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ORIGINAL RESEARCH PAPER

Improving photocatalytic properties of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ modified by PANI

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ABSTRACT

In this research, preparation of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (polyaniline) (0.5%, 1% and 1.5% PANI) nano composites was performed by synthesis of pure polyaniline and adsorption of resulted organic chains on the structure of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nano particles. The as-prepared samples was characterized by X-ray diffraction (XRD), fourier transform infrared (FTIR), field emission scanning electron microscopy (FESEM) and BET techniques. According to the X-ray diffraction analysis, pure PANI has a semi crystalline structure while all of the composites showed the characteristic peaks of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ with hexagonal wurtzite structure. The FTIR spectroscopy approved the interactions of PANI chains and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nano particles. Field emission scanning electron microscopy analysis revealed amorphous structure of PANI and the spherical shape of nano composite. The BET analysis attributed the largest specific surface area of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1% PANI) nano composite. The photocatalytic results showed that the dye can be effectively decolorized by $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1% PANI) nano composite. The enhancement of photocatalytic performance is due to the decrease of specific surface area and the higher separation efficiency of photo-induced electron-hole pairs.

Keywords: *BET Analysis, Nano Composite, Photocatalytic Activity, Polyaniline*

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INTRODUCTION

Zinc oxide (ZnO), one of the inorganic semiconductors which has favorite traits such as chemical and thermal stability, low cost and environment friendly [1]. The photocatalytic activity of these compounds in the presence of both UV and visible lights has been extensively investigated in degradation of toxic water pollutants caused by textile dyes [2]. When ZnO is exposed to light with equals or higher energy than its band gap, yields electron- hole pairs which react with water and generate hydroxyl and superoxide anion radicals and the supplied radicals are responsible for the color removal. [3]

Some of ZnO deficiencies such as the short lifetime of producing electron-hole and high band gap which is suitable for absorption of UV light (while UV light is about 5% of solar energy) was modified by entrance of single or multiple elements or transitional metals as an impurity of ZnO lattice. In order to speed up the photocatalytic activity of these doped compounds or composites, researchers focused on Synergistic or complementary properties which are raised from combining the inorganic compounds with organic polymers [5-7]. Polyaniline is a stable, environmentally and eco-friendly polymer with high conductivity, light weight, flexibility, facile fabrication and low cost which can act as a stabilizer or surface capping agents when combined with semiconductors [8-

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12]. Due to the mentioned preferable characteristics, the ZnO/PANI nano composite has been studied by several investigators [13]. But no study has been focused on hybridation of polyaniline with modified M-M′-ZnO nano particles (M and M′= transitional metals).

In this work, we synthesized pure polyaniline by in situ polymerization technique and afterward by adsorbing the PANI chains on the structure of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nano particles; $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ / PANI nano composites were prepared with different concentration of polyaniline. The morphology, structure and specific surface area of synthesized samples was characterized by XRD, FTIR, FESEM and BET. The photocatalytic activity of all samples was studied by decolorization of solution under UV-light.

MATERIALS AND METHODS

The precursors were purchased from Sigma-Aldrich Company: Aniline, ammonium peroxydisulfate, hydrochloric acid, sodium hydroxide, tetrahydrofuran (THF) (98%). The $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nano powder was obtained in our previous work (particle size: 45.9-59.4 nm) [14].

Synthesis of pure PANI

1.8 mL aniline was dissolved in 100 mL of 0.1 M hydrochloric acid. Then, 2.05 g ammonium persulfate was dissolved in 90 mL of 0.1 M hydrochloric acid and the obtained solution was slowly added into the above mixture under 18 hours stirring at 0–4°C. After completion of polymerization, the precipitant was filtered and washed several times, respectively with distilled water, 0.1M hydrochloric acid solution and ethanol for removing remained sulphate ions, monomer aniline and lighter oligomers. Eventually residuum was dried at 60°C for 24 h to obtain green polyaniline.

Synthesis of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (0.5%, 1% and 1.5% PANI)

$Zn_{0.95}Ni_{0.04}Co_{0.01}O_4$/PANI nano composites were synthesized via hybridization. 2.2 g $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ was added to 50 ml PANI solution using THF solvent. The mixtures were sonicated for 30 min in the dark and then were stirred for 24 hours in the room temperature to obtain homogeneous and uniform suspensions in which PANI chains were adsorbed on the surfaces of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nano particles. Finally $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites were filtered and washed with water for 3 times and dried at 60°C for 2 days.

Characterization

The X-ray diffraction patterns of samples were recorded by the usage of a X-ray diffractometer (Philips PW 1730) with λ = 0.154 nm in 2θ range of 20–80°.The formation of pure PANI and composites were confirmed by fourier transform infrared spectroscopy (Thermo-Nicolet 8700) in the range of 400–4000 cm^{-1}. The morphologies of pure PANI and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (0.5%, 1% and 1.5% PANI by weight) were characterized by scanning electron microscopy (KYKY SBC-12 EM3200). The absorption spectra of dye solutions were recorded with a UV-Vis spectrophotometer (CARY 100 Bio). Zeta potential of prepared nano composites was determined by Zeta potential meter (Malvern ZEN 3600). Specific surface area (BET) of the synthesized nano composites was determined by single point surface area analyzer (BELSORP).

Measurement of photocatalytic activity

The photocatalytic activity of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites (0.5%, 1% and 1.5% PANI by weight) was evaluated by measuring the photo decolorization of organic dye pollutant (Congo red). The light was provided by four lamps with lambda max= 254 nm, manufactured by Holland (6 W, PHILIPS) and the lamps were placed in the reactor in four directions at a distance of 10 to 15 cm from the vessel. All of the photocatalytic processes were performed at ambient temperature about 30˚C. Certain amounts of photocatalysts were added to 50 cc of Congo red (CR) solution with the proper concentration of NaOH 0.01 N and HCl 0.01 N solutions for adjusting the pH values. Before irradiation, the suspension was magnetically stirred in the dark for 30 min to establish adsorption–desorption equilibrium [15]. By starting photocatalytic oxidation under UV light, every 10 min, 5 ml of sample was centrifuged at 3000 rpm to remove photocatalyst and the concentration of Congo red was determined by recording the changes of lambda max at 497 nm by using UV-Vis spectrophotometer. The photo decolorization efficiency was calculated according to the following equation:

$$\%\ \text{decolorization} = \frac{C0-C}{C0}\times 100$$

Where C_0 and C respectively represent the initial absorbance of the Conge red and absorbance at time t [16].

RESULTS AND DISCUSSION

XRD results

Fig. 1 was illustrated the XRD patterns of PANI and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (0.5%, 1% and 1.5% PANI). Polyaniline exhibited broad peaks around 2θ= 18.45° and 2θ= 25.4° which was attributed to the periodicity parallel and perpendicular to the PANI chain. Actually, presence of rigid aromatic rings made PANI a semi crystalline polymer [17].

The XRD patterns of $Zn_{0.95}Ni_{0.04}Co_{0.01}O_4$/PANI nano composites was represented the characteristic peaks of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ with hexagonal wurtzite structure of ZnO which was matched with ICCD card no 01-075-0576. The appearance of new peaks with low intensity in the baseline can be raised from the adsorption of a thin layer of PANI to the surface of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nanoparticles. Hence the wurtzite structure of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nano particle has not been changed after encapsulating with PANI molecules.

Nevertheless the characteristic peaks of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nanoparticle shifted to the lower angles due to the increasing of the distance between levels of diffraction lattice of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nanoparticles. By incorporating of polymeric chains between the spaces of crystalline planes in $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ structure and interaction between oxygen group of Ni-Co-ZnO and NH group of PANI chain, the peaks shifted in nanocomposite XRD pattern [9].

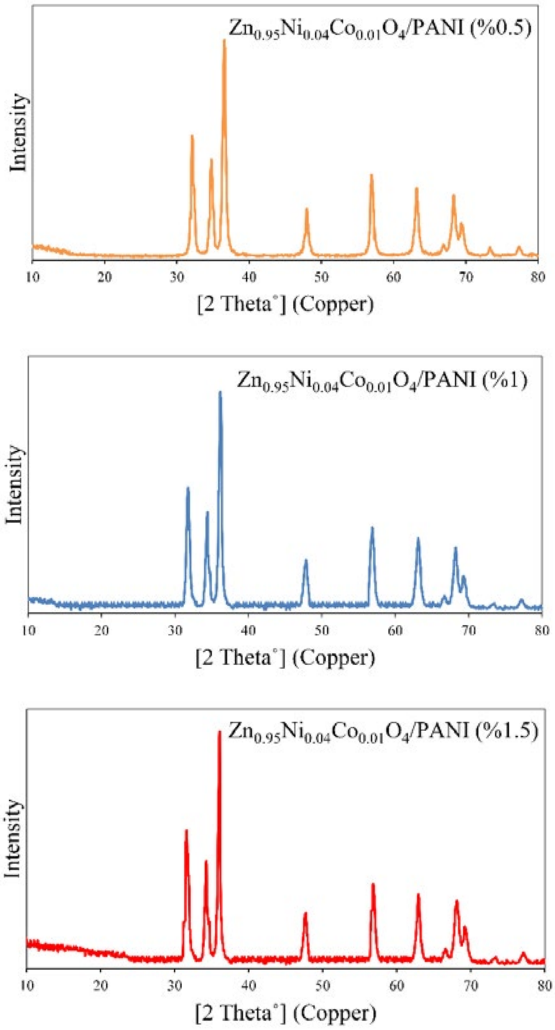


Fig. 1. XRD patterns of PANI and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (0.5%, 1% and 1.5% PANI)

FTIR

The FTIR spectrum of PANI and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (0.5%, 1% and 1.5% PANI) was shown in Fig. 2. PANI exhibits main peaks at 3442 cm^{-1} (N-H stretching mode of benzenoid ring), 1580 cm^{-1} (C=C stretching modes for quinoid unit), 1472 cm^{-1}(C=C stretching modes for benzenoid units), 1297 cm^{-1}(C-N stretching mode of benzenoid ring), 1121cm^{-1}(stretching mode of N=Q=N, Q represents the quinoid ring) and 802 cm^{-1} (out of plane bending vibration of C-H and N-H bonds). In FTIR spectrum of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (0.5% PANI) the mentioned characteristic peaks are shifted to the 3443 cm^{-1}, 1580 cm^{-1}, 1465 cm^{-1}, 1296 cm^{-1}, 1110 cm^{-1} wavenumbers. In $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (1% PANI) the characteristic peaks are presented at 3442 cm^{-1}, 1578 cm^{-1}, 1465 cm^{-1}, 1295 cm^{-1}, 1108 cm^{-1} and in $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (1.5% PANI) the peaks were seen at 3442 cm^{-1}, 1574 cm^{-1}, 1464 cm^{-1}, 1294 cm^{-1}, 1108 cm^{-1} wavenumbers. The shifting of mentioned characteristic peaks to lower wave length related to interactions of PANI chains and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite which could affect the electron densities and bond energies of polymeric chain [9].

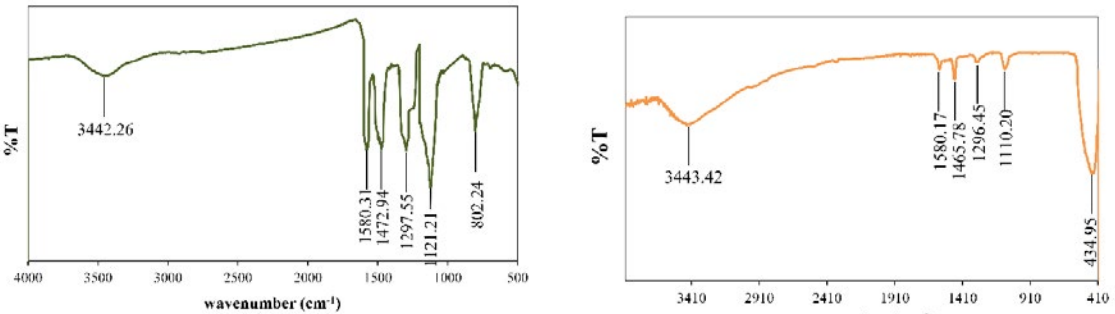
FESEM

Fig. 3 shows FESEM pictures of the PANI and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite (0.5%, 1% and 1.5% PANI). While PANI shows sphere shape, $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites exhibit spherical grains with a diameter of 50- 60 nm. Surface modification of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ by PANI, doesn't significantly change the shape and the size of inorganic nano particles. So, $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nano particles are encapsulated in only a thin layer of the polymer chains [19] .PANI has a good covering effect of the $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ nanoparticles. On the other hand by increasing the concentration of PANI up to 1.5% the particles are aggregated so the crystallinity decreases [20].

Photocatalytic studies

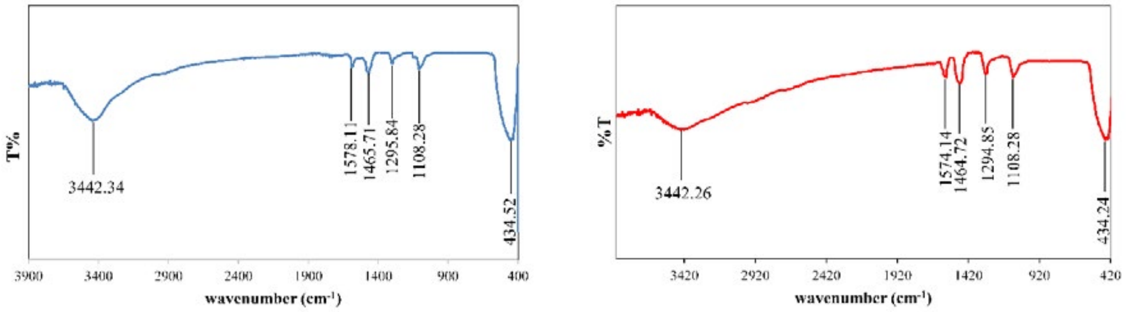
Effect of initial concentration of dye contamination

Fig. 4 illustrates the influence of initial concentration on decolorization percent of dye in the range of 10-30 ppm. Decolorization percentage decreases with an increase of initial concentration of dye contamination. By increasing the initial dye concentration, more and more molecules were absorbed on the surface of the photocatalyst and transition of light through the solution reduces.



Pure PANI

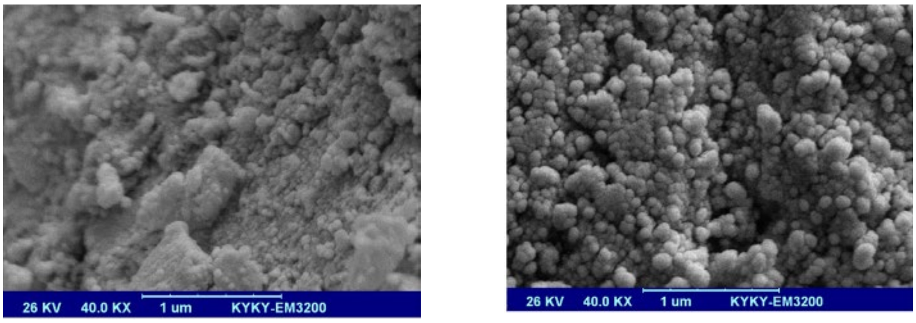
$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite 0.5



$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite 1%

$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite 1.5%

Fig. 2. FESEM micrographs of PANI and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ /PANI nano composite (0.5%, 1% and 1.5% PANI) nano composites



Pure PANI

$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite 0.5

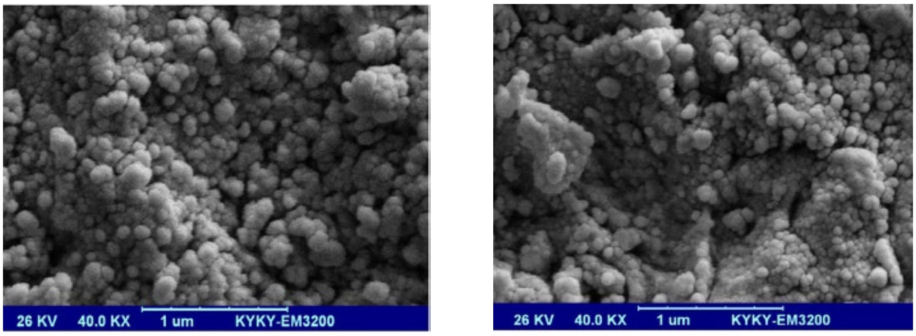


Fig. 3. Effect of initial dose of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites (0.5%, 1% and 1.5% PANI by weight) on photo decolorization activity

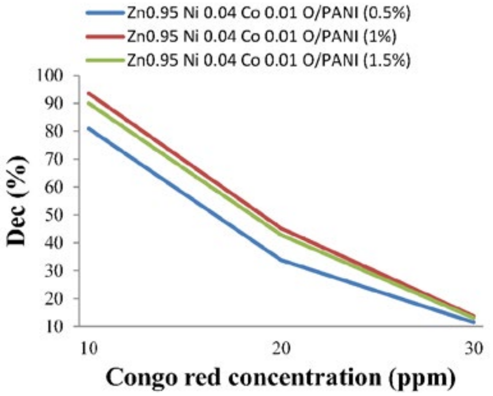


Fig. 4. Effect of pH changes in decolorization activity of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites (0.5%, 1% and 1.5% PANI by weight)

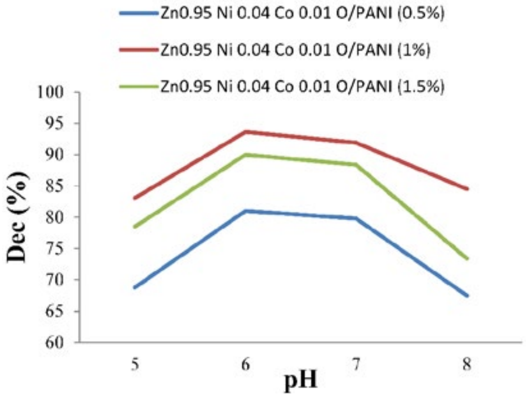


Fig. 5. Effect of concentration changes of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI photocatalyst on decolorization activity at pH: 6

Also the large amount of adsorbed dye molecules inhibits the direct contact between the dye and photo generated hydroxyl groups [21]. On the other hand due to hydrophobicity of aromatic rings in dye molecules, they can form dimmer or higher molecules and reduce the photo decolorization efficiency [22].

Effect of pH

One of the main controlling factors that occur on the semiconductor surface is pH value. This parameter influences the decolorization efficiency by affecting on the surface charge properties of photocatalysts.

Fig. 5 shows the photo decolorization of CR at different pH values from 5 to 8 in 15 min, which obviously presents that the best results was obtained in an acidic solution (pH: 6). The zeta potential values of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites (0.5%, 1% and 1.5% PANI by weight) at pH 6 were measured ≈+27 *mev* so in an anionic dye can simply adsorb the positive surface of used photocatalysts. Zeta potential of PANI polymer was reported +30 at pH ≈ 6 in previous works [23].

Although the positive charge on $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI photocatalysts surface restricts the aggregation of nanocomposites [24, 25].

Effect of Photo catalyst concentration

Finding the minimum dosage of photocatalyst with the highest efficiency of dye decolorization is very important [18]. The effect of amount of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites (0.5%, 1% and 1.5% PANI by weight) as photocatalyst on the decolorization percent of the solution was investigated. Different amounts (0.3–0.7 g) of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites were used for decolorization of 10 ppm dye solution in 15 min light irradiation at pH: 6. According to the results, the optimum amount of all samples was 0.4 g/l. By applying more amount of photocatalyst, the decolorization efficiency decreases in other word usage of 0.4 g/l of each photocatalyst can provide the maximum surface area for adsorbing dye molecules and by over dozing of photocatalysts, turbidity of solution and light scattering inhibit the penetration of UV-light through the dye solution [26]. Furthermore, in our previous work the optimum value (0.5 g/l) was determined in the case of pure $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ sample; hence hybridization of this inorganic nano particle with PANI and using the lower amount of photocatalysts can be more affordable.

The photocatalytic activity of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites (0.5%, 1% and 1.5% PANI by weight)

The photocatalytic activity of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (0.5%, 1% and 1.5% PANI by weight) samples was investigated by decolorization of 10ppm of o.4g/l of each photocatalyst under light (pH: 6 and 30˚C). Fig. 6 shows the decolorization trend of Congo red solution in presence of photocatalysts. Monitoring the changes of characteristic absorption peak of CR at 497 nm illustrated that Congo red has been decolorized completely under UV light in 45 min, 25 min and 35 minutes, respectively in the presence of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (0.5%), $Zn_{0.95}Ni_{0.04}Co_{0.01}O_4$/PANI (1%) and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1.5%). Photocatalytic activity of all three photocatalysts has been better than pure $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ in our previous work (in presence of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ color removal was completed in 70 min) [14].

The order of photocatalytic activities was as following:

$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1%) > $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1.5%) > $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (0.5%)

Study of kinetics

Photo decolorization rates of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composite was described by pseudo-first-order kinetics [27]. The rate equation is expressed as follow:

$$\ln\left(\frac{c_0}{c}\right) = kt$$

K= rate constant, C_0= initial concentration of Congo red, C= concentration of at time t

According to Fig. 7 the Plots of *Ln C0/C* versus irradiation time in presence of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (0.5%, 1% and 1.5% PANI by w eight) samples are linear.

For investigating the nature of the photochemical activity of samples the apparent rate constants (*k*)

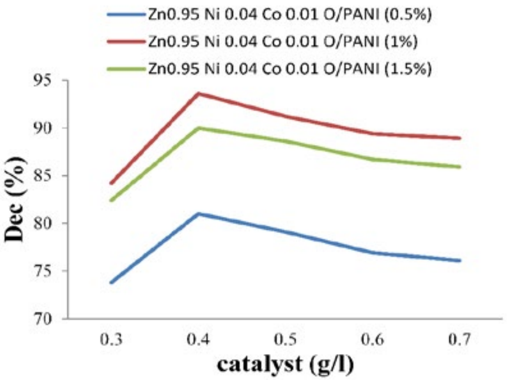


Fig. 6. Decolorization trend of 10 ppm in presence of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (0.5%, 1% and 1.5% PANI by w eight) photocatalysts under light irradiation

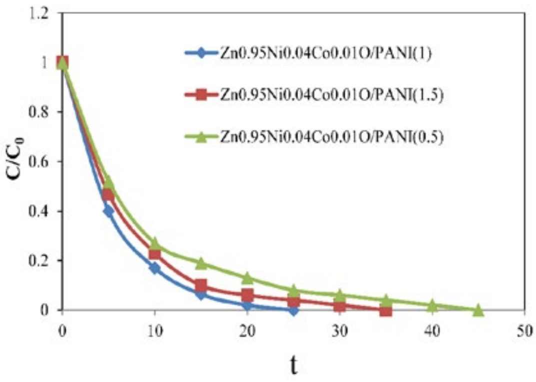


Fig. 7. Plots of LnC_0/C solution versus time for $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ /PANI (0.5%, 1% and 1.5% PANI) in optimum concentrations

are calculated from the slopes of the plots. sThe (*k*) values are summarized in Table 1 in all cases the *k* values were greater than pure $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ (K_{app} = 0.0647) .The values of R^2 for all samples are about 99%. $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ /PANI (1% PANI) nano composite is evidently the best photocatalyst among synthesized samples so it was used for photo stability experiments.

Photo stability of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ /PANI (1% PANI) nano composite

Photo stability of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1% PANI) nano composite was evaluated by reusing it in the several photocatalytic decolorization. For this purpose 0.4 g/l of this sample was added to 10 ppm of dye solution and after completing the decolorization process, the photocatalyst was separated from solution after washing with deionized water for several times, it was dried at 100˚c in the air and the same experiment was repeated. Regarding to Fig. 8 after three runs, process efficiency was 97% and this result proved high stability of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1% PANI) photocatalytic experiments. The negligible decrease of color removal efficiency can be due to losing sample during washing. R^2 values for all curves in Fig. 8 are 0.9.

According to Fig. 9 the similarity of FT-IR spectrums of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI photocatalyst before and after photocatalytic reactions, is obvious. So the structure of photocatalyst was not affected while photocatalytic activity or it was not transformed to other chemical compounds [9]. The high photo stability of this photocatalyst can be a good evidence for the effective charge carrier separation and the increasing the lifetime of charge carriers [29].

BET

To find further information about the surface area of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites (0.5%, 1% and 1.5% PANI), BET analysis was applied and the results are present in Table 2. The surface area value of 29 m^2/g was reported for pure $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ in our previous paper, therefore hybridization of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ and PANI increased this parameter [30]. By increasing the concentration of PANI from 0.5% to 1% the surface area increased, but by reaching its concentration to 1.5% the surface area value decreased due to aggregation of particles. The results of SEM analysis confirmed the aggregation of particles in the case of 1.5% PANI too. One of the most important steps in photocatalytic decolorization of dyes under light irradiation is the adsorption of dye molecules on the surface of photocatalyst and increasing of surface area can lead to improvement of the photocatalytic activity [30]. In this work $Zn_{0.\ 95}Ni_{0.04}Co_{0.01}O$/PANI (1%) has the most specific area among the synthesized samples and its well matched with the results of photocatalytic experiments.

Table 1. Apparent constant rate and R^2 values of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$ /PANI (0.5%, 1% and 1.5% PANI)

sample	K_{app} (min^{-1})	R^2
$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (0.5% PANI)	0.0965	0.99
$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1% PANI)	0.1701	0.99
$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1.5% PANI)	0.1355	0.99

Table 2. The specific surface area of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (0.5%, 1% and 1.5% PANI by) nano composites

photocatalyst	BET Surface area (m^2/g)
$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1%)	39.2
$Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1.5%)	35.1
$Zn_{0.\ 95}Ni_{0.04}Co_{0.01}O$/PANI (0.5%)	35.7

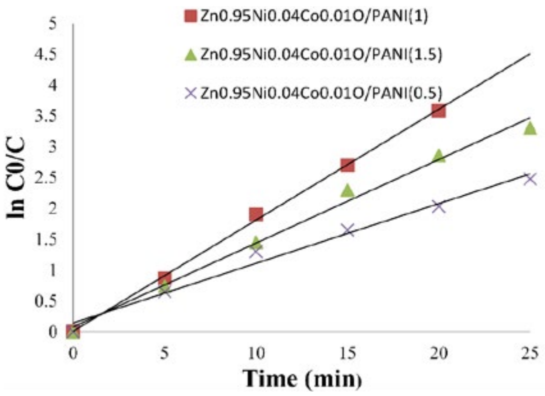


Fig. 8. Reusability of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1% PANI) with initial concentration of 0.4 g/l

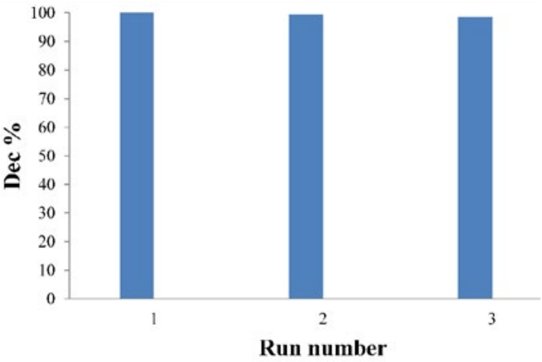


Fig. 9. FTIR spectra of $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI (1% PANI) nano composite (a) before photocatalytic activity, (b) after three runs in photocatalytic process

CONCLUSIONS

After synthesizing of polyaniline by in-situ polymerization method, the $Zn_{0.95}Ni_{0.04}$ $Co_{0.01}O$ (0.5%, 1% and 1.5% PANI) nano composites were synthesized. The XRD and FTIR results proved the formation of composites. With respect to SEM micrographs, pure PANI had typical amorphous morphology and $Zn_{0.95}Ni_{0.04}Co_{0.01}O$/PANI nano composites exhibited spherical grain with a diameter of 40- 60 nm. Photocatalytic decolorization of Congo red solution determined the PANI composite (1%) as the best photocatalyst among samples and the BET results showed the maximum amount of 39.2 m^2/g for it. The high decolorization efficiency of $Zn_{0.95}Ni_{0.04}$ $Co_{0.01}O$ (1% PANI) nano composite (98.5%) after three times reusing of photocatalysts demonstrated the high photo stability of the sample.

CONFLICT OF INTEREST

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

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