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Ultra fast and effective treatment of dyes from water with the synergistic effect of Ni doped ZnO nanoparticles and ultrasonication

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ABSTRACT

The current research work focuses on the synergistic effect of Ni doped ZnO nanoparticles and ultrasonication for the degradation of anionic (Fast Green) and cationic (Victoria Blue) dyes. Well crystalline monodispersed Ni doped ZnO nanoparticles have been synthesized by quick and simple co-precipitation technique at low temperature. Synthesized nanoparticles have been characterized by X-ray diffraction, UV–vis spectroscopy, transmission electron microscopy and energy dispersive X-ray spectroscopy. The effects of operating parameters such as catalyst dosage, pH, power dissipation, temperature and dye initial concentration have been investigated, and the enhancement in degradation capability of Ni doped ZnO with undoped ZnO has also been discussed. The degradation of both the dyes follows pseudo-first-order kinetics. In concert with superior activity and reuse performance, the current route is promising for the application of ZnO-based catalysis for water decontamination.

1. Introduction

With increasing industrialization, contamination of water by organic or synthetic pollutants has been a major environmental problem worldwide for nearly a century. In textile industries the process of dyeing results in the production of wastewater that exhibit intense coloration [1,2]. Conventional technologies used for purification of dye wastewater entail high operation and maintenance cost, compromising of limitation in complete decontamination, post treatment management of by-products and high energy consumption [3,4]. To conquer this shortcoming an alternative treatment technique focuses on the use of materials, which is both environment friendly and economical viable.

In the past few years, advanced oxidation processes (AOPs) such as ozonation, photocatalysis, and Fenton process have been widely developed for the elimination of organic dyes [5], but they cannot attain complete mineralization of contaminants due to some technical limitations. Therefore, it still not gained acceptance as an efficient and successful stand-alone technology for the decontamination of wastewater at commercial level. Among other AOPs, sonocatalytic degradation is receiving interest towards the mineralize of dyes in non-or low-transparent effluents and has very strong capability to penetrate any water medium, which is one of the main drawbacks faced by other photocatalytic treatment techniques [6,7]. So, sonocatalysis has attracted attention as a novel, fast and efficient method of degrading water contaminants. During ultrasonication (US), acoustic cavitation effect from ultrasonic irradiation causes the formation, growth and collapse of microbubble in an extremely small interval of time, liberating large magnitude of energy. The effects of bubble collapse are the creation of hot-spots, the release of free radicals, surface cleaning. The collapse of bubbles generates extremely high local temperature and pressure temperatures of about 10,000 K and pressures of about 1000 atm [8]. It should also be noted that though the release of energy is over very small pocket, cavitation events occur at multiple locations in the reactor simultaneously. The generation of active radicals ·OH released by the dissociation of H_2O molecules, induced by the cavitation effect during US is an important species for degradation mechanism [9,10]. Furthermore only sonocatalysis is not effective for complete mineralization of all categories of dyes and therefore its effect can be intensified by using some additives. The other means to attain better degradation is to combine ultrasonic cavitation with other advanced oxidation schemes viz. ultrasonic/ozone, ultrasonic/H_2O_2, ultrasonic/Fenton process, ultrasonic/UV irradiation and ultrasonic/semiconductor catalysis [11–14]. When the two systems are combined into an integrated one, it is supposed to produce synergistic effect between the sonochemical and catalytic reactions, which markedly accelerate the degradation of organic pollutants by supplying the additional cavitational effect.

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The present work has been devoted to study the synergistic effect of ultrasonication and semiconducting nanoparticles (NPs) for the degradation of toxic dyes. The existence of additives (doped ZnO NPs) during sonocatalysis results in faster degradation due to provision of extra nuclei, which enhances the cavitational effect by providing additional deformities in the liquid medium leading in the generation of more free radicals or additional oxidizing species in the system [15,16]. To the best of our knowledge very few papers are available in literature for ultrasonic degradation of dye by pure and doped ZnO NPs [9,17–19]; however their results showed that more time was required for the maximum mineralization of dyes. The most remarkable feature of the present work is that; using synergistic effect of doped ZnO NPs and ultrasonication the degradation of dyes has been achieved in comparatively minimum time span.

As an important wide and direct band gap semiconductor, ZnO is a versatile and promising nanomaterial because it plays a vital role in emerging technologies for environmental and energy related applications [2]. To achieve complete mineralization of dyes and that too in very short time, the activity of ZnO must be improved further. Doping of a metal ion in a semiconductor is known to influence both photophysical behavior and photochemical activity. Transition metal ion doping improve the trapping of electrons and inhibited the recombination of ·OH radical ion needed for the degradation reaction [20,21]. Wang et al. [22] have studied the role of Fe(III)/TiO_2 for the degradation of azo dye in combination with the ultrasonic radiation. They have reported that doping of Fe(III) ions showed enhanced degradation efficiency when used in combination with ultrasonic irradiation.

The present investigation assesses the applicability of Ni doped ZnO NPs (Ni-ZnO) for the ultrasonic degradation of Victoria blue (VB) and Fast green FCF (FG) dyes at short time scale. Compared with preceding methods, the present synthesis is green (no use of toxic and expensive reagents), high-yielding and economical. The effect of the catalyst dosage, pH, power dissipation, temperature and initial dye concentration w.r.t to contact time has been particularly elucidated on sonocatalytic degradation of both the dyes. The kinetic rate coefficients of FG and VB dyes have been evaluated and found to have excellent degradation efficacy than the reported literature values. An attempt has also been made to regenerate the used NPs after sonocatalytic degradation. In addition, the comparison of degradation efficiency of the doped NPs with that of undoped NPs has also been executed.

2. Experimental

2.1. Materials

Zinc acetate, ZnAc (CDH, 99.5%), Nickel acetate, NiAc (Himedia, 99%) Sodium hydroxide, NaOH (Qualigens, 97%), Cetyltrimethylammonium bromide, CTAB (Sigma–Aldrich, 99%), Fast Green FCF (Sigma–Aldrich), Victoria Blue (Sigma–Aldrich), Dimethyl sulfoxide, DMSO (Qualigens, 99%), and absolute ethanol (Changshu Yangyuan Chemicals, China, 99.9%) were used in the present work. All the reagents were used as received. All the solutions were prepared in double distilled water.

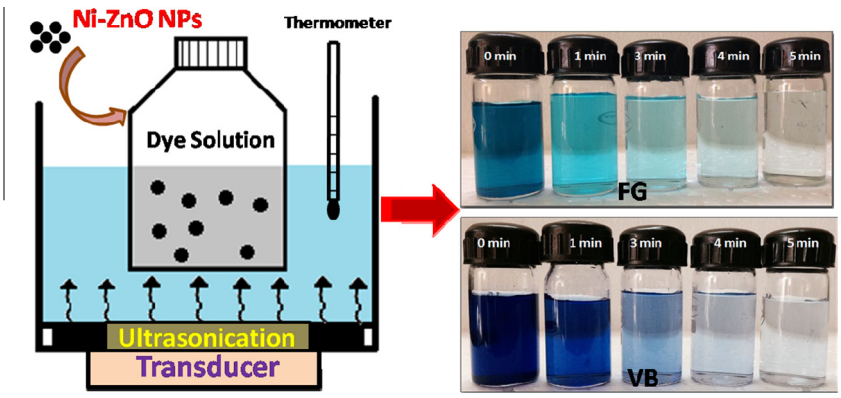
2.2. Synthesis and characterization of Ni doped ZnO NPs

Ni-ZnO NPs have been prepared by a precursor-based route via chemical precipitation method by using surfactant CTAB at low temperature. Detailed synthetic procedure has been provided in Supplementary Material.

The X-ray powder diffraction (XRD) patterns, obtained on a Panalytical X'Pert Pro X-ray diffractrometer equipped with Cu-kα radiation (1.5406 Å) operating at 40 kV, with scanning speed of 8°/min was used to identify the phase constitutions in samples. The Raman-scattering experiments were carried out by using JY-HORIBA (iHR 550) at room temperature. The 488 nm line of an Ar ion laser was used for excitation. UV–vis absorption spectra of catalyst was measured with Jasco V-530 spectrophotometer in 1 cm optical path quartz cuvette over 200–800 nm range at room temperature. Transmission electron microscopy (TEM) investigation was performed with a Hitachi (H-7500) electron microscope operating at 80 kV. Samples were prepared by drying a drop of dilute dispersion of synthesized particles on a carbon coated copper grid and then letting the solvent to dry. To check the chemical composition of the material, energy dispersive X-ray (EDS) spectroscopy analysis was performed on a JEOL model JEOL JSM-6610LV. Fourier transform infrared (FTIR) analysis was performed using Thermo scientific Model (IS50) over a spectral range of 4000–400 cm^{-1} for the determination of degraded products left in the solution after treatment.

2.3. Sonocatalytic degradation reaction procedure

Batch experiments were conducted to understand the mechanism for the degradation for both the dye using Ni doped ZnO NPs. The dye solutions were stirred in dark for 30 min prior to US to ensure that the equilibrium adsorption/desorption of the substrate on the catalyst has been attained as well as eliminating the effect of adsorption during sonocatalysis. The initial pH of the dye solutions was adjusted with HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}) solution using pH meter (Cyberscan 510). Schematic representation of the ultrasonic bath apparatus has been given in Scheme 1. Afterwards, these suspensions were placed in a commercially ultrasonic bath apparatus (PCi Analytics) producing 50 kHz ultrasonic waves for definite time interval of 5 min. After ultrasonic irradiation, samples were withdrawn from the reservoir,



Scheme 1. Schematic diagram of the sonocatalytic experimental set up and decolorization of dyes.