Role of N-ZnO/GO and Fe$_2$O$_3$-ZnO in Photocatalytic Activity

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Abstract: Present research work reports the synthesis of visible light-active ZnO photocatalyst through modification with N/GO and Fe$_2$O$_3$/GO. Modified ZnO samples are characterized by XRD. Photocatalytic activities of samples are measured in waste water consist of organic pollutants such as Malachite green (MG). N-ZnO/GO samples exhibited better photocatalytic degradation as compared to Fe$_2$O$_3$ doped ZnO. Dye degradation follow first order kinetic and rate constants are also measured.

INTRODUCTION

Treatment of organic pollutants in waste water is very necessary because it develop adverse effects on the human being and ecosystem [1]. Besides agriculture waste, the dyes and dyes intermediates get secondary category of pollutants in waste water[2]. Literature revealed that the leather and textiles are leading industries which produces dyes effluents in large amounts [3]. Moreover, it is quite demanding to degrade synthetic dyes through conventional methods such as chemical and biological methods into less harmful degraded products [4]. To solve this problem, the photocatalytic decomposition processes are being used by many researchers to degrade the organic pollutants of industrial wastewater before discharging into the environment [5]. In this method, semiconductor nanoparticles such as ZnO, TiO$_2$ etc. and its nanocomposites act as a photocatalyst and light is used to degrade the pollutants[6]. Photocatalytic degradation is achieved by high oxidative power of OH radicals (2.83 V) which ease the degradation of the dyes. These radicals are generated during the process and it can be further improved by using dopant and modification of materials. Zinc oxide (ZnO) is one of the promising II–VI semiconductors, which has gained much attention due to its wide and direct band gap of 3.37eV at 300K, large exciton binding energy of 60 MeV at room temperature [7] less toxicity, high electron mobility, and strong oxidizing power [8]. However, using ZnO as a photocatalyst exhibits some drawbacks which include its wide band gap that restricts its application in the UV range and only ~5% of visible radiation, the low surface area of the bulk form, and high rate recombination of electron and hole pair. In order to overcome this problem, various modifications have been made on ZnO in literature which extends its light absorption tendency to the visible light region and enhances its photocatalytic capability. ZnO is modified by organic materials, mono- and co-doping methods, and coupling with other semiconductors [9]. Non-metal doping does not lead to the formation of recombination centers. Unlike metal doping, it narrows the band gap by creating a new valence band through rising of the upper valence band. Hence, non-metal doping is preferred in introducing impurities to semiconductors which enhance their photocatalytic activity in the visible region [10]. Among the non-metals, nitrogen is the most promising candidate for doping due to its similarity with oxygen with regard to ionic radii and electronegativity [11] and doping of N in ZnO can improve the properties of ZnO, which is desirable for a photocatalyst as an enabler to use the maximum solar radiation [12]. On the other hand, hematite (α-Fe$_2$O$_3$) is the most thermodynamically-stable phase of iron oxide under ambient conditions with low cost, high resistance to photo-corrosion, environment friendly and absorbed visible light up to
600 nm due to the narrow band gap of 2.2 eV [13]. ZnO with Fe₂O₃ have been investigated in order to enhance the photocatalytic activity of ZnO on organic compounds degradation [14].

Recently, Graphene and Graphene oxide (GO) are considered the most promising powerful materials, with multiple potential applications in several fields[15]. GO is an environment friendly shows preferable adsorption due to the large surface area (p-p interaction) and enhanced electrostatic interaction with adsorbates and removes organic pollutants in the aqueous system via adsorption and photocatalytic degradation [16].

Thus, a synergetic effect of GO with metal oxide increases the efficiency of photocatalyst required for specific applications. N-ZnO-GO photocatalyst is prepared over N-ZnO nanoparticles which were loaded on the platform of a Graphene oxide nanosheets [17]. Malachite Green dye (MG) is an organic dye having chemical formula C₅₂H₅₄N₄O₁₂. MG is a green crystal powder with a metallic luster, highly soluble in water and ethanol with blue green solutions[18]. MG is used as a food coloring additive and as a dye in silk, wool, paper, jute, cotton, leather and acrylic industries. Wastewater containing MG dye emanating from textile mills and food industries is strongly colored and carcinogenic in nature. To decrease pollution load on mainstream water, it is desirable to degrade the dye into nontoxic form before its discharge into environment [11].

**METHODOLOGY**

- Graphene oxide (GO) are synthesized by modified Hummer’s method.
- ZnO and Fe₂O₃ NPs are synthesized by sol-gel method.
- For the preparation of 0.7(Fe₂O₃)/0.3(ZnO) nanopowder was synthesized by traditional wet chemistry method followed by calcination. A mixture of iron and zinc hydroxides was obtained by adding ammonia solution to the solution of proper amount of Zn(NO₃)_2·6H₂O and Fe(NO₃)_3·4H₂O in water. The obtained hydroxides were filtered, dried and calcined at 573 K during 1 h.
- For the preparation of N-ZnO/GO (0.5 wt % of GO), 0.5g of GO in 50mL of distilled water and ultrasonicated for 30 min. 0.1M solution of urea is added slowly into the solution of 0.9 M Zn (O₂CC₂H₅)₂ (H₂O)₂. The resulting solution was added slowly into GO solution followed by 1M NaOH until pH≈12 and stirred for 13 h. A grey precipitate was obtained which was dried at 50 °C overnight.
- For the photocatalytic activity, aqueous dye solutions (1 × 10⁻⁵ M) of MG (20mL )containing suspended 0.01 g of powdered nanocatalyst samples ZnO, N-ZnO/GO and Fe₂O₃ doped ZnO/GO nanocomposites were taken in separate 100 mL beakers and simultaneously irradiated with solar light with intensity of 60mW/cm² with continuous stirrer. At regular intervals of 45 min, 5 mL of aliquot samples were withdrawn from the reaction mixture and absorbance was measured data wavelength of 617nm (λmax) using a UV-Vis spectrophotometer to follow the degradation of MG dye.

**RESULTS AND DISCUSSION**

(Figure, 1a and b) shows the XRD patterns of N-ZnO/GO, Fe₂O₃ doped ZnO nanocomposites. All the diffraction peaks revealed that the wurtzite phase of ZnO (JCPDS: 79-0205) and hematite of Fe₂O₃ (JCPDS: 82-1503). The apparent broadening of these peaks indicates crystalline size of the nanoparticles.
The photocatalytic study was performed using MG dye. For the photocatalytic performance study of prepared different nano catalyst (N-ZnO/GO, ZnO-Fe$_2$O$_3$) 0.01g catalyst and 20 mL aqueous dye solution were taken. The time-dependent degradation of MG for the samples under visible light irradiation is shown in (Figure 2. a,b). A plot of log absorbance ($A_t$) vs. time was linear and followed pseudo-first-order kinetics (Figure-3).

\[ \ln \frac{A_0}{A_t} = kt \]  

\[ k = 2.303 \times \text{Slope} \]
The degradation efficiency as determined using the following relation:

\[
\text{%Degradation} = 100 \times \left[ \frac{(A_0 - A_t)}{A_0} \right]
\]  

(iii)

where, \(A_0\) = initial concentration of dye; \(A_t\) = dye concentration after irradiation at time, \(t\)

CONCLUSION

In this work, N-ZnO/GO, Fe\(_2\)O\(_3\) doped ZnO nanocomposite prepared by Sol-gel method are nanometric size. XRD pattern shows the presence of nitrogen, Fe\(_2\)O\(_3\) and GO. The maximum degradation has been obtained by N-ZnO/GO and Fe\(_2\)O\(_3\) doped ZnO nanocomposite were 93.8 and 51.1 \% respectively. The rate constant R square value were for N-ZnO/GO 0.00395 min\(^{-1}\) and 0.949 and Fe\(_2\)O\(_3\) doped ZnO 0.0154 min\(^{-1}\) and 0.975. The reaction kinetics is pseudo-first order reaction.
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