial Design of Experiments. Journal of Water Sustainability. 2011;1(1):75-84.

[10] Neppolian B, Choi HC, Sakthivel S. Solar/UV-induced photocatalytic degradation of three commercial textile dyes. Journal of Hazardous Materials. 2002;89(2-3):303-317.

[11] Kanai Y. Admittance Spectroscopy of Cu-Doped ZnO Crystals. Jpn J Appl Phys. 30;1991:703-707.

[12] Benjamin S, Vaya D, Punjabi PB, Ameta S C. Enhancing Photocatalytic Activity of Zinc Oxide by Coating with Some Natural Pigments. Arabian Journal of Chemistry. 2011;4:205-209.

[13] Egzar HK, Mashkour MS, Jude AM. Study the Photo degradation of Aniline Blue in Aqueous Phase by Using Different Photocatalysts. Asian Transactions on Basic and Applied Sciences. 2013;3:23-28.

[14] Ahmad M, Ahmed E, Zhang Y, Khalid NR, Xu J, Ullah M, Hong Z. Preparation of Highly Efficient Al-Doped ZnO Photocatalyst by Combustion Synthesis. Current Applied Physics. 2013;13:697-704.

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