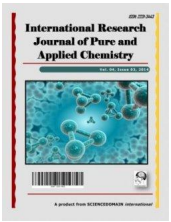

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Synthesis and Characterization of Co-doped Nickel-ZnO/Polypyrrole Nano-composites, and Their Effect on Photo-catalytic Degradation of P-nitrophenol under Solar Irradiation

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Nickel-polypyrrole co-modified ZnO nano-composites (Ni-ZnO/Ppy) were synthesized by two methods, metal impregnation of nickel (Ni) and In-situ chemical polymerization of polypyrrole (Ppy) on ZnO nano-particles. The crystal size, band gap energy and bond structure of as-synthesized nano-composites were investigated by using x-ray diffraction(XRD),UV-Vis and Fourier transform infrared (FT-IR) spectroscopic techniques respectively. Photo-catalytic degradation efficiency of synthesized photo-catalysts was investigated on p-nitrophenol dyes under solar irradiations and Co-doped photo-catalysts shows better catalytic degradation efficiency than both ZnO and Ni-ZnO nano-particles. Ni-ZnO/Ppy photo-catalysts effectively degraded 96.04% of p-nitrophenol dye on 180 minute visible light irradiation. Highest photo-catalytic activity of Ni-ZnO/Ppy nano-composites over ZnO photo-catalysts was attributed due dopants to the lower rate of recombination of the photo generated electrons- holes as well as its lower crystal size and band gap energy. The photo-catalytic degradation of p-nitrophenol kinetically follows pseudo first-order reactions for Ni-ZnO/Ppy photo-catalysts.

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Keywords: Co-doped photo-catalyst; Kinetic degradation, nano-composite; p-nitrophenol.

1. INTRODUCTION

One of the major challenges of a developing country like Ethiopia is solving environmental issue with newly booming industries in different industrial zones and costs of waste water treatment especially from wastes from textile and leather industries. The textile industry is amongst all the industries in Ethiopia is the largest consumer of high quality fresh water and with the nature of their production processes significantly contributing to pollution. Wastewater from the textile industry is also a significant environmental pollution source of persistent organic pollutants. Not only textile wastewater but also textile products often contain chemicals such as formaldehyde, azo-dyes, dioxins, pesticides and heavy metals, which might pose a risk to humans and the environment. These compounds have been found in wastewater after home washing, in organic solvent after dry-cleaning and also in the atmosphere after incineration [1].

In recent years, photo-catalytic degradation of organic pollutants in water and air using semiconductor materials has received more attention. Under light irradiation, the semiconductor generates electron/hole pairs, with electrons excited from the valence band to the conduction band and leaving positive holes in the valence band. Therefore, photo generated holes in the valence band and photo generated electrons in the conduction band are formed, respectively. The generated electron/hole pairs initiate a complex series of oxidative and reductive reactions on the surface of the semiconductor. Organic pollutants adsorbed on the surface of the semiconductor are partly or completely degraded [2].

Among the semiconductors, TiO_2 is the most widely used for photo-catalysis due to its high photo-catalytic activity, non-toxicity, and good stability. ZnO as a potential semiconductor with similar band gap energy to $TiO_2$and ZnO exhibit a better efficiency than TiO_2 in photo-catalytic degradation of some contaminations are receiving more attention [3]. To overcome these disadvantages, significant efforts has been devoted to preventing the recombination of photo-generated hole/electron pairs and improving the utilization efficiency of solar light during photo-catalytic reactions by doping with metals and surface modification by polymers gets attention to solve the challenge of catalytic efficiency and stability of photo-catalysts [4]. Polypyrrole (Ppy), as a traditional conducting polymer, is widely used in batteries, super capacitors, electrochemical or biological sensors, conductive textiles and fabrics, actuating mechanism, electromagnetic screen, anti-static paint and drug delivery systems. Besides superior conductivity, electrochemical reversibility and high polarizability, Ppy displays good chemical and thermal stability to avoid being dissolved in acidic and neutral solution, and under goes only slight photo-catalytic degradation in ambient atmosphere due to oxidation [3-5]. Thus the present study has been designed to increase efficiency of photon harvesting by reducing band gap energy of bare ZnO nano-particles by co-modification with metal, nickel(Ni) and conduction polymers, polypyrrole and its photo-catalytic activities of p-nitrophenol was investigated under visible irradiation.

2. MATERIALS AND METHODS

2.1 Synthesis of Ni-ZnO Materials

The Ni-doped ZnO is prepared by a modified homogeneous precipitation using zinc acetate, oxalic acid and nickel chloride as precursors [5]. Then 4.8 g of zinc acetate and 2.5 g of oxalic acid were dissolved in 50 ml of distilled water under stirring for 2h at room temperature. An amount of nickel chloride, which corresponds to Ni to ZnO molar ratio equal to 1, 5 and 10%, respectively was added to the solution. The obtained precipitate was filtered, washed with methanol, dried in an oven at 80°C for 24 h, and then heated at 400°C for 3 h to get a Ni doped zinc oxide (Ni-ZnO) [5,11].

2.2 Synthesis of Ni-ZnO/Ppy Nano-composites

The Ni-ZnO/Ppy composites were prepared by the direct impregnation method [16]. In a typical procedure, 1 g of Ni-ZnO nano-particles was dispersed in 10% M.wt of 30 mL of aqueous Ppy solution during one hour-stirring. The obtained Ni-ZnO/Ppy nano-composite powders were filtered, washed three times with ethanol and water respectively, and dried for 24 h at 80°C. Then dried precipitate was calcinated in furnace at 500°C for 2 hours.

2.3 X- Ray Diffraction (XRD) Analysis

The average crystallite size of the as-synthesized Ni-ZnO and Ni-ZnO/Ppy nano-composites was calculated using the Debye-Scherrer formula [8-12].

$$D = \frac{0.9\,\lambda}{\beta\cos\theta}$$

where D is the average crystallite size, λ is the wavelength of the X-ray = 0.15406 nm for Cu target Kα radiation, β is the full width at half – maximum of an XRD peak and θ is the Bragg's angle.

2.4 UV–Vis Absorption Spectral Analysis

Band gap energy (eV) of as–synthesised photo-catalysts was obtained using the equation given bellow [9,10].

$$E_g\ (ev) = \frac{1240}{\lambda}\ ev$$

Where, Eg is band gap energy in electron volts and λ is wavelength (nm) corresponding to absorption edge

2.5Photo-catalytic Degradation Studies

250 ml of dye solution was mixed with a given amount of photo-catalyst and allowed to equilibrate for 30 min in the dark to obtain adsorption/desorption equilibrium before irradiating the dye in the reactor. The solution was separately done under visible irradiation sources and magnetically stirred. Air was continuously bubbled through the reactor tube.

5 mL of each reaction mixture was withdrawn at 20 minutes time interval. The suspension was centrifuged at 3000 rpm for 5 minutes and filtered off to remove the catalyst particles and absorbance of p-nitrophenol solution was determined spectrophotometrically at 325 nm. Percentage degradation of nitrophenol was calculated using the relation [6].

$$\%\ \text{Degradation} = \frac{A0-At}{A0}\ x100$$

Where, A_o is absorbance of dye at initial stage, A_t is absorbance of dye at time "t".

2.6 Photo-catalytic Reactor

The photo-catalytic reactor consists of a quartz tube with an inlet tube for provision of air purging during photo-catalysis and outlet tube for the collection of samples from the reactor at regular time intervals.

The Visible lamp (Philips) with definite power of 40W, 220 V, 0.18 A and 50 Hz frequency was employed as visible source, and positioned 9 cm above and parallel to the reactor [8,12].

2.7 Factors Affecting Efficiency Photo-catalyst

2.7.1 Effect of Ph

Effect of pH for degradation of p-nitrophenol on synthesized photo-catalytic was investigated over a pH range from 3 to 12 keeping other parameters constant.

2.7.2 Effect of catalyst load

The effect of catalyst load on photo-catalytic degradation of p-nitrophenol was observed by taking different amounts of Ni-ZnO/Ppy / (35 mg to 175 mgL^{-1}) each time at constant dye concentration (16 mgL^{-1}) and pH of 3.

2.7.3 Effect of dye initial concentration

The effect of initial concentrations of p-nitrophenol for degradation on synthesized photo-catalyst was observed by taking different dye initial concentrations 16 mgL^{-1} to 80 mgL^{-1}, and by fixing other parameters constant (photo-catalyst load =175 mgL^{-1}, pH = 3).

2.7.4 Effect of irradiation time

The relation between the percent degradation of p-nitrophenol with irradiation time was studied over a reaction time of 180 minutes, using optimized concentration of dye 16 mgL^{-1}, photo-catalyst load 175 mgL^{-1} and pH of 3.

2.8 Kinetic Degradation Studies

The kinetics of the photo-catalytic degradations of p-nitrophenol solutions was investigated using optimized photo-catalysts load (175 mgL^{-1}), dye initial concentration (16 mgL^{-1}) and pH=3 under visible light irradiations. The graph was plotted for each case with $\ln C_o/C_t$ as a function of time (t). Where, C_o is the initial concentration of dye and C_t is concentration of dye at time t. From the slope of the respective plots, the rate of photo-catalytic degradation of p-nitrophenol was determined.

3. RESULTS AND DISCUSSION

3.1 X- Ray Diffraction (XRD) Analysis

The XRD patterns of calcinated ZnO and Ni-ZnO and Ni-ZnO/Ppy nano-particles were shown in Fig. 1(A, B and C) respectively. The diffraction peaks at scattering angle in Figure.1C (2θ); 32.125°, 34.481°, 36.525°, 47.483°, 57.117°, 63.058° and the corresponding Miller indices are (100), (002), (101), (102), (110) (103) and (112) respectively for Ni-ZnO/Ppy nano-particles.

Whereas in Fig. 1b ($\boldsymbol{2\theta}$); 31.837°, 34.479°, 36.495°, 47.480°, 56.724° and 62.891° corresponding to the reflection from crystal planes for as –synthesized Ni-ZnO respectively and also both the synthesized photo-catalysts are suggesting hexagonal crystal structure [7-12].

The most intense peak at 2θ; 27.480° for Ni-ZnO/Ppy in Fig. 1(C), 36.525° for Ni-ZnO in Fig. 1 (B) and 36.429° for ZnO nano-particles, Fig. 1 (A) as shown in their XRD patterns were used to calculate the average crystalline size. The values of calculated average crystallite size (D) of the photo-catalysts are given in Table 1. As Debye-Scherrer formula calculation shows, the higher crystalline size obtained was 37.35 nm for ZnO then 31.47 nm for Ni-ZnO nano-particles. However, the lowest crystalline size was obtained for co-doped Ni-ZnO/Ppy nano-composite which is 18.23 nm. Doping with metals like nickel and conducting polymer, polypyrrole may reduce the size and help to control the morphology of synthesized nano-composites similar reported [9].

Table 1. Average crystalline size (D) of as-synthesized Ni-ZnO and Ni-ZnO/Ppy nano-composites photo-catalysts

Sample	2θ(degree)	β(radian)	D(nm)
ZnO	36.429	0.00408	37.35
Ni-ZnO	36.525	0.00490	31.47
Ni-ZnO/Ppy	27.4801	0.0051	18.23

3.2 Fourier Transform Infrared (FT-IR) Spectroscopic Study

Fig. 2A shows the FT-IR spectrum of the ZnO, and Ni-ZnO and Ni-ZnO/Ppy over 400-4000 $cm^{-1.}$ IR spectroscopy gives qualitative information about the way in which the adsorbed Polypyrrole (Ppy) molecules and Nickel metals are bonded to the surface of ZnO nano-particles. Fig. 2B and Fig. 2C compares the IR spectra of Ni-ZnO and Ni-ZnO/Ppy nano-composites.

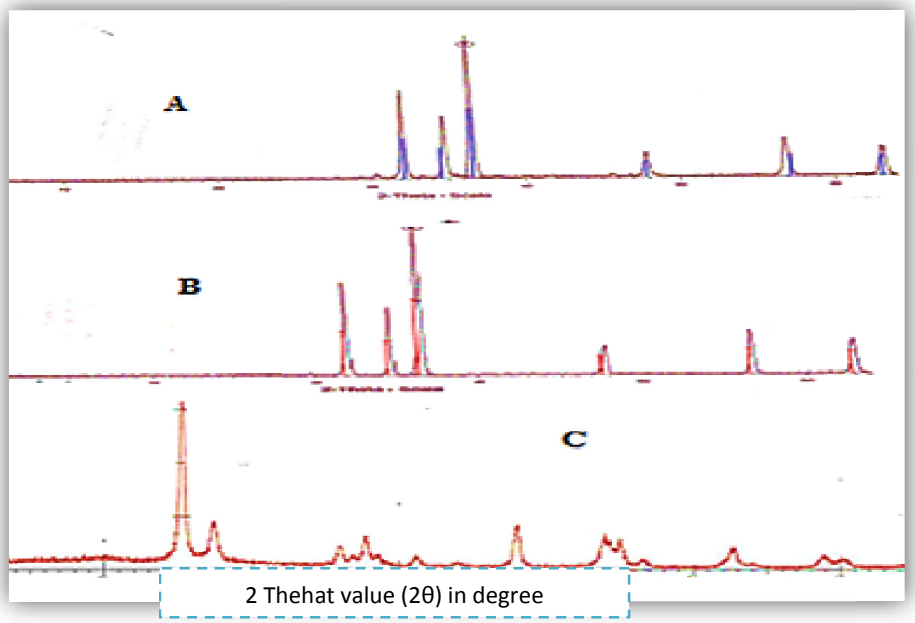


Fig. 1. XRD spectral of; A) ZnOnano-particles, B) Ni-ZnOnano-particles and C) Ni-ZnO/Ppy nano-composite

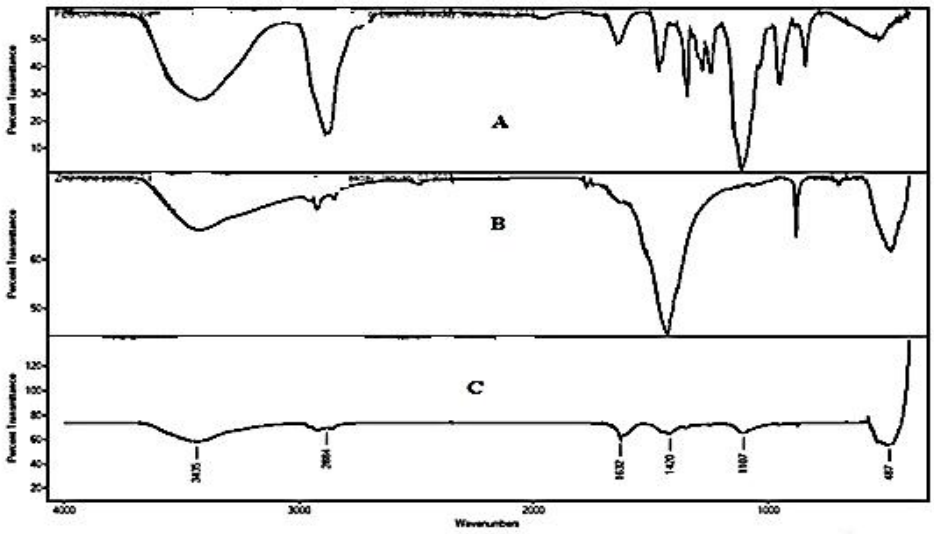


Fig. 2. FTIR spectra of (A) ZnO, (B) Ni-ZnO nano-particles and(C)Ni-ZnO/Ppy nano-composite respectively

From Fig. 2 comparing, Fig. 2(C) with Fig. 2(B), it could be found that for the Ni-ZnO nano-composite there is a new absorption peak at 1107 cm^{-1}, which can be attributed to the flex vibrations of CH_2–O–Zn[4, 9]. It demonstrated that ZnO nano-particles bonded with Ppy.

The absorption peak at 2853 cm^{-1} in ZnO Fig. 2(A).That corresponds to 2856cm^{-1} in Ni-ZnO/Ppy Fig. 2(C) is due to the CH group stretching vibration shifts to higher wave length the case of Ni-ZnO nano-particles. The broad band peak appearing at 3435 cm^{-1} for Ni-ZnO/Ppy in Fig. 2(C) due to OH group, has shifted higher wave numbers in comparison with the hydroxyl group peak in the ZnO nano-particles (3429 cm^{-1}). It indicates that covalent bonds have been formed between the Ppy, $Ni^{+2}$and ZnO nano-particles in Ni-ZnO/Ppy [17].

The strong absorption band formed at the 483 cm^{-1} for ZnO in Fig. 2(a) correlated to metal oxygen bond in ZnO is shifted to lower wave length for ZnO, 480cm^{-1} for Ni-ZnO in Fig. 2(C). The peaks in the range of 1400-1500cm^{-1} corresponds to the C=O bonds. The most intense absorption peak at 1431cm^{-1} in Fig. 3a and 1420 cm^{-1} in Fig. 2(C) due to O-C-O stretching of mono-dentates carbonates originated during synthesis of ZnO nano-particle. The adsorbed band at 1635 cm^{-1} is assigned O-H bending vibrations. The intense peak at 1800-1600 cm^{-1} corresponds to C=O stretching frequency and 700- 990 cm^{-1} is due to C-H bending vibrations respectively.

3.3 UV–Vis Absorption Spectral Analysis

The optical absorption of ZnO nano-particles, Ni-ZnO and Ni-ZnO/Ppy nano-composite are given in Fig. 3. The adsorption edge for ZnO, Ni-ZnO and Ni-ZnO/Ppy nano-particles are obtained at 383nm, 418 nm and 510 nm respectively. The band gaps of the synthesised photo-catalyst, Ni-ZnO and Ni-ZnO/Ppy nano-composites are well extended to visible region of spectrum as compared to ZnO nano-particles (Table 2). This may be due to the modification of electronic levels of ZnO by Ni^{+2} and Ppy as similarly reported [8,9,14].

Table 2. Absorption on wavelength and band gaps energy of ZnO and Ni-ZnO and Ni-ZnO/Ppy nano-composite photo-catalysts

Photo-catalysts nano-particles	Wavelength in (nm)	Band gap energy (Eg) in (ev)
ZnO (calcinated)	383	3.23
Ni-ZnO	418	2.96
Ni-ZnO/Ppy	510	2.43

Band gap energy of (eV) of Ni-ZnO/Ppy is less than that of Ni-ZnO and ZnO nano-particles. Thus, absorption peaks of ZnO were shifted from 383 nm to 418 nm and 510 nm wavelength for Ni-ZnO and Ni-ZnO/Ppy respectively. As compared to bare ZnO nano particle both nano composites were shifted to visible region. The extension of absorption in the visible range can be attributed due to the nickel doping. Additional co-doping Ni-ZnO by polypyrrole (Ppy) account further shift in wave length of nano composites to visible region as seen Fig. 3 of Table 2. The narrowing band gap energy of former nano composites Ni-ZnO/Ppy are due to delocalized Ni 3d states of doped Ni, intermix with O 2p of ZnO and Ppy of Nitrogen (N) 2p states of photo-catalyst ZnO. Such intermixing of doped metal 3d and ppy, N 2p states with energy states of photo-catalyst near valence band (VB) narrows down the band gap energy of photocatalyst [18]. Further reduction in the band gap of the Ni-ZnO/Ppy nano composites might be due to the synergetic effect of the two dopants; Ppy and Ni^{+2} generating electrons to reduce the band gaps [7,9,16,17].

3.4 Atomic Adsorption Spectroscopic (AAS) Analysis

Table-3 shows the observed data for AAS analysis for Ni-ZnO and Ni-ZnO/Ppy nano-composites photo-catalysts. Fairly good correlation (R^2 =0.998) to the AAS data of the synthesized photo catalysts was found from AAS calibrations curve linear equations, y = 0.013 x + 0.032; as shown in Fig. 4.Wherey is absorbance and x is the concentration of Nickel in ppm per samples.

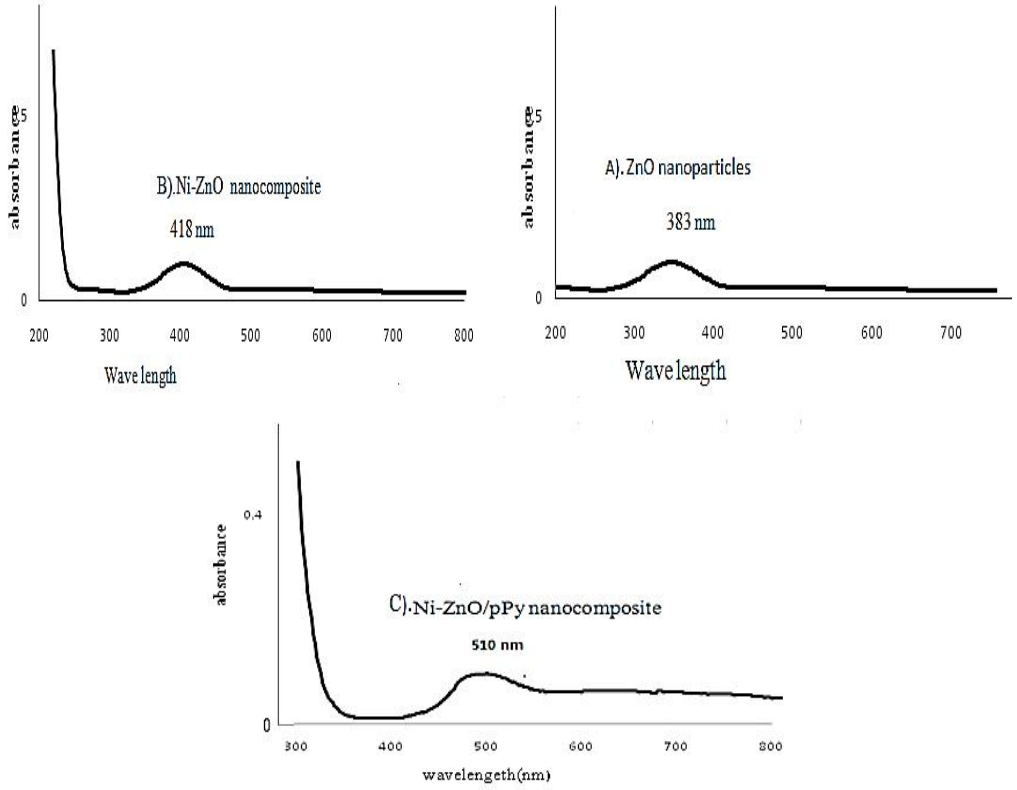


Fig. 3. UV-Visible diffuse absorption spectra and the absorption edge wavelength a) ZnO nano-particles, b) Ni-ZnO, c) Ni-ZnO/Ppy nano-composites

Table 3. Zinc concentration in the as-synthesized Ni-ZnO and Ni-ZnO/Ppy nano-composite

Photo-catalysts at (20 mg)	Element	Absorbance	Concentration (ppm)	% metal
Ni-ZnO	Ni	0.809	59.77	59.77
Ni-ZnO/Ppy	Ni	0.735	54.07	54.07

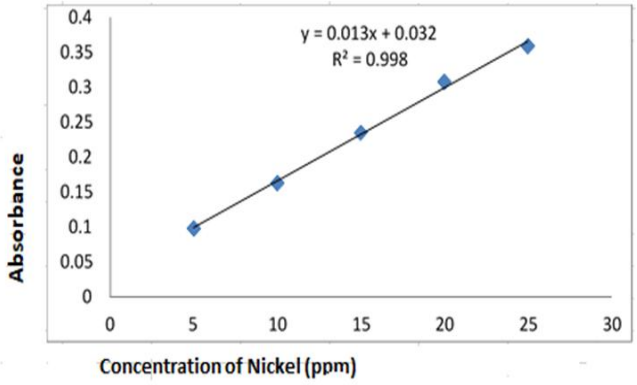
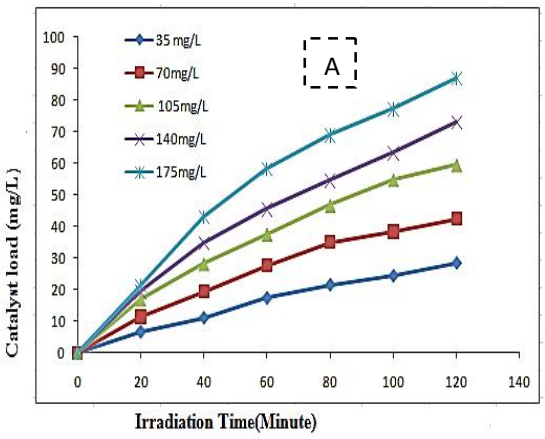


Fig. 4. AAS Calibration curve for Nickel

3.5 Factors Affecting Efficiency of Photo-catalysts

3.5.1 Effect of photo-catalyst load

Series of experiments were carried out to find the optimum amount by varying its amount the photo-catalysts (Ni-ZnO/Ppy) load from $^{-1}$to 175mgL^{-1}.To achieve highest photo-catalytic reaction rate, the optimum amount of the photo-catalysts was set to175mgL^{-1} as shown in Fig. 5. The observed dependence of reaction rate on the amount of photo-catalysts can be explained in terms of the availability of active sites at the adsorbent surface and the level of light penetration possibly through the reaction medium. With increasing the amount of photo-catalysts up to 175 mgL^{-1} the percent degradation dyes were increased with in increasing the adsorbent total surface area and thus, the number of active sites made available for the photo-catalytic reaction to take place very easily. However, increasing excess photo-catalysts (above the optimal load) may account for inducing more aggregation (particle–particle interactions) between photo-catalysts and also accounts for reducing photon penetration through the sample and reduces removal abilities of photo-catalysts. The degradation efficiency decreases after achieving an optimum value of photo-catalyst load [8,9]. Therefore, 175 mgL^{-1} of photo-catalyst was selected as the optimum amount of the Ni-ZnO/Ppy nano-composites photo-catalyst for the subsequent experiments.



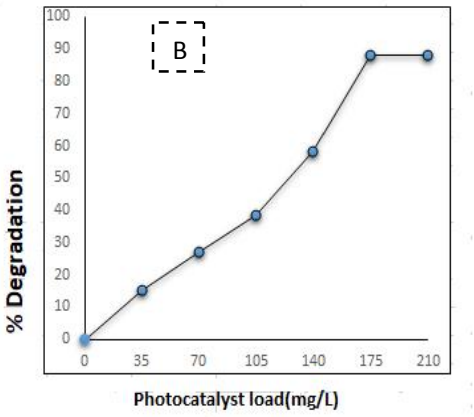


Fig. 5(A).Plot of catalyst load versus visible light irradiation times for degradation of p-nitrophenol at optimized parameters like (Dye = 16 mgL^{-1}, pH = 3),
Fig. 5 (B).Plot of percent degradation of p-nitrophenol versus Ni-ZnO/Ppy photo-catalyst load

3.5.2 Effect of pH

The pH of solutions greatly affects the rate of reaction taking place on a semiconductor surfaces due to its influences on the surface-charge-properties of the photo-catalysts. The effect of on pH on the photo-catalytic degradation rate of para-nitrophenol was investigated in the range of pH 3.0 –12.0. The photo-degradation efficiency of synthesized photo-catalysts was investigated on p-nitrophenol dye probe solution with an initial concentration of 16 mgL^{-1} using Ni-ZnO/Ppy nano-composites photo-catalyst (175 mgL^{-1}) show maximum degradation at acidic medium pH=3. The highest photo-catalytic degradation of p-nitrophenol was observed at pH = 3.0 as shown in Fig. 6.

3.5.3 Effect of initial dye concentration

The photo-degradation efficiency of synthesized photo-catalysts was investigated on p-nitrophenol dye probe solution with an initial concentration of 16 mgL^{-1} using Ni-ZnO/Ppy nano-composites photo-catalyst (175 mgL^{-1}) show maximum degradation at acidic medium pH = 3 as show in Fig. 7. As the dye concentration was increased degradation activity is kept constant and then little decrease in degradation activity of photo-catalysts was observed as similarly reported [8, 9]. At higher dye initial concentration, the approach of the radiation photons to the catalyst surface is hindered and screened off, thereby, reducing the photo-catalytic activity in the system [12]. Moreover, at the higher dye concentration, the number of collisions between dye molecules increases at the cost of required collisions between dye molecules and OH radical and therefore, the rate of reaction is retarded [13,22].

3.5.4 Photo-catalytic degradation study

Photo catalytic degradations of p-nitrophenol on synthesized photo catalysts, Ni-ZnO/Ppy was higher than Ni-ZnO and lesser in case of ZnO nano particles comparatively. This could be due to the slightly lower particle size of the former may accounts for high degradation activities than Ni-ZnO nano particle photo catalysts. In addition doping nickel and polypyrrole on surface of ZnO nano particles reduces the band gap energy modified once and also the both dopant nickel and polypyrrole under solar irradiation generates electrons to conduction band of ZnO which accounts best photocatalytic action of co-doped ZnO nano composites under solar irradiation. Thus, the π-electron of polypyrrole after receiving solar radiation due to lower band gap than ZnO particles, they generated electrons create new energy levels between conduction and valence bands of ZnO, thus, decreasing the band gap in zinc oxide[15]. The observed highest degradation of p-nitrophenol over Ni–ZnO/Ppy photo catalysts were due to dopants Ppy and Ni that can account for better performance co-doped photo catalysts.

3.5.5 Mechanism for degradation of dyes on synthesized photo-catalyst

Under visible light irradiation, both nickel and Ppy absorbed the visible light and induced excited-state electrons. The photo-excited electrons were injected into the conduction band of ZnO nano-particles, The electron in the conduction band (e^{-}CB) of ZnO nano-particle is transferred to molecular oxygen, leading to the formation of •OH and $•O_2^-$ radicals, which are active oxidizers capable of degrading organic pollutants and oxidized the dye contaminations as shown in proposed mechanism in Fig. 8.

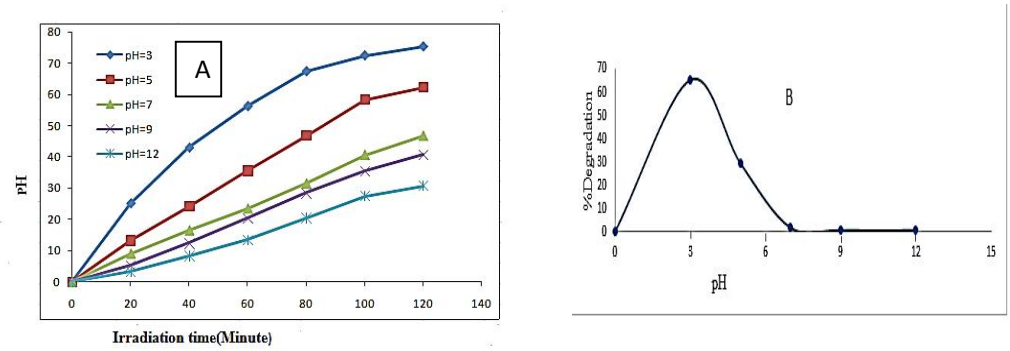


Fig. 6 (A). Plot of pH versus visible light irradiation time for degradation of p-nitrophenol
Fig. 6(B). Plot of percent degradation of p-nitrophenol as function of pH under visible light irradiation at fixed other parameters of (Dye = 16 mgL^{-1}, Ni-ZnO/Ppy = 175 mgL^{-1})

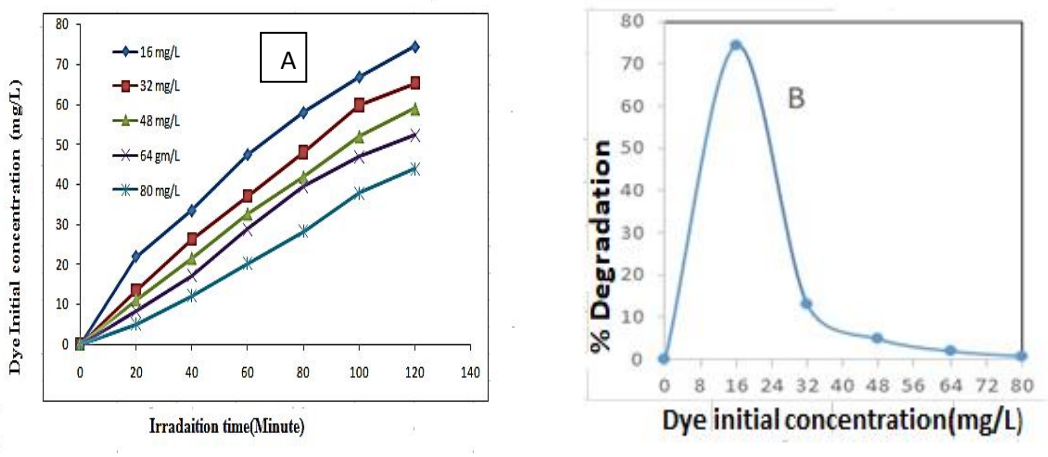


Fig. 7 (A). Plot of dye initial concentration versus visible light irradiation for degradation of para-nitrophenol

Fig. 7(B). Plots of percentage degradation of para-nitrophenol as a function of Dye initial concentration under Visible light irradiation (at constant Ni-ZnO/Ppy load of 175 mgL^{-1} and pH = 3)

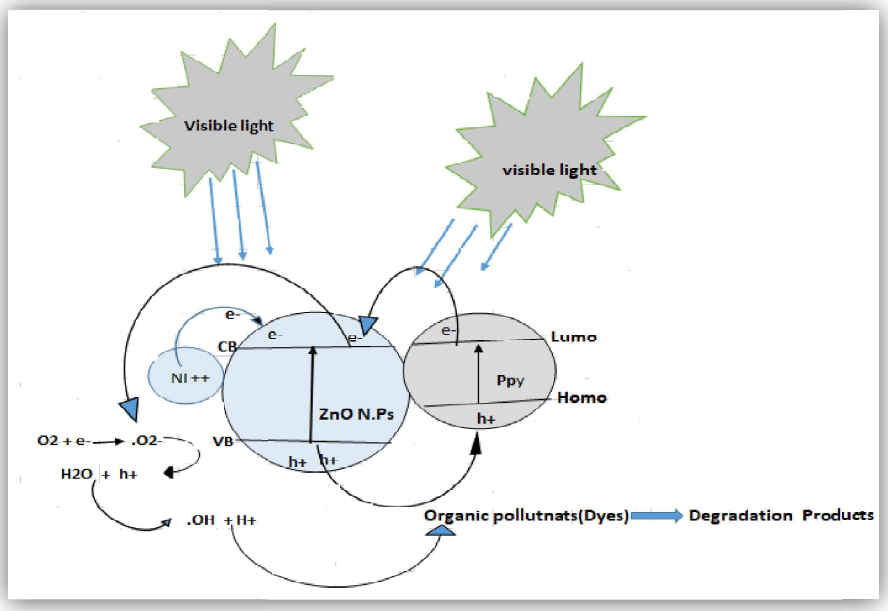


Fig. 8. Proposed mechanism of photo-catalytic activities of Ni-ZnO/Ppynano-composite under visible radiation in aqueous solution

The result shows that the percent photo-catalytic degradations of p-nitrophenolat 180 min contact time under visible radiation using ZnO, Ni-ZnO and Ni-/ZnO/Ppy nano-particles are 7.35 and 83.37 and 96.04%, respectively (Fig. 9). Higher photo-catalytic degradation activities Ni-ZnO/Ppy nano-particles photo-catalysts on p-nitrophenol dye is due to co-doping of ZnO, both metal doping by Ni and surface modification by conducting polymers, polypyrrole contributes positively, in enhancing the photo-catalytic degradation of the substrate p-nitrophenol [19-21]. Also, nickel traps the electrons at the conduction band and prevents electro-hole recombination [22].

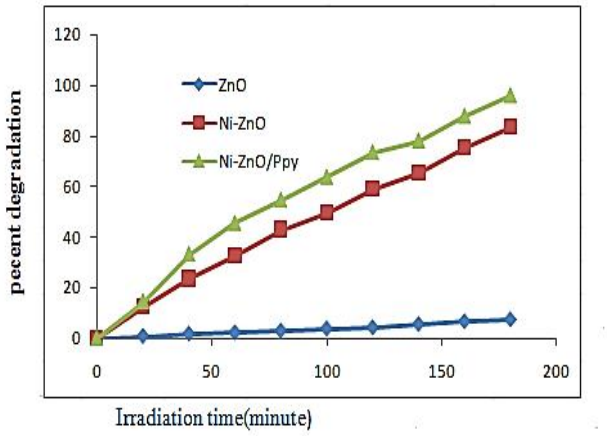


Fig. 9. Plot of percentage degradation of p-nitrophenol as a function of time under visible irradiations by photo-catalysts, ZnO, Ni-ZnO and Ni-ZnO/Ppy nano-composite

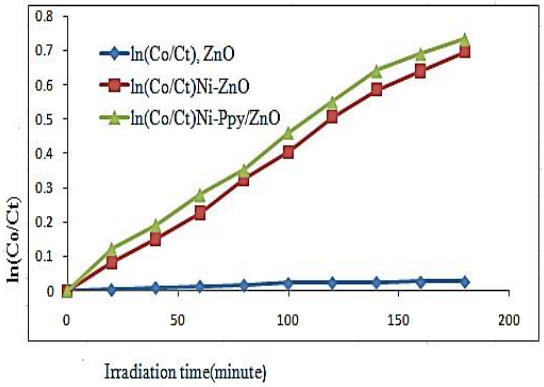


Fig. 10. Plot of $\ln(C_o/C_t)$ versus irradiation time for photo-catalytic degradation of 4-NPs using under Visible irradiation at (dye initial concentration = 16 mgL^{-1}, photo-catalyst load = 175 mgL^{-1}, pH = 3)

3.6 Kinetic Studies of Photo-catalytic Degradation

The adsorption rate constants of 4-NPs degradations under visible irradiation using Ni-ZnO and Ni-ZnO/Ppy photo-catalysts were obtained as; $4.33x10^{-4}$ and $5.39x10^{-3}$ min^{-1}, respectively as shown in Fig. 10. Fairly good correlations to the pseudo-first Order adsorption and photo-catalytic degradation reaction kinetics were obtained for all cases [18,21].

4. CONCLUSION

Present study concludes that doping of Ni in ZnO reduces e^- - h^+ recombination and implies high energy harvesting effect for photo-catalytic degradation of p-nitrophenol. 83.31and 96.04% of p-nitrophenol were degraded over Ni-ZnO and Ni-ZnO/Ppy nano-composite photo-catalyst under solar radiation respectively. Enhanced photo-catalytic activities of Ni-ZnO/Ppy a nano-particle is due to dopants, Nickel and polypyrrole under solar irradiation they generate electrons to conduction bands of ZnO nano particles and enhances photo-catalytic activities of Ni-ZnO/Ppy and photo-catalytic degradation of p-nitrophenol follows pseudo-first order reaction mechanism.

COMPETING INTERESTS

Authors declare that no competing interests exist among them.

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