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Research Paper

PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE DYE BY NICKEL DOPED ZINC OXIDE NANOPARTICLES

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Abstract:

Nanoparticles (NPs) of nickel doped zinc oxide (NiZnO) have been fabricated through auto combustion synthesis scheme consuming zinc nitrate and citric acid. Employing X-ray diffraction examinations, the structure of synthesized nanoparticles was confirmed. The synthesized NPs' photo catalytic capabilities were evaluated with methylene blue (MB) dye degradation, in presence of natural sunlight. About 91% of MB dye solution was degraded by prepared nano powder in 90 minutes of sunlight irradiation.

Keywords: Zinc oxide nanoparticles, photocatalyst, dye degradation, methylene blue.

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I. INTRODUCTION

The industrial processes generate massive number of organic pollutants, including organic dye which is heavily utilized in textile industries, paper manufacturing, rubber, leather, and printing industries posing a substantial threat to environmental sustainability [1]. Textile dye the main source for aquatic pollution for coloured compounds that approximate amount of 1-15 % discharged in waste water during the dyeing process and textile industries. The contamination of waste water with this dye dissolved oxygen and therefore affects the aquatic life [2]. Discharge of waste water from textile industries into water bodies is causing a huge environmental hazard. The waste water not only depletes the aesthetic quality of water, but also renders it detrimental for aquatic flora and fauna. So, elimination of these recalcitrant dyes from the water bodies is an imperative issue [3]. The water from industries goes into the river or ocean, it is very important to degrade the dye. One such a dye methylene blue is extensively utilized in textile manufacturing for dyeing cotton, wool, and silk [4,5]. Methylene blue is a water-soluble azo dye. It contaminates environment and potentially harms to human health, leading to the symptoms such as rapid breathing, tissue necrosis, jaundice, vomiting and cyanosis [6]. It is often used as a test model dye for photo degradation studies [7]. Industrial discharge contains high concentration of dyes characterized by toxicity, non-degradable and refractory for traditional treatment method [8]. Photocatalysis is a promising technology for complete destruction of organic pollutants without formation of secondary pollutants [9]. In photocatalysis one can use the source of UV radiations from sunlight and in the presences of catalyst (such as semiconductors) conduct the chemical reactions to degrade the organic pollutants present in waste water [10]. Various semiconductors have been tested for their efficiencies towards the dye degradation. Some of these include ZnO, TiO_2, V_2O_5, CuO, CdS, WO_3, ZrO_3 and their impregnated forms [11]. Among these metal oxide semiconductor nanoparticles, ZnO have attracted much attention for the degradation of toxic dyes and destruction of the bacteria which was mainly due to narrow band gap energy (3.3 eV). It is used as a catalyst for the waste water treatment [12]. ZnO is also characterized by excellent optoelectronic properties, high chemical stability, abundance in nature, inexpensiveness and ease of nano-fabrication. Owning to the strong oxidation potential and fast charge transport properties, the photocatalytic properties of ZnO has been investigated for elimination of various organic dyes and pollutants. It was found out by researchers that doping a ZnO NPs with transition metals enhance various properties including photocatalytic performance [13]. So, to check the photocatalytic performance of doped ZnO, we propose here the synthesis of Nickel doped ZnO nanoparticles from facile auto combustion mode and its photocatalytic studies against MB dye. Owning to the strong oxidation potential and fast charge transport properties, the photocatalytic properties of ZnO has been investigated for elimination of various organic dyes and pollutants [14]. Although ZnO nanomaterials exhibit exceptional catalytic properties, their overall performance has been hindered. The main limitations stem from ZnO's wide bandgap, which restricts its ability to absorb solar energy, and its tendency to undergo photo-corrosion in aqueous solutions due to the recombination of charge carriers [15]. Doping strategies of ZnO with other elements increased light absorption properties significantly [16]. The extension of ZnO to the visible region not only increase the photocatalytic performance but also improve the antibacterial activity. Transition metals such as Fe, Co, Ni and Mn etc. use to improve the photocatalytic performance of the metal oxide semiconductor. Among various transition metals nickel is used as a dopant to increase the photocatalytic and antibacterial activity due to same valence state and ionic radii [17]. Nickel shows excellent photocatalytic and antibacterial activity when it doped with metal oxide therefore, the work is to a potential Ni doped ZnO catalyst to degrade the organic dye and alternative to the traditional antibiotic [18]. ZnO exhibited better photodegradation efficiency of some reactive dyes in aqueous solution than TiO_2. Photodegradation applications of ZnO nanoparticles and metal doped ZnO nanoparticles were reported to corroborate with the results of metal doped TiO_2 nanoparticles [19]. When a ZnO semiconductor is subjected to sunlight, within semi-conductor's valence band (VB) and conduction band (CB), electron-hole (e^-/h^+) pairs are generated [20]. The recombination or interaction of such electron-hole pairs with dye molecules individually degrades the dye [21].

II. EXPERIMENTAL SECTION

2.1 Chemicals

All chemical employed in this synthesis procedure were of analytical grade. Zinc nitrate hexahydrate [$Zn(NO_3)_2·6H_2O$] and Citric acid ($C_6H_8O_7$) were bought from SRL PVT. company, they were used precisely as they were with no purification. For photocatalytic studies, (10 mg/L) methylene blue dye was employed.

2.2 Characterization techniques

The structural and phase identification studies of prepared ZnO were confirmed by powder X-ray diffraction (PXRD) instrument (Model: AXS D8 Advance Bruker, Germany) with Cu-Kα radiation source (λ = 1.5405 Å).

2.3 Synthesis of nanoparticles

$Ni_xZn_{1-x}O$ nano powder (x = 0.025) was synthesized employing auto combustion method. Zinc nitrate and nickel nitrate were dissolved in minimum amount of distilled water and stirred. Citric acid as a fuel was also dissolved in minimum amount of distilled water and stirred. Then citric acid solution was added to nitrate solution and stirred and heated at 100℃ on hot plate magnetic stirrer. After stirring with heating, sol was formed which then converts to gel, then the gel was transferred to preheated muffle furnace at 350℃. At this stage, auto combustion reaction starts, gel bursts, swells and converts into loose powder. The obtained product was crushed in agate mortar for about 1hr and then nano powder is calcined at 800℃, for 2 hrs. The obtained grey coloured nano powder of nickel doped zinc oxide was used further for characterization and photocatalytic applications.

2.4 Investigation of photocatalytic capacity

The photocatalytic abilities of produced nano powder were assessed by testing the MB dye deterioration in an aqueous solution under daylight conditions. In actual performance, 30 mg of synthesized nanoparticles as photocatalyst has been mixed with 50 ml MB dye (10 mg/L) having pH 7 to 11. The pH of the dye solution was adjusted via solutions of NaOH and HCl. After adding the dye solution to photocatalyst, the solution was agitated on magnetic stirrer under dark condition for about 30 minutes to reach equilibrium among adsorption-desorption. After 30 minutes, the resultant mixture was exposed to natural sunshine with continuous stirring. At definite time intervals, 5 ml aliquots were extracted from the solution. These aliquots were then subjected to centrifugation. The resulting supernant solution were used to measure absorption spectra using a Shimadzu UV-1800 spectrophotometer. Distilled water was employed as the reference medium, and UV-Visible absorption spectra was recorded within the range of 200-800 nm wavelength, to observe the degradation of MB. The percentage of decomposition of MB dye was ascertained utilising an equation (1).

% degradation = $((C_0-C_t) / C_0)$ x 100 (1)

In above equation, C_0 represents dye concentrations prior to radiation exposure and the dye concentration after time t in minutes, shown by C_t.

III. RESULT AND DISCUSSION

3.1 XRD analysis of NiZnO nanoparticles

The XRD spectrum of NiZnO NPs is as shown in Fig.1. The micrographs of the sample well matched with standard data (JCPDS-36-1451) of ZnO [22]. The XRD patterns show a hexagonal wurtzite phase without any impurities and secondary phase, which ultimately indicate an effective incorporation of Ni in the ZnO lattice. The formation of the secondary phase is controlled by taking low concentrations of dopant nickel metal [23].

Debye Scherrer's equation [24] was used to measure the crystallite size (D), $D = k\lambda / \beta\cos\theta$, λ represents radiation wavelength (1.5416A˚) and k indicates shape factor (0.9). β is the full-width at half maximum (FWHM) in radians, and θ represents Bragg's angle in degree. FWHM of the prominent peak (101) used to calculate crystallite size and was determined to be 23.77 nm.

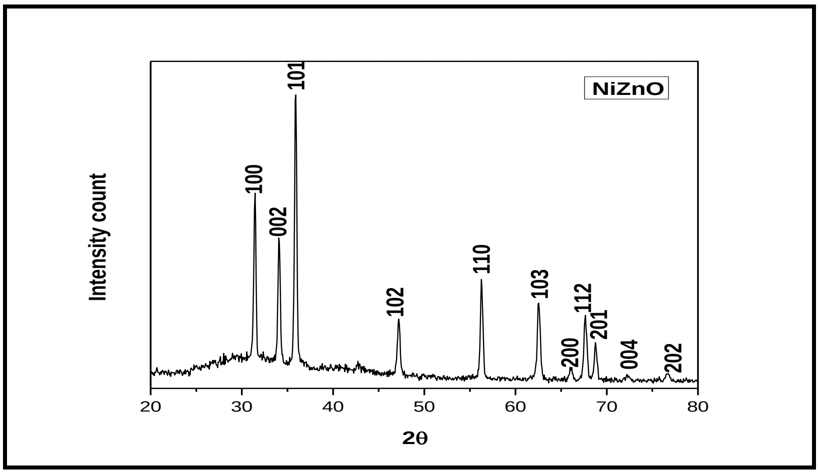

Fig.1 XRD spectrum of NiZnO nano powders

3.2 Photocatalytic activity evaluation

The photocatalytic dye degradation efficiency of prepared NiZnO nanoparticles was tested over 10 mg/L methylene blue dye. To study the effect of increasing pH on dye degradation capacity of nano powder, the pH of dye solution was varied from pH 7 to pH 11, keeping the photocatalyst loading constant as 0.030 mg for 50 ml of dye solution in all three pH conditions.

Table 1 shows results of MB dye degradation at pH 7, where it was found that about 80% of the dye was degraded in 90 min in presence of sunlight.

Table 1. Photocatalysis at pH 7

Abs.	Conc.	C/Co	Time	Ln C/Co	Degradation	% Degradation
3.245	3.241106	1	-30	0	0.79876733	79.876733
3.112	3.108266	0.95901	0	0.04184974		
2.763	2.760683	0.85117	30	0.16043644		
1.564	1.561124	0.48166	60	0.7305083		
0.653	0.652216	0.20123	90	1.6032935		

Table 2 shows MB dye degradation at pH 9, indicating about 86% dye degradation in 90 min after sunlight exposure

Table 2. Photocatalysis at pH 9

Abs	Conc.	C/Co	Time	ln C/Co	Degradation	%Degradation
3.256	3.2530928	1	-30	0	0.860872236	86.08722359
3.167	3.1631396	0.972666	0	0.027714		
2.631	2.6278428	0.808047	30	0.213135		
1.344	1.3423872	0.412776	60	0.884849		
0.453	0.4524564	0.139128	90	1.972362		

Table 3 shows MB dye degradation at pH 11, reveals 91% degradation in 90 min of sunlight irradiation.

Table 3. Photocatalysis at pH 11

Abs.	Conc.	C/Co	Time	ln C/Co	Degradation	%Degradation
3.452	3.447858	1	0	0	0.91367323	91.367323
3.233	3.22912	0.936559	15	0.0655432		
2.211	2.208347	0.640498	30	0.4455088		
1.241	1.339391	0.38847	45	0.9455381		
0.298	0.297242	0.086327	60	2.4496155		

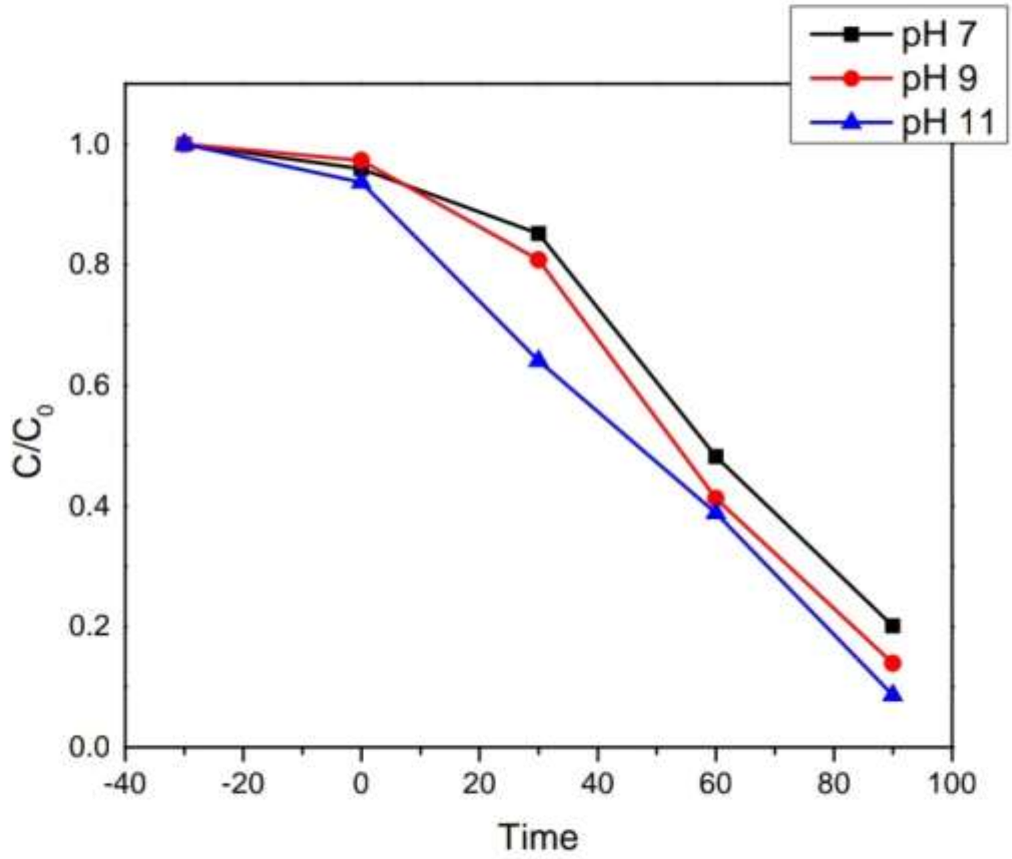

Fig. 2 % degradation of MB dye at different pH

From Fig. 2 it was clear that the dye degradation performance by prepared nano powders using sunlight irradiation was found to increase with increase in pH. Methylene blue as, a cationic dye, adsorb to less extent on photocatalyst surface in acidic environment, but when pH increased, adsorption of dye on photocatalyst takes place effectively. Production of $^{\bullet}$OH radical as an intermediate species, also increase at basic pH of dye, which has active role in mechanism of dye degradation [25].

IV. CONCLUSION

The auto combustion synthesis of nickel doped zinc oxide was successfully carried out using citric acid as a fuel. The XRD studies also proves formation of nickel doped zinc oxide with the particle size of the product within nanometric range. Absence of secondary peak in XRD spectrum proves successful doping of nickel into ZnO lattice. Prepared sample can act as a photocatalyst for the degradation of dye in presence of sunlight. The degradation studies at varying conditions indicates that, the degradation is most efficient at pH 11, and efficiency decreases with decreasing pH. This suggests that the reaction or process is more favorable in alkaline condition pH (9 and 11) as compared to neutral condition.

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