International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: SJIF: 5.995
Available Online at www.journalijcar.org
Volume 7; Issue 1(J); January 2018; Page No. 9407-9410
DOI: http://dx.doi.org/10.24327/ijcar.2018.9410.1553

Research Article

PHOTOCATALYTIC DEGRADATION OF CONGO RED UNDER NATURAL SUNLIGHT WITH ZN-TI BIMETALLIC PHOTOCATALYST

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A R T I C L E I N F O

Article History:
Received 15th October, 2017
Received in revised form 10th November, 2017
Accepted 26th December, 2017
Published online 28th January, 2018

Key words:

Advanced oxidation process, Photo catalytic degradation, Visible-light-active photo catalyst (Pure nano Titanium & Zinc), Congo red, SEM.

A B S T R A C T

Catalytic degradation of organic dye molecules has attracted extensive attention due to their high toxicity to water resources. Degradation of hazardous Congo red dye was studied using Zn-Ti bimetallic photo catalyst in this work. The aim of the present work is to study photochemical degradation of reactive azo-dye such as Congo red. Various Ti-Zn composites were used as photo catalysts for this study. The synthesized photo catalysts exhibited high photo catalytic activity for the degradation of Congo red. Scanning Electron Microscopy (SEM) and UV-VIS Analysis were done for materials characterization. We also investigated various effects like initial pH, catalyst loading and concentrations of the dyes on the rate of degradation. Complete degradation of 0.1M Congo red dye was achieved for 60min of irradiation in presence of pure nanoTi&Zn(1:1).

INTRODUCTION

Dyes and pigments are widely used in the textiles, paper, plastics, leather, food and cosmetic industry to colour products. The effluent from the above mentioned industries containing various hazardous dyes is reveals very harmful effects on living things. Dye molecules are non-biodegradable, intense colour and some of them are toxic to environment (Daneshvar, *et al*., 2003; Rajeshwar, *et al*., 2008). They can easily form highly toxic complexes with some heavy m*etal* ions (i.e. Cr, Al and Cu) in waste water to pollute water resources. A variety of physical, chemical, and biological methods, such as coagulation, adsorption, membrane process, and oxidation-ozonation are well established for treatment of dyes from wastewater. Some dyes are difficult to degrade with standard biological methods, due to their complex aromatic structure and synthetic origin. Congo red is an azo-dye, and it is toxic to many organisms. It represents a significant effluent problem along with related dyes from textile, printing, dyeing, paper, rubber and plastic industries. It is entirely undesirable in the environment due to its toxic nature, and it is highly resistant to biodegradation because of its structural stability. It is necessary to develop highly efficient, non-toxic and chemically stable photo catalyst to improve future environment.

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The conventional process is insufficient to rectify of this problems, these process causes the secondary pollutions. To overcome of this problem the new "advanced oxidation processes" (AOPs) such as photo catalysis constitute one of the emerging technologies for dye degradation is developed. It includes photo catalysis systems such as a combination of a metals semiconductor (TiO_2, ZnO, etc.) and UV/visible light. Dyes organic bulk molecules can be degraded in the presence of photo catalyst upon irradiation with UV/visible light because of their absorption in the UV/visible region.

Organic dyes are commonly present in wastewater effluents of different industries, such as textile, leather goods, cosmetics, food, plastics, consumer electronics, etc. Therefore, there is considerable interest in the degradation of dyes, in particular photo catalytic degradation (Rajeshwar, *et al*., 2008; Rauf, *etal*., 2009; Han, *et al*., 2009). The catalytic degradation of dye molecules has attracted more and more attention in recent year. Photo catalytic degradation of dyes has affected by different factors, initial concentration of dyes, photo catalyst particle size, the adsorption of the dye onto the photo catalyst is typically considered to play an important role. Titanium dioxide is generally considered to be the best photo catalyst and has the ability to de-toxificate water from a number of organic pollutants (Fox, *etal*., 1993; Kusvuran, *et al*., 2005). TiO_2 and ZnO have the best photo catalytic activities as compared to other semiconductors (Hoffmann, *et al*., 1995; Fox, *et al*., 1993; Kansal, *et al*., 2007). ZnO/TiO_2 semiconductor couples possessing more efficient catalytically

active sites degrade pollutants, such as dyes, pesticides, detergents, and volatile organic compounds, effectively by photo catalytic processes. (Fujishima, *etal*., 2000; Fujishima, *etal*., 2007; Yawalkar, *etal*., 2001). Composite made of ZnO and TiO_2, both have similar band-gap energies at around~3.2eV seems to be higher reaction rates as compared to other semiconductor couples(Bhatkhande, *etal*., 2002; Hasnat, *etal*., 2007; Akyol, *etal*., 2010). Pure nano particles have a great advantage to apply to a catalytic reaction process due to their large surface area hence have ability to adsorb small molecules and high catalytic activity (Chen, *etal*., 2007). M*etal* containing nanoparticles functional materials for water purification. TiO2,"the epitome of best" semiconductor photo catalyst due to its photo resistive nature, easy and economic availability, high absorption cross section and suitable electronic structure (Yin, *etal*., 2005). In recent years, nano sized particles wide applications in other modern scientific and technological field because of its wide direct band gap, strong excitonic binding energy and promising application for UV-laser with low threshold, field emission array (Xu, *etal*., 2003; Xu, *etal*., 2004). surficial acoustic device (Zhao, *etal*., 2004) and transistor and biosensor (Arnold, *etal*., 2003) in nanoscales. Other higher achievable, more efficient photo catalyst material is ZnO, its nanostructures can be prepared by very simple, low cost, and low temperature techniques, which contributes to the attractiveness of this material.

Experimental Procedure

Materials

Powder form of synthesized pure Ti:Zn nano composite, Congo red (M.Wt= 696.665 g/mol, $C_{32}H_{22}N_6Na_2O_6S_2$: λ_{max} =497nm)

Procedure

Dye solution preparation

The photo catalytic degradation efficiency of as-synthesized nanocomposite Ti:Zn catalyst was evaluated by performing the Congo red dye degradation reaction under direct sunlight irradiation in the month of April–May 2016 between 11:00 am to 3:00 pm. In photo catalytic dye degradation experiment prepared 100 ml of 20 PPM dye solution in 250 ml beaker and 20 mg of catalyst semiconductor was added and mixture was stirred to obtain uniform suspension and kept it in dark under stirring around 30 min. After 30 min we have to take 5 ml of dye solution and centrifuge and measure the absorbance by UV it is noted as initial concentration. Then we have to shift the reaction to sunlight (should be in sunlight better to do the experiment after 10 AM to 4 PM) and have to use continues stirring and have to measure the absorbance for every 10 min interval up to clear solution.

The photo degradation of Congo red follows the first-order reaction kinetics that obeys the equation ln(C0/C) = kt, where k is the rate constant, t is the irradiation time, C0 and C are the initial and concentration at time t. The first order rate constant value is higher for the Ti:Zn(1:1) compare to 1:2,2:1,1:0,0:1,composition, among of these catalysts 1:1(Ti:Zn) has the highest rate constant has highest activity, highly efficient, nontoxic and chemically stable photo catalyst because of larger surface area of this catalyst causes greater adsorption of the dyes, degree of dispersion of the Tio2,Zno solution greatly further studies were carried out by using the same catalyst Ti:Zn(1:1). Comparative graph of Ti:Zn nanocomposite have been represented in Fig 1

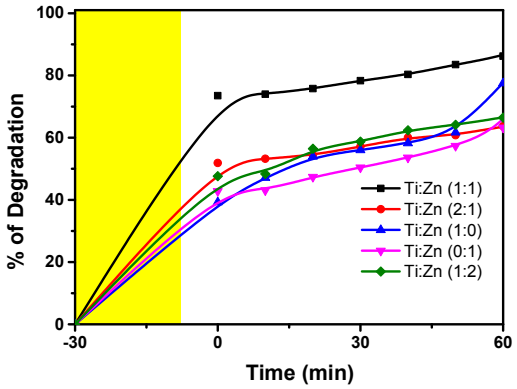

Fig 1 Comparative graph of Ti:Zn nanocomposite

Characterization

SEM (Scanning electron microscope)

The morphology of the as-synthesized samples was investigated by field emission scanning electron microscopy (FE-SEM, LEO1550).The nano structures and morphologies of samples are examined by SEM characterization. SEM may offer better performance for surface and shape analysis, particularly in applications such as quality control of colloidal nano-precipitates or for measuring surfaces and microstructures of nano sized powdered materials. For many nanotechnology developers looking at fundamental size and shape properties.

UV Visible spectral changes

Single Monochromator UV-2600 (optional ISR-2600Plus, λ up to 1400nm) spectroscopy can be used to study reaction rates. It was employed to record the spectra. If a reagent or a product of the reaction absorbs radiation at a particular frequency the spectrometer can be set to measure the absorption at that frequency as a function of time. The absorption peaks, corresponding to dye, diminished and finally disappeared under reaction which indicated that the dye had been degraded.

RESULTS AND DISCUSSIONS

SEM (Scanning electron microscopy)

Morphology study

The nanostructures and morphologies of samples are examined by SEM characterization, carried out on field emission scanning electron microscopy (FE-SEM, LEO1550). Morphology study Figure 2 (a to j) shows the SEM picture of the different ratios of nano Ti:Zn samples. From the images it can be clearly observed that the prepared our samples consists of nano particles in the size of <100 nm. SEM studies were carried out to find out the surface morphology of synthesized Ti&Zn nanocomposite. SEM micrographs of the Ti&Zn nanocomposite have been represented in Fig. 2

UV –Visible spectral changes

Effect of initial concentration of Congo red on photo catalytic degradation

The degradation efficiency of Congo red is found to decrease with an increase in the initial dye concentration.

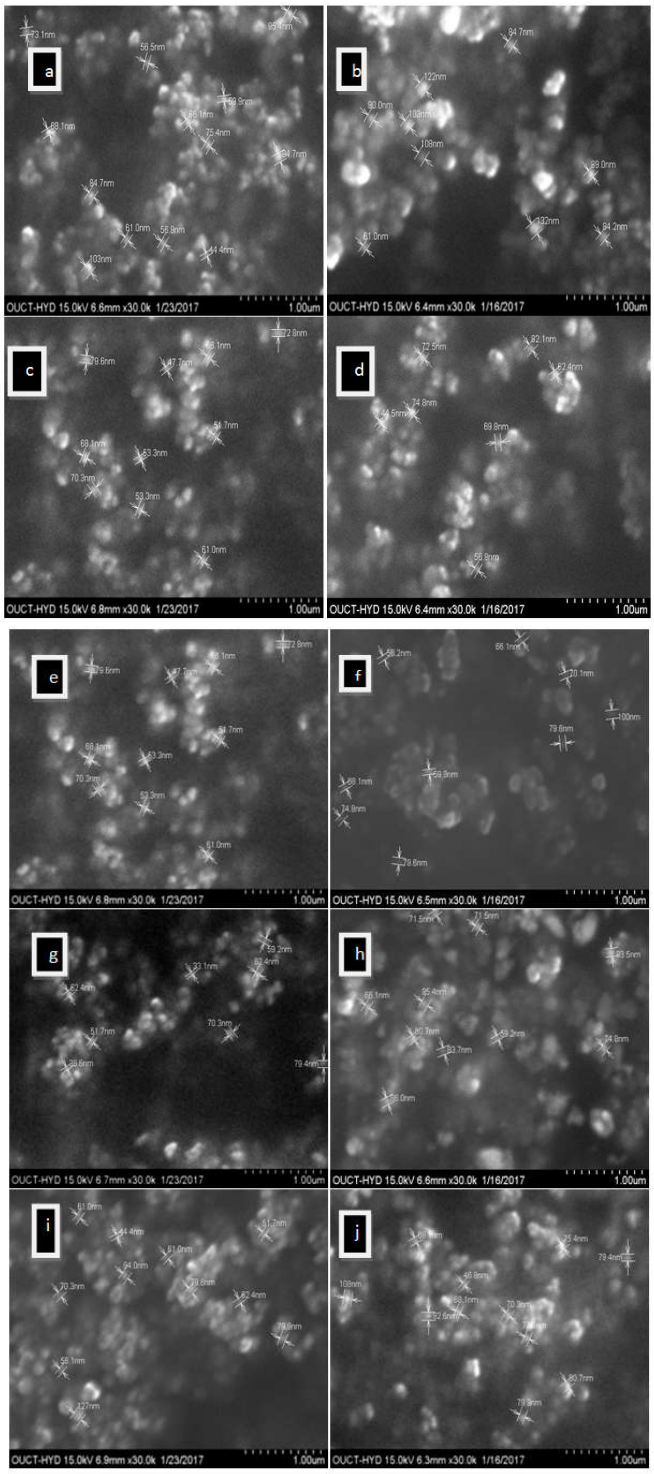

Figure 2 SEM images of Ti:Zn nano composite a) before calcination (0:1) b)after calcination (0:1) c) before calcination (1:0) d) after calcination (1:0) e) before calcination (1:1) f) after calcination (1:1) g) before calcination (1:2) h) after calcination(1:2) i)before calcination (2:1) j) after calcination (2:1)

The influence of dye initial concentration, photo catalytic degradation of Congo red was studied in the concentration range of 10ppm to 40ppm.Concentration has a significant effect on the degradation of Congo red. After illumination for 60 min, the rate constant 'k'10, 20, 30, 40 ppm was found to be it clearly shows that as the concentration decreases rate constant increases. This can be attributed to the hindering of photons with the increase in concentration of Congo red to reach the surface of photo catalyst. Moreover, as the concentration of dye Congo red increases, the molecules adsorbed on the surface of photo catalyst might increase. This decreases the active sites on the photo catalyst which results in a decrease in generation of hydroxyl radical, and hence the lower activity. Comparative graph havebeen represented in Fig 3

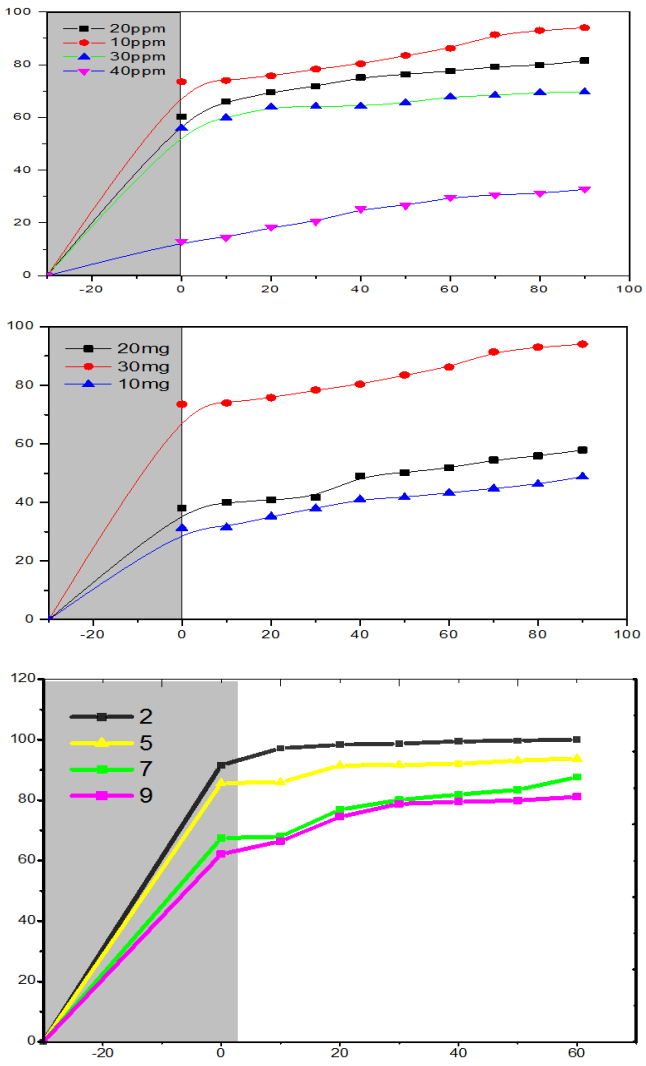

Fig 3 Effect of initial concentration of Cango red on photo catalytic degradation
Fig 4 Effect of catalyst amount on degradation rate
Fig 5 Effect of PH on degradation

Effect of catalyst amount on degradation rate

The degradation efficiency of Congo red is found to increase with an increase in the catalyst loading. The total active surface area increases with increasing catalyst dosage. When the dye concentration is increased the catalyst amount is constant, it results fewer active sites for the reaction, with the increased dye molecule the solution become more intense colour**.** This increase in degradation rate with the photo catalyst amount can be explained in terms of availability of active sites on the catalyst surface. The tendency of adsorption of the dye to the surface of the catalysts. When catalyst amount is increases photo degradation efficiency increases. Comparative graph have been represented in Fig 4

Effect of PH on degradation rate

The effect of pH on the decolourization of dye experiments were carried out at various pH values, ranging from 2-9 for constant dye concentration (20ppm) with catalyst loading (20mg). It has been observed decolourization efficiency

increases with increase in PH. We are observed Maximum rate of degradation at pH8. Similar behaviour has also been reported for the photo-catalytic efficiency of (Ti:Zn) for decolourization of azo-dyes. (Mckay, *etal*., 1988). The interpretation of pH factor on the efficiency of photo catalytic degradation process can be explained on the basis of acid base property of metal oxide surface and the ionization state of ionisable organic molecule (Gonclaves, *etal*., 1999). In acidic solutions photo degradation efficiency was more than that in alkaline solutions. It is because photodecomposition of ZnO takes place in acidic and neutral solutions. The experimental results showed that higher degradation of dye occurred in acidic region than in a basic solution. The rate of photo decolourization increased with increase in pH, exhibiting maximum efficiency (98.5%) at pH2. Although the adsorption of dye molecules are low at alkaline pH, the possible reason for this behaviour may be the formation of more *OH radicals. At alkaline mediums, excess of hydroxyl anions facilitate photo generation of •OH radicals which is accepted as primary oxidizing species responsible for photo catalytic degradation, resulting in enhancement of the efficiency of the process. Comparative graph have been represented in Fig 5

CONCLUSIONS

In this work, a study has been carried out on the identification of nanostructures &morphology of Pure Ti/Zn powders using SEM technique. From the results, SEM can confirm the Ti & Zn sizes. The results presented in this paper indicated that Pure nano Ti/Zn could be efficiently used to degrade the Congo red dye. The degradation kinetics of Congo red dye was fast with maximum efficiencies of 95.02% for CR and within 60 min using Ti:Zn(1:1) catalyst for CR. The degradation rate of dyes was obviously affected by the operating parameters (illumination time, initial dye concentration, and amount of photo catalyst, pH of semiconductors). Study of effect of pH revealed that the acidic pH favours the degradation of Congo red due to better TiO_2 surface. The aim of this research is to study the degradation efficiency of the commercially available photo catalysts in the market in term of percentage of dye removal from real textile wastewater of ZnO/TiO2. In addition, effect of particles size on photo catalytic activity was also reported and discussed.

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