SYNTHESIS AND PHOTOCATALYTIC PROPERTIES OF NIZNO NANOPARTICLES FOR DEGRADATION OF METHYL ORANGE DYE

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ABSTRACT:
Nanoparticles (NPs) of nickel doped zinc oxide (NiZnO) have been fabricated through auto combustion synthesis scheme consuming zinc nitrate, nickel nitrate and citric acid. Employing X-ray diffraction examinations, the structure of synthesized nanoparticles was confirmed. With methyl orange (MO) dye, the created NPs' photocatalytic capabilities were analyzed by irradiation of natural sunlight. About 92 % of MO dye solution was degraded by prepared nano powder in 150 minutes of sunlight irradiation.

Keywords: Zinc oxide nanoparticles, photocatalyst, dye degradation, Methyl Orange.

1.INTRODUCTION

The dye industry has grown at a tremendous pace in recent years. Some of these colour dyes are especially harmful and constitute a serious threat to the environment [1]. Textile, paper, leather, printing, and other industries frequently utilise dyes [2]. The wastewater discharged from these industries contains a high concentration of dyes, which can be toxic, non-biodegradable, and resistant to conventional treatment methods. When this wastewater is discharged into water bodies, it may have a profound effect on the environment, human health and aquatic life [3]. It is water soluble azo dye, causing serious environmental pollution. Although it is not particularly dangerous, it can cause rapid breathing, tissue necrosis, jaundice, vomiting, distress, and cyanosis in humans [6, 7]. Taking such dangerous colours out of water bodies is one of the main concerns for environmental protection agencies. Researchers have developed various innovative methods such as adsorption, coagulation, oxidation, filtration, and ultrafiltration for dye removal [8]. One of the best strategies is heterogeneous photocatalysis applied for the decline of a large number of organic contents from water bodies [9, 10]. The chemical properties of numerous representative dyes that are normally utilized in the textile industries [21]. Among the major dye classifications, Azo dyes are considered to exhibit the largest group of colourants and over 50% of all industrial dye utilized is azo dyes [22]. Dyes are classified into cationic and anionic dyes according to the chemical structure. The cationic dyes are categorized as methylene blue (MB), malachite green (MG), Rhodamine B (RhB), crystal violet (CV), Rhodamine 6G (Rh6G), and safranin O (SO),which exhibit cationic functional groups that can dissociate into positively charged ions [23]. Whereas, the Anionic dyes comprising the reactive, direct and acid dyes [24]. Methyl orange (MO) and tartrazine (TA) anionic azo dyes are the most commonly used substances for dyeing cotton, wood, and silk [25]. These substances are usually present in the effluent water of many industries, such as

textiles, leather, paper, printing, foodstuffs and cosmetics. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents discharged into water bodies [26] Although methyl orange is not considered to be very toxic, it can cause some harmful effects such as vomiting, increased heart rate, diarrhoea, shock, cyanosis, and tissue necrosis in human beings . The present work concerns nanoparticles of Ni doped ZnO, a material belonging to the spintronic class. Some of its uses have been shown in a recent work that this nanomaterial presents both interesting magnetic and photo-luminescent properties . Most of the studies reported in the literature deals with the removal of dyes or organic compounds by a photo-catalytic process in the presence of Ni doped zinc oxide thin films, nanopowders and nanorods . This work lies within a more general goal we are presently developing, which pertains to propose a depollution process including several steps based on the multifunctionality of such material (high surface/volume, ferromagnetic and photo-luminescent characters). Indeed, to our knowledge there is no study which compared the adsorption process of dyes onto nickel doped zinc oxide nanoparticles of small size and a low specific surface area. ZnO has attained tremendous attention of researchers because of its chemical stability, non-toxicity and inexpensive nature. The present paper reports a simple and efficient method for the synthesis of nickel doped ZnO nanoparticles. The photocatalytic behaviour of synthesized nanoparticles has been evaluated using Methyl Orange (MO) as probe molecule under UV irradiation.

2. EXPERIMENTAL SECTION

2.1 Chemicals

All chemical used in this synthesis procedure were of analytical grade. Zinc nitrate hexahydrate [Zn $(NO_3)_2 \cdot 6H_2O$], Nickel nitrate [Ni $(NO_3)_2 \cdot 6H_2O$] and Citric acid ($C_6H_8O_7$) were purchased from SRL PVT. Company, and used as it is without any purification. For photodegradation studies, (10 mg/L) methyl orange dye was employed.

2.2 Characterization techniques

The structural 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 and citric were taken in stoichiometric proportion and dissolved in minimum amount of distilled water and stirred separately. After adding citric acid solution to nitrate solution, the obtained sol was stirred and heated at 100℃ on hot plate magnetic stirrer. After stirring with heating, sol then converts to gel, then the gel was shifted 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 degradation studies of produced nano powder were examined by testing the methyl orange dye deterioration in presence of sunlight, with nano powder

as photocatalyst. In actual procedure, 30 mg of prepared nanoparticles as photocatalyst has been mixed with 50 ml MO dye (10 mg/L) having pH 7 to 11. NaOH and HCl solution were used to adjust pH. After adding the dye solution to photocatalyst, the solution was stirred 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 sunlight with continuous stirring. At fixed time intervals, 5 ml aliquots were extracted from the solution. These aliquots were then subjected to centrifugation. The resulting supernant solution was 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 decomposition percentage of MO dye was calculated using an equation (1).

% degradation = $((C_0-C_t) / C_0) \times 100$ (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.

3. RESULT AND DISCUSSION

3.1 XRD analysis of NiZnO nanoparticles

The XRD spectrum of NiZnO is as shown in Fig.1. The micrographs of the sample well matched with standard data (JCPDS-36-1451) of ZnO . 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.

Debye Scherrer's equation 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.

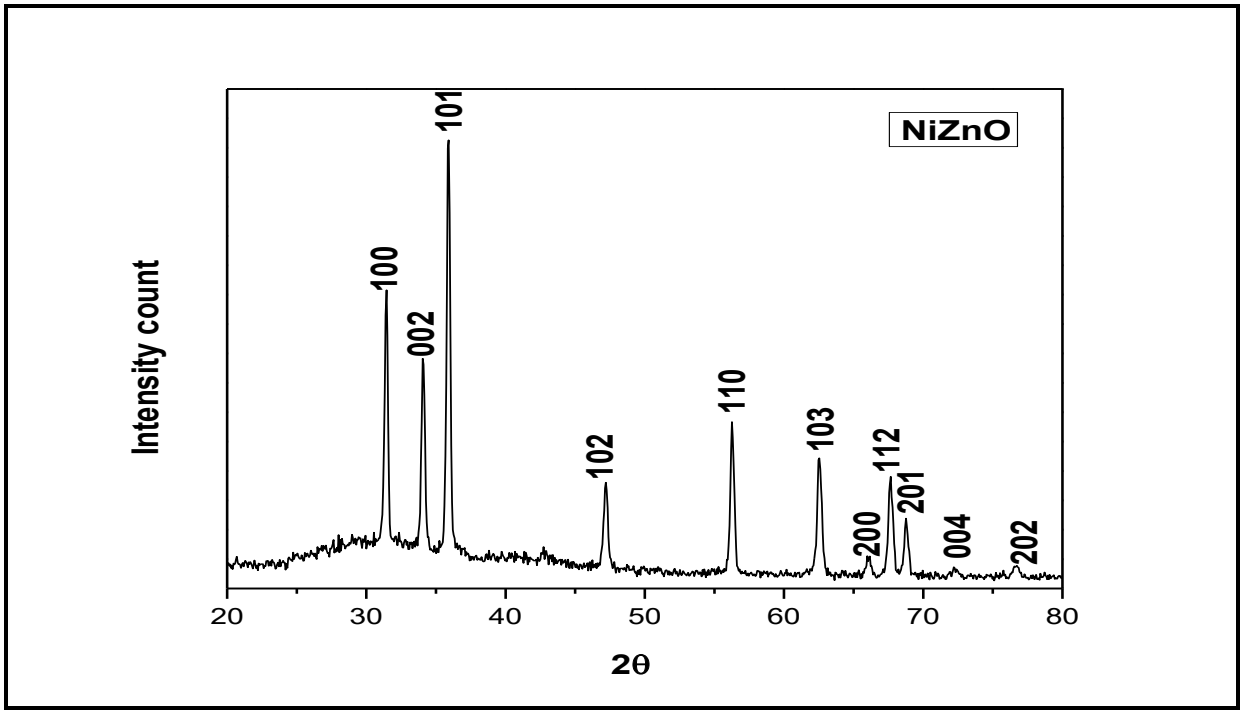

Fig.1 XRD spectrum of NiZnO nano powders

3.2 Photocatalytic activity evaluation

The photocatalytic dye degradation efficiency of prepared NiZnO nanoparticles was tested over 10 mg/L methyl orange 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 MO dye degradation at pH 7, where it was found that about 80% of the dye was degraded in 92 min in presence of sunlight.

Photocatalysis by 0.03 g NiZnO at pH 7 on 10 ppm MO dye

Abs.	Conc.	C/Co	Time	ln C/Co	Degradation	%Degradation
2.466	2.4630	1	-30	0	0.9184914	91.849148
2.311	2.3082	0.93715	0	0.064917		
1.713	1.7109	0.69465	30	0.364351		
1.718	1.1765	0.4777	60	0.738779		
0.988	0.9868	0.40065	90	0.9146699		
0.522	0.5213	0.21168	120	1.5526851		
0.201	0.2007	0.08151	150	2.507047		

Table 1 shows results of MO dye degradation at pH 9, where it was found that about 80% of the dye was degraded in 89 min in presence of sunlight.

Photocatalysis by 0.03g NiZnO at pH 9 on 10 ppm MO dye

Abs.	Conc.	C/Co	Time	ln C/Co	Degradation	%Degradation
2.646	2.6428	1	-30	0	0.89569161	89.569161
2.487	2.4840	0.9399	0	0.061971		
1.909	1.9067	0.7214	30	0.326469		
1.321	1.3194	0.4992	60	0.694660		
1.104	1.1026	0.4172	90	0.874109		
0.744	0.7431	0.2811	120	1.268763		
0.276	0.2756	0.1043	150	2.260403		

Table 3 shows results of MO dye degradation at pH 11, where it was found that about 80% of the dye was degraded in 88 min in presence of sunlight.

Photocatalysis by 0.03g NiZnO at PH 11 on 10 ppm MO dye

Abs.	Conc.	C/Co	Time	ln C/Co	Degradation	%Degradation
2.451	2.448059	1	-30	0	0.88127295	88.12729498
2.403	2.400116	0.98042	0	0.019778		
1.919	1.916697	0.78295	30	0.244691		
1.401	1.399319	0.5716	60	0.559309		
1.197	1.195564	0.48837	90	0.716671		
0.768	0.767078	0.31334	120	1.160461		
0.291	0.290651	0.11873	150	2.130928		

The concentration ratio C/Co (where C concentration of methyl orange at time t and Co is initial concentration) was calculated for all pH levels.

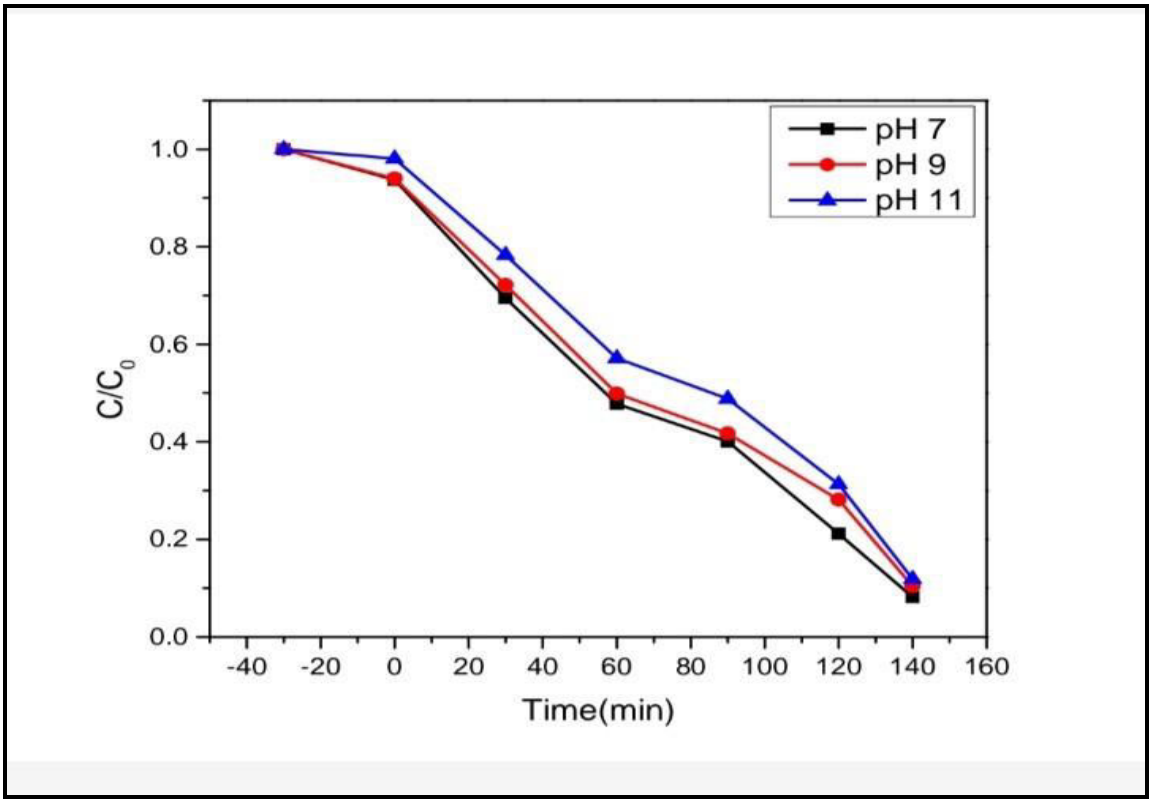

Fig.2 Photo degradation of MO dye at various pH

Fig. 2 shows photodegradation of methyl orange dye at pH 7 to 11. The results in graph clearly indicate maximum degradation of dye takes place at pH 7, i.e. at neutral pH of dye solution. As per studies reported, the point of zero charge (PZC) of nano-sized ZnO particle is about a pH of 9.30. Nanoscale ZnO particles have negatively charged surfaces above the PZC level. Nanoscale ZnO particles have positively charged surfaces below the PZC. In a broad range of pH values, methyl orange molecules are negatively charged. Consequently, the MO anions ought to be easily adsorbed on the surfaces of nano-sized ZnO particles when the pH of the MO solution is lower than the PZC [AA]. Thus, it supports maximum degradation at pH 7 compared to pH 9 and 11 of methyl orange dye solution.

CONCLUSION

The fabrication of nickel doped zinc oxide nanoparticles was done successfully using auto combustion synthesis taking citric acid as a fuel. The XRD analysis proves formation of wurtzite hexagonal structure of nickel doped ZnO nanoparticles. The photodegradation studies reveal that maximum degradation of methyl orange dye takes place at pH 7. About 92 % of the dye was degraded by nanopowders in 150 min of sunlight irradiation.

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