

Multi-doped ZnO Photocatalyst for Solar Induced Degradation of Indigo Carmine Dye and as an Antimicrobial Agent

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Received: 7 May 2019 / Accepted: 30 July 2019 © Springer Science+Business Media, LLC, part of Springer Nature 2019

Abstract

Multi-doped photocatalysts are among the new class of materials employed for photocatalysis and as an antimicrobial agent. Lower band gap energy due to the metal dopant and lower electron–hole recombination because of non-metal dopant increase the overall efficiency of photocatalyst. Furthermore, these dopants directly influence optical shift, crystallinity and surface area. A Ni, C, N, S multi-doped ZnO photocatalyst was synthesized by simple hydrothermal co-precipitation method by using thiourea as a non-metal precursor and was characterized by XRD, SEM, TEM, EDAX, FTIR techniques. Ni, C, N, S dopants were detected in EDAX, FTIR and XRD. The average particle size was found 12.82 nm from particle size distribution studies, TEM and XRD analysis. The synthesized catalyst showed highest photocatalytic efficiency of Indigo Carmine dye at higher pH and minimum catalyst dose in 120 min of solar light exposure by obeying pseudo first order kinetics. Furthermore, the catalyst was also employed as an antimicrobial agent and showed higher antimicrobial activity against *Escherichia coli* and *Staphylococccus saprophyticus* pathogenic bacteria at different concentrations.

Keywords Photocatalyst · Antimicrobial activity · Multi-doped · Dye degradation · Indigo carmine dye

1 Introduction

Water is an important resource for all living organisms on earth, but currently industrialization, urbanization and other anthropogenic activities are utilizing and contaminating large amount of hydrosphere [1]. One of the main cause of water pollution is the organic chemicals used in various industrial operations, especially organic dyes are among the most used chemicals in different types of industries like textile, paint, paper, food, cosmetic, pharmaceutical [2]. More

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mg water pollutants and in all mentioned industries the main hazard is proving to be a textile industry since, it uses large amount of water soluble dyes in various industrial operations such as scouring, washing, dyeing, bleaching, sizing and finishing with little or no care and due to the high water solubility textile effluent contain large amount of organic matter in the form of organic dyes [4].
 These dyes are very hazardous when they enter into the water bodies since, very small amount (ppm) of dye can be visible in water system and is able to create hazardous

be visible in water system and is able to create hazardous effects to living organisms [5]. These organic contaminants are most of the times made up of aromatic framework and due to their non-biodegradable nature, incorporate into the living organisms and may cause carcinogenic and mutagenic towards living organisms and human being [2, 6]. Essential sunlight is trapped in these conjugated organic moieties which is necessary for aquatic life. Furthermore, chemical oxygen demand of the system increases and leads to serious consequences such as low dissolve oxygen, false

than 100,000 different types of dyes are commercially available, out of this annually greater than 1.6 million tons of

dyes are produced and 10-15% volume goes as a waste in

the form of industrial effluent [3]. Therefore, dyes are major

Different methods and techniques such as adsorption [7], biodegradations [8], reverse osmosis [9], coagulations–flocculation [10], nano-filtration [11], ozone treatment [12] etc. are known and employed for the removal of these hazardous organic substances from waste water effluents. However, the problems related to most of these methods are high cost, less efficiency and secondary waste products generation which require further treatment which is again a daunting and costly task [4, 13]. Hence, there is a need for the effective, fast and eco-friendly process which utilize minimum resources and produce maximum efficiency for the complete removal of the organic moieties from industrial waste water effluents.

In order for complete elimination of organic dyes from water, eco-friendly, cost effective and fast methods are advanced oxidation processes (AOPs) [13]. In these method free radicals are produced, which break down larger, polycyclic, macromolecules into smaller and less harmful substances [2, 14]. Most of the times these molecules mineralize into nontoxic micro molecules like water (H₂O), carbon dioxide (CO_2) and nitrogen (N_2) etc. [15, 16]. However, there are some drawbacks related to the AOP's are reported and must not be ignored. The energy required for the AOP's is the important issue since most of the photocatalysts utilize UV radiation which only accounts for less than 5% of entire solar spectra and the alternate option is UV lamps which may prove costly [2, 14, 15]. Furthermore, the process is carried out at laboratory scale but to employ it on pilot scale is difficult [13]. The amount of photocatalyst, concentration of contaminant, reaction time and rector set up must be appropriate for efficient degradation, most of the photocatalysts synthesis requires higher temperature, pressure and low yield is observe in many processes, in addition to that real industrial effluents contain mixture of dyes which are complicated to degrade since photocatalyst are selective in many cases [3, 14]. By considering these aspects it is important to develop an efficient AOP's for complete destruction of organic contaminants.

The generation of oxidizing species is carried out in aqueous medium with the help of various types of nanomaterials which utilize light as an energy source commonly known as photocatalyst [17]. Photocatalyst like TiO_2 , SnO_2 , V_2O_5 , Nb_2O_5 , Fe_2O_3 , ZrO_2 and many others are popular and employed in AOPs [4, 6, 18]. The main problems with these photocatalysts are high cost, toxicity and less efficiency in visible solar radiation range which is the major part of total solar flux [18]. ZnO is one of the promising contender in this field, since it is nontoxic, cheap, easily available and has wide band-gap range especially near-UV–Vis region which is 90 to 93% of total

solar radiation having high stability and high potential as photocatalyst [19], but still it can be improved to harness radiation within visible range and this drawback of ZnO can be eliminated by doping it with metal as well as non-metal dopants [20].

Variety of metal dopants like Fe, V, Nb, Au, Ag, Pd, Ce and many more are extensively used as a doping agent in many metal oxides [21, 22] in which Nickel stands out because it promotes visible-light absorption by decreasing band gap, generate electron-hole pair, decrease the recombination of these photo induced charge carriers, provides strength, improves morphology and supports major metal oxide for photocatalysis process [23, 24]. Apart from that, currently non-metals like B, N, C, S, F etc. are used as a dopant which are introduced by simple ion source like urea, thiourea, various amino acids etc. to minimize electron hole recombination, improve grain size, increase surface area by the synergic effect of non-metal multivalent ions [24]. Furthermore, non-metal 2p states mix with O2p of parent oxide states in the valence band narrows the band gap which helps to generate electrons-holes pairs and facilitates the generation of oxidizing species [25].

Doping of metal and non-metal has remarkable effect on antimicrobial activity of ZnO [21]. Antimicrobial activity of any nanomaterial is carried out by various mechanisms such as generation of reactive oxygen species (ROS) especially dioxygen radical $(O2^{-1})$, these oxidizing radicals are highly reactive and generally react with the macromolecules such as DNA, enzymes (protein), lipids and other cellular mater and ultimately kill the microorganism [26]. Metal Cation Release, Membrane dysfunction and particle internalization are size dependent mechanism in which metal ion directly alter the transportation and other cell membrane related processes [21]. Doping of metal and non-metal helps to generate ROS and increase the antimicrobial proficiency of NP's [27]. Furthermore, doping also controls the size and morphology of nanoparticles which is an important property of efficient antimicrobial agent [28].

In the present work, we report the photocatalytic activity of a multi-doped photocatalyst in which nickel is a metal and C, N, S are non-metal dopants in ZnO system. The photocatalytic efficiency of the synthesized multidoped photocatalyst was tested in solar radiation for the degradation of Indigo Carmine anionic dye by applying various parameters such as, pH of dye solution, initial concentration of dye, catalyst dose, contact time etc. It is observed from the study that prepared catalyst show high degradation efficiency 98.85% for Indigo Carmine under solar radiation at higher pH and minimum catalyst dose in 120 min obeying pseudo first order kinetics. Furthermore, it shows good antimicrobial efficiency against common Gram-positive and Gram-negative pathogenic bacteria.

2 Experimental Methods

2.1 Materials

All chemicals used were of analytical grade and used without further purification. Zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O)$ (97%), Nickel nitrate hexahydrate $(Ni(NO_3)_2 \cdot 6H_2O)$, Nitric acid (HNO_3) and Indigo Carmine (IC) Fig. 1, were purchased from Fisher Scientific, India. Thiourea, CS(NH₃)₂ (99%) and polyethyleneglycol-200 (PEG) (99.8%), was purchased from Merck, India. Mueller–Hinton agar (MHA) and Mueller–Hinton broth (MHB) media for the antibacterial study were purchased from BD diagnostic, France.

2.2 Synthesis of Photocatalyst

Ni, C, N, S multi-doped ZnO was prepared by adding $Zn(NO_3)_2 \cdot 6H_2O$ (1.0 mmol) to 0.1 mol L⁻¹ of HNO₃ up to complete dissolution of $Zn(NO_3)_2 \cdot 6H_2O$. Then, drop wise polyethyleneglycol-200 (1.0 mL) was added and the mixture was stirred for 1 h after complete addition of PEG. Thereafter, calculated amount of Ni(NO₃)_2 \cdot 6H_2O by considering Ni:Zn ratio as 1.0% was added and stirred for 1 h. Thiourea (3 grams) was added and the mixture was stirred for 2 h. The homogeneous solution was dried in an oven at 100 °C for 12 h then black residue obtained was claimed at 600 °C for 3 h at the rate 10 °C per min to obtain yellowish-green powder of 1% Ni, C, N, S doped ZnO [29].

2.3 Characterization

The morphology of synthesized material was characterized by transmission electron microscopy (TEM) with selected area electron diffraction (SAED), elemental composition detected by energy dispersive X-ray (EDAX) on the field-emission scanning electron microscopy (FESEM), Crystallite nature detected by X-ray diffraction (XRD) and finally functional groups present in material



Fig. 1 Structure of indigo carmine dye

were analyzed by fourier transform infra-red spectroscopy (FT-IR). The antimicrobial activity of prepared sample was tested against Gram-positive, and Gram-negative pathogenic bacteria.

2.4 Antimicrobial Activity of Prepared 1% Ni, C, N, S Doped ZnO

The Gram positive (Staphylococcus saprophyticus KCTC 3345) and Gram-negative (Escherichia coli KCTC 1682) pathogenic bacteria were procured from Korean Collection for Type Cultures (KCTC), Republic of Korea. Agar well diffusion assay for antibacterial activity of 1% Ni, C, N, S multi-doped ZnO was performed [30]. A 24 h old bacterial culture suspension diluted in MHB medium and adjusted 0.08-0.1 optical density at 625 nm (equivalent to 0.5 McFarland-standard) using spectrophotometer (Libra S22, Biochrom Ltd, Cambridge, England) and used for antibacterial assay. Briefly, 100 µL of diluted bacterial suspension spreaded over the surface of MHA media plates with the help of sterile L-shaped glass rod and wells were prepared by 8 mm gel puncture borer. Different concentrations of synthesized material (12.5, 25, 50, and 100 mg mL⁻¹) samples were prepared in sterile water and 100 µL of each were dropped in wells. After that, MHA plates were incubated at 37 °C for 24 h. After incubation, zone of inhibition (ZOI) diameter were measured in mm. These experiment was performed in triplicate.

3 Results and Discussion

3.1 XRD Analysis

XRD study was carried out with a monochromatic high intensity Cu Ka radiation (1.54060 Å) and X-ray diffractometer (45 kV and 40 mA) with goniometer radius 240 mm. The intensity data were collected at 25 °C in a 20 range from 10° to 90° with fixed divergence slit size 0.8709° with angular type of slit opening having step size of $0.017^{\circ} 2\theta$ and scan rate of 0.2° s⁻¹ with continuous scanning. The XRD characterization is useful for the detection of crystallinity and to get information related to average crystallite size of synthesized material. The XRD pattern of multidoped ZnO is given in Fig. 2. The pattern is resembling to a typical, highly crystallite ZnO. High crystallinity is evident from sharp peaks in XRD pattern. Peak observed at 32.70°, 33.55°, 35.38°, 46.68°, 57.23°, 61.99°, 65.53°, 67.09°, 68.24° corresponding to (100), (002), (101), (102), (110), (103), (200), (112) and (201) are representative of characteristic hexagonal wurtzite ZnO structure [31]. NiO-base phase is dissolved at high temperature (600 °C) and incorporated in ZnO lattices forming Ni doped ZnO is evident from small



Fig. 2 X-ray diffraction patterns 1% Ni, C, N, S multi-doped ZnO

Table 1 XRD parameters of prepared photocatalyst

Multi-doped ZnO						
20°	(hkl) Planes	FWHM (β)	Size (nm)			
32.70	100	1.2623	6.85			
35.38	101	0.2998	29.05			
57.23	110	3.7076	2.55			
Average crystal- lite size			12.82			

peak at 42.206° corresponding to (200) [32] and 50.901° for Ni/NiO [33]. This is a clear indication of successful doping of nickel ions into the ZnO wurtzite structure.

Fig. 3 TEM images and SAD pattern of 1% Ni, C, N, S multi-doped ZnO

By using high intense peaks from XRD spectrum, the crystallite size of the multi-doped ZnO was calculated by Debye–Scherrer's formula (Formula 1) [34]. The average crystallite size of 1% Ni, C, N, S multi-doped ZnO was calculated by considering high intense peaks from XRD spectrum given in Table 1 and it was found 12.82 nm.

$$D = \frac{0.94\lambda}{\beta\cos\theta} \tag{1}$$

where, λ is 1.54060 Å, K is constant = 0.94, β is full width half maxima (FWHM) and θ is diffraction angle (Cu-K α).

3.2 TEM and SAED Pattern Analysis

TEM measurements provide decisive information related to crystallite size, morphology and crystallinity of the synthesized multi-doped photocatalyst. TEM analysis was carried out with the help of FEI Tecnai G2, F30 model. Figure 3a, b shows the nanospheres morphology having size within the range of 10-25 nm. Nanoparticles are agglomerated and forming cluster of nanospheres of different sizes. The hexagonal wurtzite single-crystal nature of the prepared nanospheres is evident from TEM images. Figure 3c, d depict SAED patterns which are obtained by focusing the beam vertically on a single crystal. The hexagonal diffraction pattern of (101) plane confirms the single wurtzite structure of the multi-doped ZnO [33]. The polycrystallite nature of material is reviled from multiple rings of electron diffraction pattern and blurring of diffraction rings (Fig. 3d). The lattice spacing shows (101) plane of wurtzite ZnO [35].



3.3 SEM and EDAX Analysis

Field emission scanning electron microscope with high resolution and magnification is used and it is observed from the high resolution SEM image (Fig. 4a) that the surface is heterogonous morphology with agglomeration and the particles size is fairly consistent and large number of cavities are observed due to the agglomeration of particles may show interconnected pores which indicate high porosity in the synthesized material [35]. The particle size distribution study from SEM image reveals the average crystallite size is within 15 nm given in Fig. 4b. The highly porous material is beneficial since, it adsorbs the dye molecules in the cavities and then degradation takes place, this adsorptiondegradation combination overall increases the photocatalytic efficiency of the photocatalyst [35]. EDAX analysis was useful to know the elemental composition in the prepared sample. From the spectra, given in Fig. 4c, it can be observed that all the expected elements were present, there were no signal related to any unexpected element, confirming the purity of synthesized 1% Ni, C, N, S multi-doped ZnO. The weight percentage of the compositional elements are given in Fig. 4c. The successful doping of C, N and S is confirmed from the table and value to be noticed is the percentage of Ni in the prepared sample which is 1.12% by weight which confirms the successful 1% doping of Ni into the Ni, C, N, S multi-doped ZnO sample.

3.4 FTIR Analysis

The chemical bonding in a material can be studied using FT-IR spectroscopy. FT-IR spectra was recorded by 3000 Hyperion Microscope with Vertex 800 FT-IR System, Bruker, Germany. The measurements were taken in the range of 400–5000 cm⁻¹. The obtained spectrum of synthesized material is given in Fig. 5. The interruption of water molecules is unavoidable and it is confirmed by the broad absorption band around 3454 cm⁻¹ and the peak at 1640 cm⁻¹ are corresponding to O–H stretching and H–O–H bending vibrations of water molecules respectively [36]. The



Fig. 5 FT-IR transmittance of 1% Ni, C, N, S multi-doped ZnO



Fig. 4 a SEM image, b particle size distribution and c EDAX analysis with elemental composition of 1% Ni, C, N, S multidoped ZnO (w%) broad peak at 1350 to 1000 cm⁻¹ attributed to nitrate groups and carbonyl group of carboxylate ions proving the presence of carbon and nitrogen in prepared sample [37, 38]. The small peaks around 750 to 650 cm⁻¹ corresponding to NH₂ and C–S stretching [39]. The peak intensity around 550 cm⁻¹ correspond to stretching mode of Zn–O bonding [39, 40].

3.5 Optical Properties

Figure 6 shows the absorbance spectra and band gap graph of 1% Ni, C, N, S doped ZnO. An absorption peak appears at 363 nm which is less than 378 nm for the pure ZnO observe elsewhere, indicates the shifting of absorption maxima towards blue shift, this minor modification in band structure is observe due to doping of metal and non-metals [23]. The UV/Vis absorbance data was utilized to calculate the band gap using Eq. 2.

$$(\alpha h\nu) = A(h\nu - Eg)$$
(2)

where, α is the absorption coefficient, A is a constant and h ν is the photon energy [32]. The prepared photocatalyst has Eg=3.25 eV which is less than pure ZnO shows decrease in band gap [23, 29]. The study provides sufficient information about the decrease in band gap of prepared photocatalyst compare to pure ZnO which eventually help photocatalysis process.

3.6 Photocatalytic Studies

The photocatalytic study of the prepared photocatalyst was tested under solar radiation which is an eco-friendly approach. The ideal time in subcontinent region for the high instance radiation especially in central India is in the month



Fig. 6 UV/Vis absorption spectra and optical band gap of 1% Ni, C, N, S multi-doped ZnO

of May. For the study the time was chosen from 12 am to 3 pm in the sunny summer afternoons in the month of May, when the intensity of solar radiation is at the peak and the average solar flux during the experiment days was recorded by digital solar sun meter ranged from 1200 to 950 W m⁻² during 3 h of experiment. As discussed below, various parameters were tested by placing the reaction assembly in the solar radiation. The experiment set up is given in Fig. 8b.

3.7 Effect of pH of Solution

The pH of the dye solution is one of the most important parameter to study the photocatalytic performance of any synthesized material. Before the experiment the point zero charge (pHpzc) of the photocatalyst was determined by using 1 M NaCl solution by monitoring the change in pH of photocatalyst immersed solution for 48 h [41]. pHpzc of multidoped photocatalyst was calculated about 7.8 (pHpzc = 7.8). At this pH photocatalyst acquires net zero charges. When, the pH of solution is below 7.8 the surface of the photocatalyst is positively charged and when it is greater than 7.8 the surface is negatively charged given in Eq. 3. [42, 43]. The pHpzc value indicates the higher degradation efficiency must be at lower pH since, the dye is negatively charged and catalyst surface is positively charged which will increase adsorption and eventually degradation.

$$M-OH^{2+} \stackrel{(pH<7.8)}{\longleftarrow} M-OH \stackrel{(pH>7.8)}{\longrightarrow} M-O^{-}$$
(3)

The photocatalytic efficiency at various pH ranges given in Fig. 7. It was found that the efficiency of prepared catalyst was higher at basic pH (pH 9) though IC is less adsorbed on the surface. The reason behind less degradation efficiency at acidic pH is probably due to dissolution of catalyst in acidic medium [44]. Neutral and slightly alkaline media up to pH 9 favoured the degradation of IC, probably due to increase in the free radicles generation [2, 45]. pH greater than 9 decrease the degradation, possibly due to less effective H₂O₂ and HOO generation, formation of OH scavenging carbonate and bicarbonate from CO₂ [45] and radicle–radicle pair neutralization [46].

3.8 Effect of Initial Dye Concentration

The effect of initial dye concentration was studied by considering the highest degradation pH (pH 9) and varying the initial dye concentration 10 to 30 mg L^{-1} (Fig. 8a). The 100 mL solutions of all mentioned concentrations was prepared by serial dilution, the pH was adjusted to 9 with the help of 0.1 N HCl and 0.1 N NaOH solution and 2 mg L^{-1} of catalyst was introduced into the solution. Figure 8a shows the change in absorbance with time. It is observed that, as the concentration of dye solution increased the degradation percentage decreased. Generally, efficiency of catalyst



Fig. 7 Effect of pH on degradation of indigo carmine by multi-doped ZnO photocatalyst (initial dye concentration is 15 mg L^{-1} and catalyst dose is 2 mg L^{-1})

is inversely proportional to initial dye concentration [44] because, the number of dye molecules is increased and the availability of surface for the absorption of light and formation of oxidized species like OH, O_2^{-1} were decreased due to

the adsorption of dye molecule on the surface furthermore, as the dye concentration was increased the penetration of light was also decreased [44, 47]. The pH 9, 2 mg L^{-1} catalyst dose and 10 mg L^{-1} of dye concentration combination proved most effective for the degradation of IC dye under solar radiation.

3.9 Effect of Irradiation Time

The optimum conditions obtained from previous experiments were utilize for the investigation of effect of contact time on the degradation of IC. The pH was kept at 9, 2 mg L^{-1} catalyst was introduced and the concentration of dye solution was kept at 15 mg L^{-1} . The steady increase in the degradation is observed as the time progressed. The degradation of IC under solar radiation was completed in 120 min and as the time progressed the degradation also increased especially after 60 min of irradiation it was visible that the color started to fade and the degradation completed at the 120th min of the irradiation time were the recorded absorbance was almost zero. The effect of contact time and gradual decrees in absorbance with time is given in Fig. 9a, b. Progressive fading of color from zero minute to 120th min is visible in the image Fig. 9c. The Langmuir-Hinshelwood kinetics model was used to study the degradation of



Fig. 8 a Effect of initial dye concentration on indigo carmine degradation (pH 9.0, catalyst dose 2 mg L^{-1}). **b** Experiment setup in solar radiation



Fig. 9 a Effect of irradiation time on indigo carmine degradation (initial dye concentration is 15 mg L^{-1} , pH 9.0, catalyst dose 2 mg L^{-1}). **b** Spectral variation during indigo carmine degradation, **c** Progressive fading of color from 0 to 150 min

IC dye [47]. The kinetic study of photocatalytic degradation was carried out by plotting the graph $\ln C_0/C_t$ versus time (min) given in Fig. 10. In which C_t is the concentration of dye at time t (mg L⁻¹), C_0 is the initial concentration of the IC dye (mg L⁻¹) solution. The rate constant K (min⁻¹) is obtain from the slope of the linear plot between $\ln C_0/C_t$ and irradiation time (t). It is evident from the K value that dye concentration is inversely proportional to rate of the reaction hence, gradual decrease in the value of K is observed from 5 to 15 mg L⁻¹ depicted in Table 2. The results confirmed the kinetics of IC dye degradation obeyed the pseudo first order rate kinetics [48, 49].

3.10 Effect of Catalyst Dose

Effect of catalyst dose was examined by keeping pH at 9 and dye concentration at 15 mg L⁻¹. It is clear from Fig. 11, the highest catalytic efficiency was observed at 2 mg L⁻¹ of catalyst dose and as the catalyst dose was increased the degradation efficiency was decreased. It was observed during experiment that, after 2 mg L⁻¹ the catalyst wasn't dispersed



Fig. 10 Pseudo-first order decolorization rate constant of indigo carmine (dye concentration is 5, 10, 15 mg L^{-1} , pH 9.0, catalyst dose 2 mg L^{-1})

5 mg/L

10 mg/L

▲ 15 mg/L

Table 2 Pseudo first order decolorization rate constant of IC dye

Catalyst (mg L ⁻¹)	Conc. of dye $(mg L^{-1})$	Rate const. (K) min ⁻¹	(R ²)
2	5	2.83×10^{-2}	0.9919
2	10	1.69×10^{-2}	0.9921
2	15	1.36×10^{-2}	0.9678



Fig. 11 Effect of catalyst dose on indigo carmine degradation (dye concentration is 15 mg L^{-1} , pH 9.0)

completely in the 100 mL dye solution even at higher stirring speed. The less proficiency is probably attributed to the saturation of catalyst into the dye solution which leads to the non-uniform distribution of catalyst throughout the dye solution resulting less degradation [50] also, less penetration due to the scattering brought about by excess of catalyst particles resulting in less utilization of solar radiation and eventually less degradation efficiency [51].

3.11 Reusability of Multi-doped Photocatalyst

The stability of synthesized photocatalyst was tested by the reusability experiment. After each photocatalytic experiment (that is the first cycle), degraded dye solution was filtered to remove catalyst with the help of Wattman filter paper. The catalyst was washed with distilled water and ethanol and collected in silica crucible and dried in oven at 150 °C for 2 h [51]. The obtained dry catalyst sample was subjected to three cycles of photocatalysis by maintaining the optimum condition pH 9, 3 mg L⁻¹ of catalyst dose and 15 mg L⁻¹ of dye solution for the degradation of IC dye under solar radiation. The reusability of prepared catalyst was efficient up to three cycles by marginal decrease in photocatalytic efficiency up to fourth cycle where the percent degradation



Fig. 12 Reusability of prepared catalyst for degradation of indigo carmine (initial dye concentration is 15 mg L^{-1} , pH 9.0, catalyst dose 3 mg L^{-1})

drops by 6% which is depicted in Fig. 12. This may be because of decrease of active sites on catalytic surface and loss of catalyst [45, 52] and loss of catalyst during the recovery process.

3.12 Mechanism of Photocatalysis

Metal and non-metal dopants promote generation of photo induced charge carries that is electron-hole pair. Metal dopant like nickel form shallow level donor impurities create energy levels near the conduction band edge and acceptor impurities create energy levels near the valence band edge and forms a continuum of states just like in the bands and effectively the band gap decreases [19], shifts the absorption to UV-Vis range and traps the electrons which are utilise to generate dioxygen radical (O_2^{-}) . Non-metal dopants C, N and S promote the excitation of electron through the overlapped 2p levels of non-metal with 2p levels of ZnO oxygen, which create holes which produce strong oxidising hydroxyl radical (OH) [21, 25]. The mechanism is depicted in Fig. 13. The overall effect increases the excitation of electrons and decrease the electron-hole recombination which facilitate the formation of oxidising species and eventually increase photocatalytic degradation [19, 21].

3.13 Antimicrobial Activity

The antibacterial activity of 1% Ni, C, N, S multi-doped ZnO was evaluated by agar well diffusion method and shows significant bactericidal activity against *S. saprophyticus* and *E. coli*. After 24 h incubation ZOI were observed, as shown in Fig. 14. The results indicate 1% Ni, C, N, S multi-doped





ZnO has concentration dependent bactericidal activity. The ZOI were increased from lower to higher concentration of 1% Ni, C, N, S multi-doped ZnO in both tested microorganisms. The significant ZOI diameter observed, 10.67 ± 1.15 , 13.67 ± 0.58 , 17.0 ± 1 , and 22.0 ± 1 mm at 12.5, 25, 50, and 100 µg mL⁻¹ of 1% Ni, C, N, S multi-doped ZnO on S. saprophyticus. Similarly, ZOI diameter observed, 11.67 ± 0.58 , 14.67 ± 0.58 , 18.67 ± 0.58 , and 22.33 ± 1.15 at 12.5, 25, 50, and 100 μ g mL⁻¹ of 1% Ni, C, N, S multi-doped ZnO on E. coli. There is no significant difference in bactericidal activity against tested microorganism were observed. These findings are in good agreement with previously reported studies [53, 54]. The ion (Fe) doped ZnO NPs reported for inhibition of Salmonella typhimurium [55]. Reactive oxygen species formation cause cell membrane damage and finally inhibit growth of bacteria. Taken together, 1% Ni, C, N, S



Fig. 14 Bacterial culture showing zone of inhibition around 1% Ni, C, N, S multi-doped ZnO in wells (A, B, C and D wells indicates different concentrations, 100, 50, 25, and 12.5 μ g mL⁻¹, respectively), plates containing *E. coli* (left side) and *S. saprophyticus* (right side)

multi-doped ZnO can be applicable as efficient antimicrobial agent.

3.14 Comparison of Catalytic Ability of Synthesised Photocatalyst

Metal, non-metals and graphenes are employed to extract maximum efficiency out of ZnO. Different methods and techniques have been utilised to modify ZnO for the removal of various types of organic contaminants under different types of energy sources. It is difficult to compare synthesized material with vast number of work which has been reported, out of many such works here few materials are discussed in Table 3.

4 Conclusions

1% Ni C, N, S multi-doped ZnO photocatalyst was successfully synthesized by hydrothermal co-precipitation method and employed for the solar light induced photocatalysis of IC the anionic dye. The prepared catalyst showed higher photocatalytic efficiency at pH 9 and at minimum catalyst dose. Complete degradation was observed and the reaction obeyed pseudo first order kinetics. The catalyst was highly effective, this is attributed to lower band gap, higher generation and low recombination rate of electron-hole pair and was highly effective for multiple cycle therefore, can be utilized as an efficient photocatalyst for the removal of dye contamination from waste water. The antimicrobial activity of prepared catalyst was tested on model Gram positive and Gram negative microorganisms and it was highly effective against both the types.

Dopant	Fabrication method	Pollutant	Radiation source	Degradation efficiency (%)	Refs.
Ni, ZnS	Sol-gel	Indigo carmine	150 Ozone free xenon lamp	91% in 180 min	[56]
Nb ₂ O ₅	Electrochemical synthesis	Indigo carmine	UV and sunlight	96% in 240 min	[57]
Bi ₂ O ₃ -2C ₃ N ₄	Hydrothermal method	Indigo carmine	Xenon lamp 150 W Vis light	93% in 180 min	[58]
CuO/graphene	Hydrothermal method	Indigo carmine	UV light	96.5% in 240 min	[59]
Cu, Au–Ag	Polyol method	Diuron herbicide	1700 W xenon lamp	98% in 90 min	[60]
Fe doped nanosheets using NFC	Hydrothermal method	Tetracycline	36 W UV lamp	90% in 120 min	[61]
Ni, C, N, S	Hydrothermal coprecipitation	Indigo carmine	Sunlight	98% in 120 min	[This work]

Table 3 Comparison of 1% Ni, C, N, S doped ZnO with reported photocatalysts

Acknowledgements The author thankful to IIT Bombay and KBC North Maharashtra University, Jalgaon, India for characterization and Department of Microbiology, College of Natural Sciences, Pukyong National University, Busan, Republic of Korea for Antimicrobial studies. Authors also thankful to the Principal, G.T.P. College, Nandurbar and K.V.N. Naik College, Nashik, India for providing necessary laboratory facilities.

Compliance with Ethical Standards

Conflicts of interest The authors declare that there is no conflict of interests regarding the publication of this paper.

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