

ORIGINAL RESEARCH PAPER

Photocatalytic degradation of Congo Red dye by using nano ZnO and Ni-Co-ZnO nanocomposites

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ABSTRACT

Photocatalysis has attracted significant attention as a potential issue for the degradation of toxic organic pollutants such as Congo Red. In this research spherical Pure ZnO nano particles and Ni-Co-ZnO nano composites ($Zn_{0.95}Ni_{0.04}Co_{0.01}O$, $Zn_{0.95}Ni_{0.025}Co_{0.025}O$ and $Zn_{0.95}Ni_{0.01}Co_{0.04}O$) have been synthesized by precipitation method. X-ray diffraction, Fourier transform Infra Red, field emission scanning electron microscopy, EDX and ICP analysis confirmed the structure and composition of the samples. The x-ray diffraction analysis (XRD) showed that all samples prepared were about Wurtzite structure and average crystal size of 17nm. Field emission scanning electron microscopy (FESEM) analysis revealed the spherical shape of all samples. The Fourier transform infrared spectroscopy (FT-IR) revealed bands at 435 cm⁻¹, 480 cm⁻¹ and 525 cm⁻¹ are related to Zn-O bonds, related to the stretching vibrating bonds of ZnO. The results illustrated the Ni and Co ions substituted the Zn ions in ZnO crystal lattice successfully. The results showed that some of doped Ni-Co ZnO exhibit enhanced photocatalytic activity, as compared to pure ZnO. Kinetic of de-colorization process for all photo-catalysts followed pseudo first order. In degradation process The best photocatalyst was ($Zn_{0.95}Ni_{0.04}Co_{0.01}O$).

Keywords: Ni-Co-ZnO Nano Composite, Photocatalytic Activity, Precipitation Method, UV-C Light

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INTRODUCTION

In recent years, investigators attempt to control the contaminant caused by industrial dyes, or antibiotics by photo oxidation activity of semiconductors which are efficient and environmentally friendly [1, 2]. Most desirable semiconductors are ZnSe, CdS, TiO₂, ZnS, and ZnO. Meanwhile ZnO is an economically photocatalyst and has shown higher efficiency than others[2], additionally zinc oxide is stable in both acidic and alkaline environments[3,4]

Generally,when ZnO is irradiated by UV light with proper or higher than the band gap energy, yields an electron-hole pair which migrate to the surface of ZnO and reacts with water and oxygen

to generate reactive hydroxyl and superoxide anion radicals to oxidize and minerals the dye molecules [23].

Although ZnO has high photo-sensitization, the short lifetime of produced electron-hole is an unfavorable factor which restricts the appliance of this semiconductor [5, 6, and 2]. On the other hand wide band gap of ZnO makes it appropriate for UV-light absorption [7] while UV radiation is only 3-5 percent of the sun's light, hence reducing the band gap of ZnO is valuable for utilizing visible light [8]. Many researchers endeavor to modify the optical properties of ZnO and rectify mentioned problems by engineering band gap [9]. In this regard addition of single or multiple elements or

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transitional metals as impurity to ZnO Lattice has been effective [7, 10-17]. Cationic dopant such as Fe, Co, Ni, Nd, Ta, Ce

have attracted a lot of attention on improving the photocatalytic activity due to their unoccupied orbitals [1,3, 18-21] . But less study has been focused on Ni and Co addition simultaneously [22]. Though in previous works, incorporation of Ni and Co ions in structure of ZnO has been studied, no investigation conducted to find the optimum ratio of nickel, cobalt and zinc ions in order to have Ni-Co-ZnO nano composite with as high photo catalytic activation as possible.

In this work we synthesized ZnO nano particles and Ni-CO-ZnO nano composites with different concentration using co-precipitation method. The morphology and structure of synthesized samples were characterized by XRD, FT-IR, ICP, EDX and SEM. The photocatalytic activity of all samples was tested by decolorization of Congo red solution under UV-light .The band gap, specific area and reusability of the best photocatalyst was investigated.

EXPERIMENTAL PROCEDURES

Materials

The precursors in experimental stages which were purchased from Sigma Aldrich included: Zinc Nitrate hexa hydrate, Nickel (II) nitrate hexahydrate, Cobalt(II) nitrate hexahydrate, Sodium hydroxide, Poly (vinyl alcohol), Ethanol, Hydrochloric acid and Congo red.

Pure ZnO nano particles synthesis

ZnO nano particles were synthesized using precipitation method. The brief synthesis method is as follows: 6.7 mmol Zinc Nitrate hexa hydrate and 75 cc Ethanol were added to 2 g PVA in 50 ml H₂O. Then the NaOH 0.1 N was added drop wise in to above solution to adjust pH in 12. In order to complete reaction stirring was continued for 5 hours at room temperature 30°C. The resulted precipitant was filtered and washed with distilled water for several times and afterward was dried at 100°C for 2 hours. The powder was calcinated at 600°C for 4 hours.

Ni-Co-ZnO nano composites synthesis

To prepare Zn_{0.95}Ni_{0.04}Co_{0.01}O, Zn_{0.95}Ni_{0.025}Co_{0.025}O and Zn_{0.95}Ni_{0.01}Co_{0.04}O samples respectively 0.282 mmol, 0.176 mmol, 0.071 mmol Nickel Nitrate hexa Hydrate and 0.071 mmol, 0.176mmol,

0.282mmol Cobalt Nitrate hexa Hydrate were added to the beaker in the step of adding Zinc Nitrate hexa Hydrate and subsequently similar processes took place.

Characterization

The morphology of synthesized nano particles was studied with scanning electron microscope (SEM) (KYKY SBC-12 EM3200) which was equipped with EDX. X-ray diffractometer (Philips PW 1730) used for determination the size and structure of produced crystals and probable imperfections. The monochromatic wavelength was 1.54Å and the refractory pattern for all samples was recorded in the range of 20°-80°. The results of FT-IR analysis were obtained by using spectrometer Thermo Nicolet Nexus 870 in the range of 400-4000 Cm⁻¹. Monitoring the changes of absorption spectra of dye solutions was performed with UV-Vis spectrometer CARY 100 Bio. For recording the reflectance percent of nano particles in the range of 200-700 nm, Avantes spectrometer (Ava spes-2048- TEC) was operated. Zeta potential of samples was determined by Zeta potential meter (Malvern ZEN 3600) For measuring the Specific area of samples BET single point surface area analyzer (BELSORP) was used. Amount of amount of metal ions was measured using ICP analysis (PerkinElmer® Optima 7300 DV).

Measurement of photocatalytic activity

The photocatalytic reactions were performed using a photoreactor in which four UV-C lamps with lambda max= 254 nm, manufactured by Holand (UV-C, 6 W, PHILIPS) were operated. The UV lamps were located in four directions at a distance of 10 to 15 cm from the vessel. All of the experiments were carried out at ambient temperature at 30°C and certain amounts of catalysts were added to 50 ml Congo red solution with proper concentration. For adjusting pH values, NaOH 0.01 N and HCl 0.01 N solutions were added and sample container was stirred in dark for 30 min to nail suspension in which the adsorption-desorption processes of Congo red dye and photocatalyst completed. The reaction started using UV light irradiation and every 10 min 5 ml of sample was centrifuged at 3000 rpm for removing catalyst. The transparent solution was used for monitoring the changed of characteristic absorption peak of Congo red with lambda max at 497 nm by UV- Vis spectrophotometer. The concentration

values were obtained using calibration curve of concentration versus absorption. For calculating the photo decolorization percentage the equation of % decolorization = $\frac{C-C_0}{C_0} \times 100$ was used [24].

RESULT AND DISCUSSION

XRD

The XRD patterns of ZnO, Zn_{0.95}Ni_{0.04}Co_{0.01}O, Zn_{0.95}Ni_{0.025}Co_{0.025}O and Zn_{0.95}Ni_{0.01}Co_{0.04}O are shown in Fig. 1. The obtained peaks of ZnO and Ni-Co-ZnO are matched by the peaks of Wurtzite structure of ZnO with standard ICDD card no 98-006-5172 and 01-075-0576. The substitution of Nickel and Cobalt ions did not appear altering the crystal structure and the peaks are at the same position as ZnO, but the position of peaks are shifted to higher angles due to ionic radius of Nickel and Cobalt ions are shorter than that of Zinc ions, that seems to have resulted in slight decrease in the lattice parameter of the composites as it is shown in Table 1 [28-30]. The lattice parameters (a and c) of pure ZnO and Ni-Co-ZnO nano composites can be calculated by the following equation [44]:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + kh + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Where d is the crystal planes distance and (h,k,l)

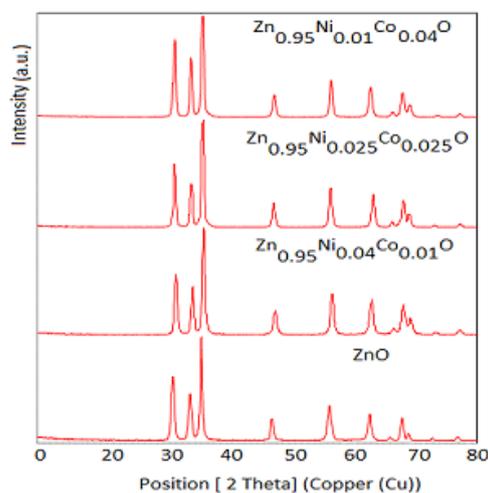


Fig. 1. XRD pattern of ZnO and Ni-Co-ZnO samples

are Miller indices. The crystalline size of particles can be calculated by Scherer formula [26,27].

FT- IR

The FT-IR spectra of the ZnO, Zn_{0.95}Ni_{0.04}Co_{0.01}O, Zn_{0.95}Ni_{0.025}Co_{0.025}O and Zn_{0.95}Ni_{0.01}Co_{0.04}O samples are presented in Fig. 2. The absorption peaks at 435 cm⁻¹, 480 cm⁻¹ and 525 cm⁻¹ are related to Zn-O bond and the shift of this functional peak is due to formation of Zn-O-Ni and Zn-O-Co bonds [26, 31-34]. No band shows the presence of nitrate means calcinations at 600°C for 4 hours have been suitable for removing it. The bands at 3440 cm⁻¹ and 1625 cm⁻¹ are related to stretching and bending vibrations of H₂O molecules and the band found at 2340 cm⁻¹ refers to stretching vibration of atmospheric CO₂ bands [34, 35]. The lack of additional bands represents the substitution of all Nickel and Cobalt ions in the structure of ZnO [36].

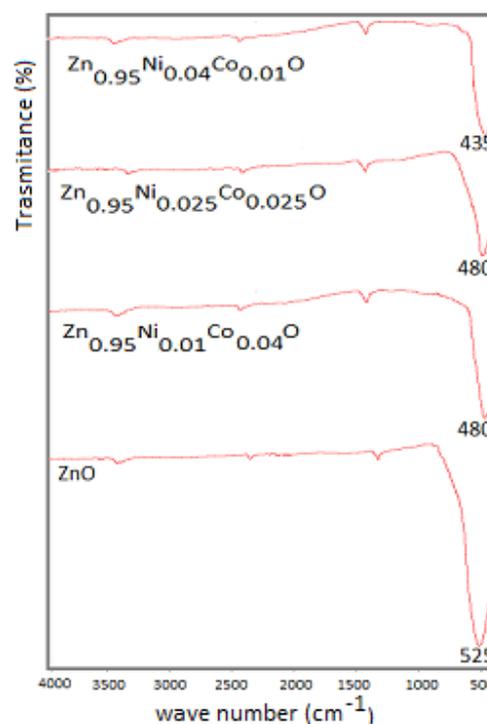


Fig. 2. FT-IR spectra of ZnO nano particle and Ni-Co-ZnO nano composites

Table 1. Calculated parameters related to XRD pattern of ZnO and Ni-Co-ZnO samples

| sample | Lattice parameter value [Å] | | Volume v(Å) ³ | Average crystal size D (nm) |
|--|-----------------------------|--------------------|--------------------------|-----------------------------|
| | a=b ₍₁₀₀₎ | c ₍₀₀₂₎ | | |
| ZnO | 3.2854 | 5.3159 | 3.2854 | 23 |
| Zn _{0.95} Ni _{0.01} Co _{0.04} O | 3.2467 | 5.19964 | 3.2467 | 17 |
| Zn _{0.95} Ni _{0.025} Co _{0.025} O | 3.2236 | 5.1590 | 3.2236 | 17 |
| Zn _{0.95} Ni _{0.04} Co _{0.01} O | 3.2174 | 5.5.1274 | 3.2174 | 17 |

SEM

Fig. 3 shows SEM images of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$, $Zn_{0.95}Ni_{0.025}Co_{0.025}O$ and $Zn_{0.95}Ni_{0.01}Co_{0.04}O$ nano composites. The morphology and size of spherical Ni-Co-ZnO nano composites with various Ni and Co contents are nearly the same with the size of 45.9-59.4 nm. It is clear that the method of synthesizing samples has almost restricted the aggregation, so the applicable factors such as pH, temperature and time of reaction, concentration of solution and surfactant and type of it and doze of inlet impurities were appropriate.[43]

EDX and ICP

The elemental analysis of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ was determined using EDX as shown in Fig. 4. The presence

of Zn, Co, Ni and O ions is confirmed and obviously there is no additional element in the network structure. In EDX pattern of sample, the peaks at 9.6 kev, 8.7 kev and 1 kev are related to Zinc, the peaks at 8.3 kev, 7.4 kev and 0.85 kev are related to Nickel, the peaks at 7.6 kev, 6.9 kev and 1.3 kev are related to Cobalt and the peak at 0.5 kev is related to Oxygen.

In order to measure the concentration of Nickel, Cobalt and Zinc ions in synthsized samples and ICP analysis was used and regarding to Table 2 there is a good correspondence between experimental and theoretical values.

Photocatalytic activity

For optimizing conditions of photocatalytic decolorization of Congo red a series of experiments

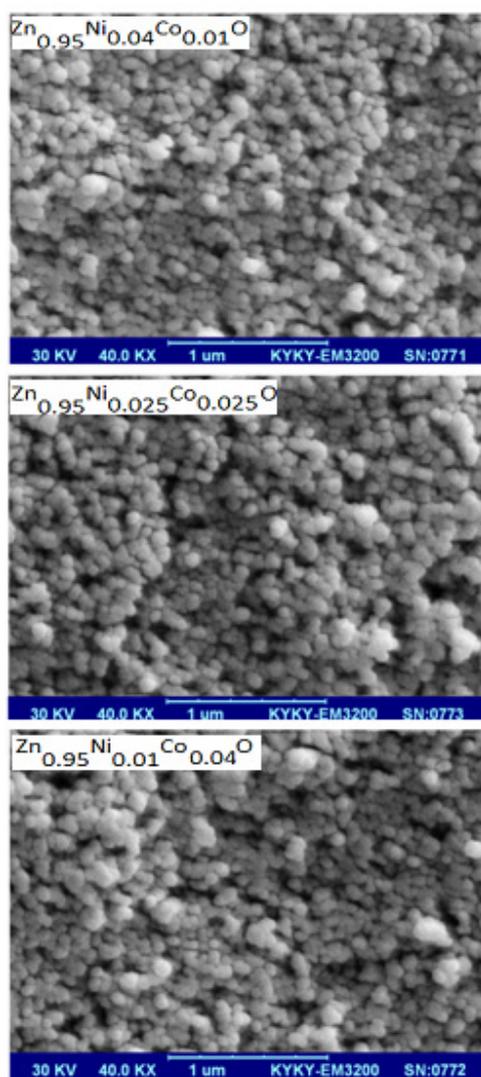


Fig. 3. SEM images of Ni-Co-ZnO nano composites

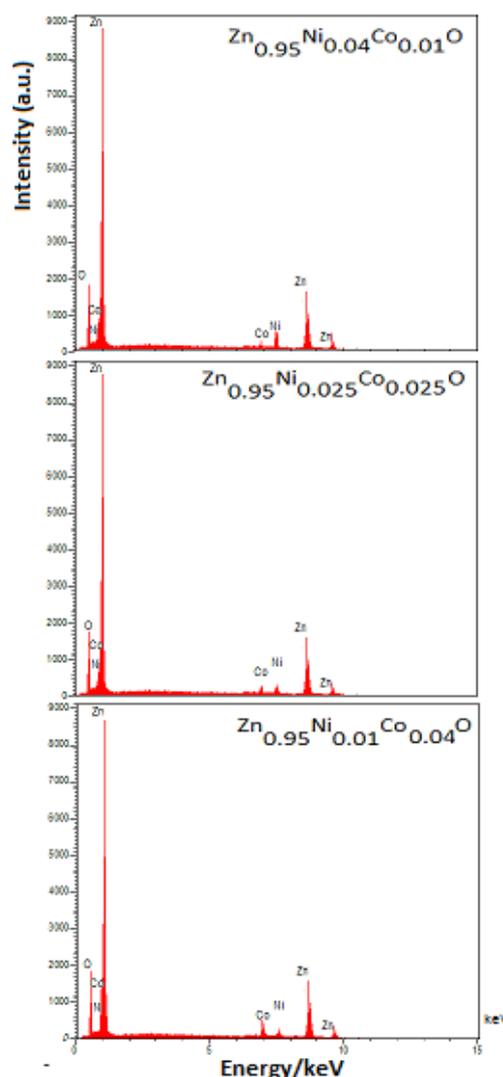


Fig. 4. EDX patterns of Ni-Co-ZnO nano composites

were conducted. In this regard the effect of initial concentration of Congo red, pH of dye solution and amount of photocatalysts were investigated.

Effect of initial concentration of Congo red

Fig. 5 shows the effect of initial Congo red concentration on photocatalytic decolorization rate of dye in the range of 10-30 ppm. As it is obvious, decolorization rate is inversely affected by initial concentration of Congo red because by increasing initial amount of dye because penetration of light reduces and the number of Congo red molecules

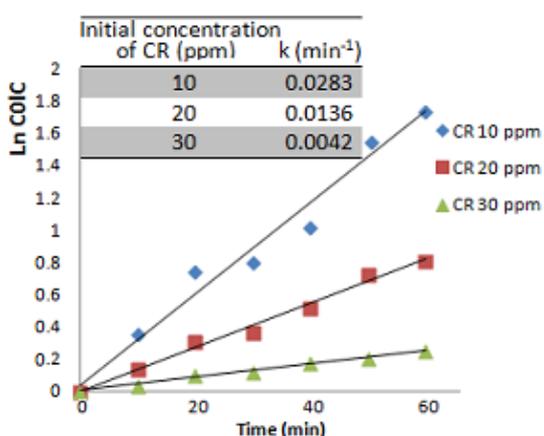


Fig. 5. Effect of initial amount of Congo red on photodecolorization activity of ZnO (0.6 g/l) under UV-C light irradiation

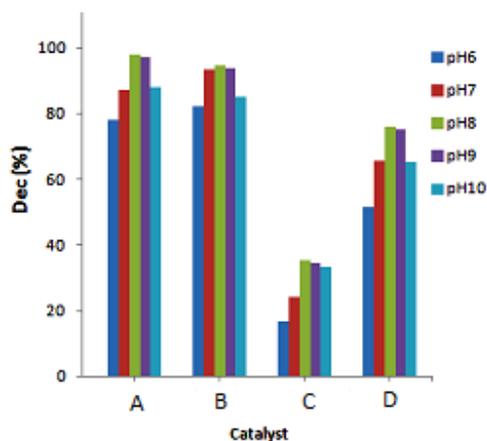


Fig. 6. Effect of pH changes on decolorization activity of 0.5 g/l photocatalysts (A= $Zn_{0.95}Ni_{0.04}Co_{0.01}O$, B= $Zn_{0.95}Ni_{0.025}Co_{0.025}O$, C= $Zn_{0.95}Ni_{0.01}Co_{0.04}O$ and D= ZnO) under UV-C light irradiation (Congo red 10 ppm).

which are absorbed on the surface of semiconductor increases so generation of OH^{\bullet} groups which act as active reagent for mineralization of organic dye, reduces [37]. Also such conditions lead to hydrophobicity of aromatic rings in dye molecules due to formation of dimer or higher molecules and the efficiency of decolorization decreases [38].

Effect of pH

To find the optimum pH for decolorization of Congo red, the pH values were changed in the range of 6-10 while other conditions such as initial Congo red concentration, dose of photocatalyst and temperature were kept constant. According to Fig. 6 in all cases by increasing pH from 6 to 8 the decolorization percent raised and after pH=8 decolorization percent decreased. Hence pH=8 was chosen as the best pH. Congo red is an anionic dye which easily absorbs on the surface of semiconductors which have been positively charged. Among the produced photocatalysts, the zeta potential of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ as the selected sample was measured at the optimum pH. As is seen in Fig. 7, at pH= 8 the value of zeta potential of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ is +17 mev. In previous researches zeta potential values of ZnO were reported as $\approx +18$ mev and +16 mev for pH 8 [39,40]. Clearly OH^- anion radicals are produced in pH=8 and with considering Zeta potential, hinder agglomeration of particles and adsorb Congo red on the surface of catalyst.

Effect of Photo catalyst concentration

For determining the optimum dosage of photocatalysts, decolorization of 10 ppm Congo

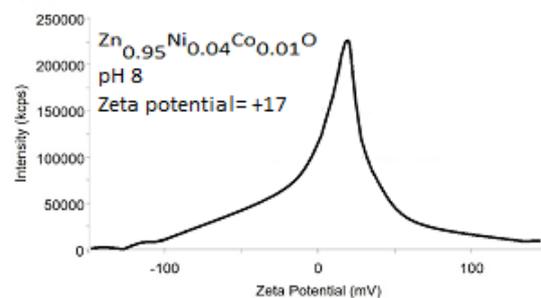


Fig. 7. Zeta potential values of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ at pH 8

Table 2. The ICP analysis results of Ni-Co-ZnO analysis

| Sample | Mole percent of metal ions in synthesized sample | | |
|----------------------------------|--|-----------|-----------|
| | Zinc (mol%) | Ni (mol%) | Co (mol%) |
| $Zn_{0.95}Ni_{0.01}Co_{0.04}O$ | 95.11 | 1.05 | 3.84 |
| $Zn_{0.95}Ni_{0.025}Co_{0.025}O$ | 95.06 | 2.49 | 2.45 |
| $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ | 95.01 | 4.03 | 0.96 |

red solution was investigated under UV light irradiation while pH of solution was fixed at 8 and exposed to UV light an hour in 30 °C. The photocatalysts concentration varied from 0.3 g/l to 0.7 g/l. According to the results in Fig. 8 the optimum amount for ZnO and Zn_{0.95}Ni_{0.01}Co_{0.04}O photocatalysts was 0.6 g/l while this value in the case of Zn_{0.95}Ni_{0.025}Co_{0.025}O and Zn_{0.95}Ni_{0.04}Co_{0.01}O photocatalysts decreased to 0.5 g/l so the second group is more economically affordable. By over dosing the photo catalysts, the efficiency of decolorization decreases due to aggregation of particles and shielding effect, decrease effective surface area and light scattering .It should be noted that the kind of photocatalyst and initial concentration of dye are also important [37,41]. Similar doze of applied ZnO in previous researches has been reported before [6, 38]

The photocatalytic activity of ZnO nano particles and Ni-Co-ZnO nano composites

To find the best ratio of doped ions in Ni-Co-ZnO nano composite the photodecolorization activity of ZnO, Zn_{0.95}Ni_{0.04}Co_{0.01}O, Zn_{0.95}Ni_{0.025}Co_{0.025}O and Zn_{0.95}Ni_{0.01}Co_{0.04}O samples was investigated in the optimum pH, optimum doze of each catalyst and 10 ppm Congo red concentration. Fig. 9 illustrates the UV-Vis spectra changes of Congo red solution. The decrease of the absorption peak intensities of the Congo red showed the degradation of dye molecules by photocatalysts under UV- light. As can be seen in Fig. 9 the disappearance of the characteristic peak of Congo red after 120 min under UV-light showed that Congo red has been decolorized completely by

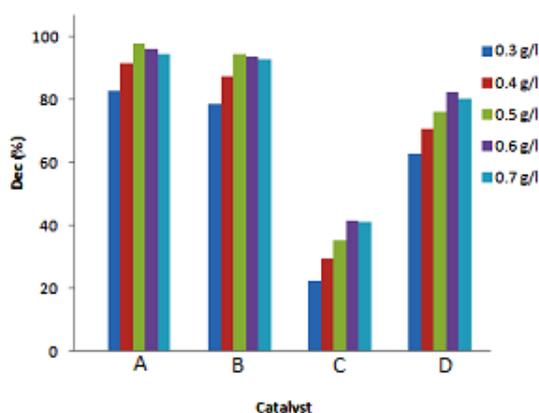


Fig. 8. Effect of concentration changes of photocatalysts (A=Zn_{0.95}Ni_{0.04}Co_{0.01}O, B=Zn_{0.95}Ni_{0.025}Co_{0.025}O, C= Zn_{0.95}Ni_{0.01}Co_{0.04}O and D= ZnO) on decolorization activity of them at pH8, and under UV-C light irradiation (Congo red 10 ppm).

pure ZnO while decolorization time decreased to 90 min and 70 min in the case of Zn_{0.95}Ni_{0.025}Co_{0.025}O and Zn_{0.95}Ni_{0.04}Co_{0.01}O photocatalysts, whereas the decolorization efficiency of Zn_{0.95}Ni_{0.01}Co_{0.04}O is only 62% after 120 min. so the order of photocatalytic activities was Zn_{0.95}Ni_{0.04}Co_{0.01}O > Zn_{0.95}Ni_{0.025}Co_{0.025}O > ZnO > Zn_{0.95}Ni_{0.01}Co_{0.04}O .

Kinetics of Congo red photodecolorization

To study the photodecolorization activity of synthesized samples, the first order rate equation was used [25]. The rate equation is given by the expression:

$$\ln(C_0/C) = kt$$

k= rate constant

C₀= initial concentration of Congo red

C= concentration of Congo red at time t

Fig. 10 shows the linear plots of Ln C₀/C against time for all catalysts and the photocatalytic activity of them under UV light can be evaluated by

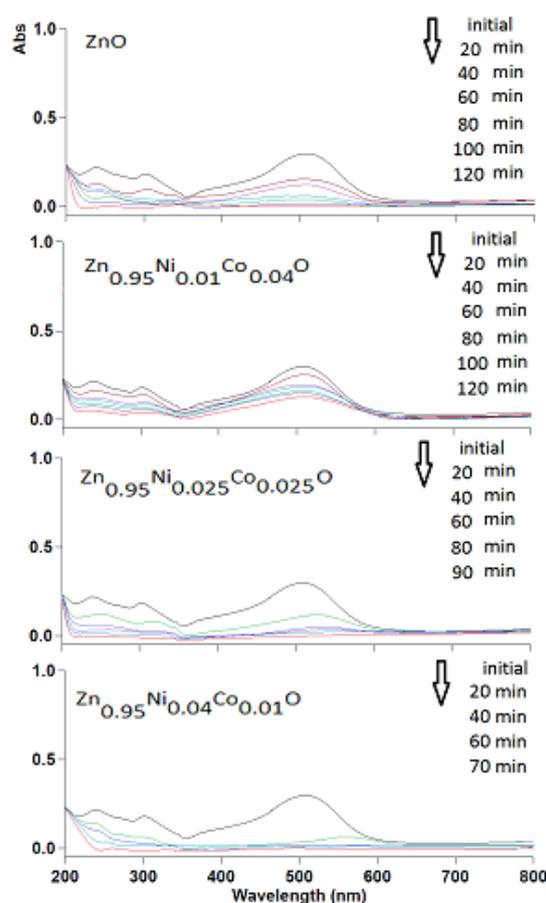


Fig. 9. Decolorization trend of Congo red 10 ppm in presence of ZnO and Ni-Co-ZnO photocatalysts under UV-C light irradiation

comparing the rate constants K. K values are the slope of the linear regressions and summarized in Table 3. The value R² of linear fitting for all of synthesized photocatalysts is more than 99%. Zn_{0.95}Ni_{0.04}Co_{0.01}O nano composite is evidently the best photocatalyst among synthesized samples so subsequent studies were conducted by using this superior photocatalyst.

Photostability of Zn_{0.95}Ni_{0.04}Co_{0.01}O nano composite

Photostability of Zn_{0.95}Ni_{0.04}Co_{0.01}O nano composite was investigated by reusing it, in other

Table 3. Apparent constant rate of synthesized photocatalysts for Congo red 10ppm decolorization at pH 8 and optimum doze of photocatalyst under UV light irradiation (0.6 g/l of ZnO and Zn_{0.95}Ni_{0.01}Co_{0.04}O, 0.5 g/l of Zn_{0.95}Ni_{0.025}Co_{0.025}O and Zn_{0.95}Ni_{0.04}Co_{0.01}O)

| Sample | k _{app} (min ⁻¹) | R ² |
|--|---------------------------------------|----------------|
| ZnO | 0.0289 | 0.99 |
| Zn _{0.95} Ni _{0.04} Co _{0.01} O | 0.0647 | 0.99 |
| Zn _{0.95} Ni _{0.025} Co _{0.025} O | 0.0457 | 0.99 |
| Zn _{0.95} Ni _{0.01} Co _{0.04} O | 00075 | 0.99 |

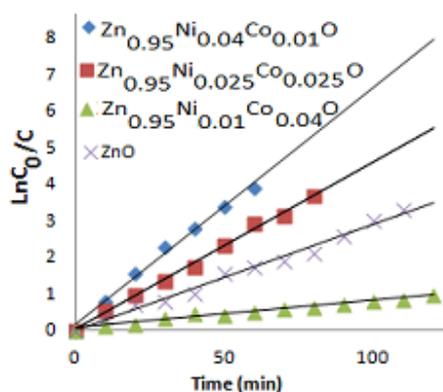


Fig. 10. LnC₀/C plots of Congo red solution against time under UV light irradiation, initial Congo red 10ppm , pH 8 , and optimum concentrations of ZnO and Ni-Co-ZnO

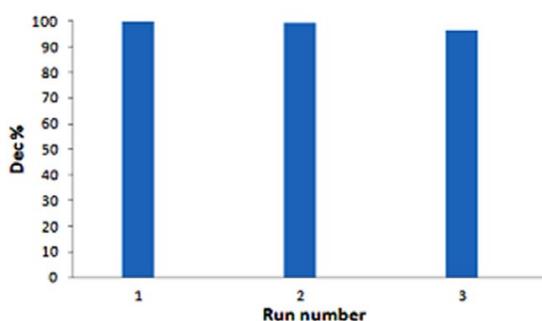


Fig. 11. Reusability of Zn_{0.95}Ni_{0.04}Co_{0.01}O with initial concentration of 0.5 g/l in photodecolorization of Congo red 10 ppm at pH8 under UV-C light irradiation

word after applying Zn_{0.95}Ni_{0.04}Co_{0.01}O in color removal of Congo red 10 ppm at pH 8, it was filtered and dried at 100 °c after several times washing with distilled water and recycled to photodecolorization process under UV light and with the same previous conditions. According to Fig. 11 after three times recycling, process efficiency was 96% and slight decrease of photocatalytic activity can be related to Sample waste during washing. High photostability of Zn_{0.95}Ni_{0.04}Co_{0.01}O indicate that charge carriers have been separated efficiently [42]. Finally the photocatalyst was studied by FT-IR analysis. Fig. 12 shows the indicator peak of Zn-O didn't change in terms of location and intensity. FT-IR analysis was applied by some researchers before [8].

DRS

Investigating optical properties of Zn_{0.95}Ni_{0.04}Co_{0.01}O and ZnO was carried out by diffuse reflectance spectroscopy in the range of 200-700nm at room temperature. According to Fig. 13 Pure ZnO shows reflectance about 80% but for Zn_{0.95}Ni_{0.04}Co_{0.01}O reflectance reduces. The Band

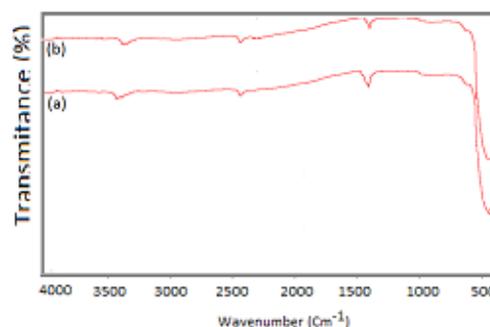


Fig. 12. FT-IR spectra of Zn_{0.95}Ni_{0.04}Co_{0.01}O (a) after synthesis, (b) after three times recovery of the photocatalytic process

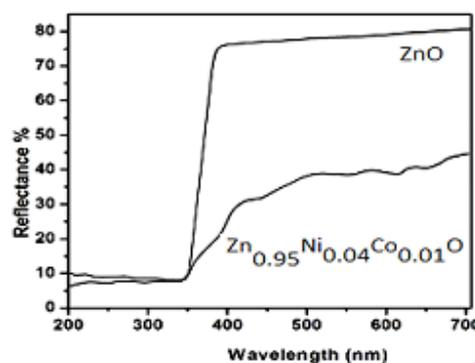


Fig. 13. Diffuse reflectance spectra of Zn_{0.95}Ni_{0.04}Co_{0.01}O nano composite in compare with pure nano ZnO

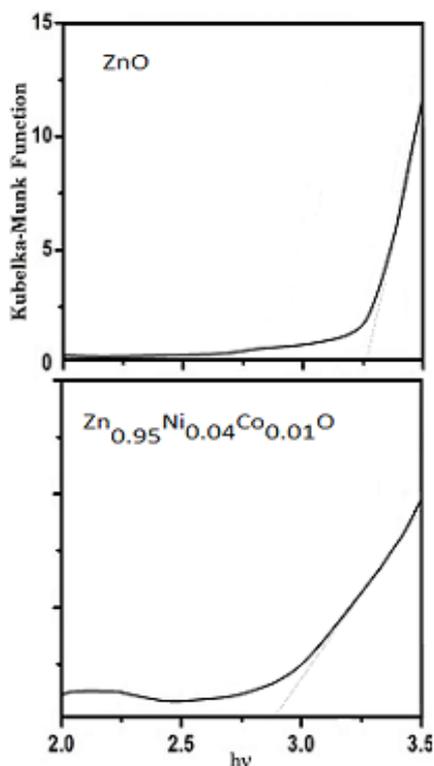


Fig. 14. The Tauc Plot of $\text{Zn}_{0.95}\text{Ni}_{0.04}\text{Co}_{0.01}\text{O}$ nano composite and pure nano ZnO

edge absorption of ZnO is at 380 nm (3.26 eV) and this value obviously shifts to longer wave length for $\text{Zn}_{0.95}\text{Ni}_{0.04}\text{Co}_{0.01}\text{O}$. Red shift of Band edge absorption is a good reason for Zn^{2+} substitution by doped ions [45-47]. For calculating the band gap energy of samples Kubelka-Munk Tauc function, $F(R)$, was applied [48]. As it is shown in Fig. 14, $F(R)^2$ was plotted against the energy and the band gap values 3.26 eV and 2.88 eV were obtained by extrapolating the linear part of curve respectively for ZnO and $\text{Zn}_{0.95}\text{Ni}_{0.04}\text{Co}_{0.01}\text{O}$ samples. In the previous research on single transitional metals substitution in ZnO structure, the interaction of band electrons and electrons which are localized in d orbitals of doped ions, or in other word sp-d exchange interaction, was interpreted as a justification for creation of new levels of energy and consequently reduction of the band gap [49-51]. Now in present work It seems that existence of two kinds of doped ions has a synergic effect on producing new levels of energy due to hybridation of half-filled d orbitals of Nickel and Cobalt ions with each other and with orbitals of host ions and the generated levels of energy has the role of impurities which decreases band gap.

BET

For assessing the Specific area of ZnO and $\text{Zn}_{0.95}\text{Ni}_{0.04}\text{Co}_{0.01}\text{O}$ samples BET analysis was applied. The results showed by entering the Co^{2+} and Ni^{2+} in the structure of ZnO surface area ranges from $18 \text{ m}^2/\text{g}$ to $29 \text{ m}^2/\text{g}$ due to smaller size of Nickel and Cobalt ions in compare with Zn^{2+} . Similar results have been reported before [52-56]. Since the adsorption on the surface of photocatalyst is one of the important steps in the photocatalytic processing increasing of surface area can lead to improvement of photocatalytic activity hence the results are suitable.

CONCLUSION

Pure ZnO, $\text{Zn}_{0.95}\text{Ni}_{0.04}\text{Co}_{0.01}\text{O}$, $\text{Zn}_{0.95}\text{Ni}_{0.025}\text{Co}_{0.025}\text{O}$ and $\text{Zn}_{0.95}\text{Ni}_{0.01}\text{Co}_{0.04}\text{O}$ nano composites were synthesized through precipitation process. XRD, FT-IR confirmed the substitution of guest ions in the ZnO lattice and ICP analysis confirmed the correspondence between theoretical and experimental of metal ions. Photocatalytic activity was investigated by decolorization of Congo red under UV-C light. $\text{Zn}_{0.95}\text{Ni}_{0.04}\text{Co}_{0.01}\text{O}$ nano composite showed the highest photocatalytic activity among all samples. High efficiency of reusing mentioned photocatalyst after three times recovery as well as lack of structure change which was affirmed using FT-IR analysis proved the good separation of charge carriers in it. SEM analysis showed the spherical and uniform morphology for this nano composite. DRS and BET analysis respectively confirmed the decreasing of band gap and increasing of surface area in $\text{Zn}_{0.95}\text{Ni}_{0.04}\text{Co}_{0.01}\text{O}$ compared with ZnO.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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