Fe³⁺ modified zinc oxide nanomaterial as an efficient, multifaceted material for photocatalytic degradation of MB dye and ethanol gas sensor

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Abstract

In the present investigation, we report the preparation of 5% Fe/ZnO nanocatalyst for organic transformations, gas sensing, and organic pollutant elimination applications via the CPT method. A broad range of analytical techniques was applied to attribute the successful modification of the nanocatalyst and to evaluate the structural and morphological properties, surface area, and chemical compositions by the x-ray diffraction, scanning electron microscopy, high resolution-transmission electron microscopy, Brunauer-Emmett-Teller, and energy dispersive spectroscopy techniques. The organic transformations of dihydropyrimidinones, gas sensing performance to ethanol and the photocatalytic degradation of methylene blue (MB) as organic pollutant were studied thoroughly. Compared with undoped ZnO and other nanocatalyst the 5 moles % Fe doped ZnO significantly shows the enhanced catalytic performance in the synthesis process of dihydropyrimidinones at high yield 98% and catalyst dose 10 mol% with ethanol as solvent. Due to enhanced gas sensing performance comparatively at low temperature to ethanol, it is known for ideal sensor, which has high selectivity, rapid response-recovery time, and high stability. It also shows the enhanced photocatalytic performance in the degradation of methylene blue dye in the aqueous heterogeneous suspension. The efficiency of the semiconductor photocatalyst is found higher at the small amount of catalyst dose (0.8 g/L) and at the contact time of 100 min and pH 8.0 as operating parameters. Further, the organic transformation mechanism, enhanced gas sensing and, photodegradation mechanism were explained as the synergic effect of the ZnO and Fe doping. The result reveals that 5% Fe doped ZnO nanocatalyst are promising approaches to aim the goal of achieving a superior heterogeneous catalyst for elimination of organic pollutant (MB) at optimum conditions and gas sensing performance for detection of ethanol.

Research Highlights

- Fabrication of undoped ZnO and Fe³⁺ ZnO by co-precipitation method.
- Comparative study of prepared catalysts for water purification techniques.
- Ethanol gas sensing application of modified ZnO material.
- Efficient removal of MB dyes under UV light irradiation.

1. Introduction

Recently the dense population of people worldwide has resulted in contamination of air and water because of the growth of industrial units. The significant source of this contamination is different gases like NO₂, CO₂, SO₂, volatile organic gases like ethanol, methanol, and formaldehyde [1–4] etc. different organic dyes due to their toxic and non-degradable nature, further the chemical waste from inefficient organic reactions also contribute to the contamination [5, 6]. To decrease the damage caused by pollutant gases, organic dyes, and chemical waste from less efficient organic reactions, investigations have been focused on efficient gas sensors to detect harmful gases, on photocatalysts to convert organic dyes to less hazardous chemicals, and heterogeneous catalyst to enhance the catalytic performance and

reduce the reaction waste [7–12]. The utilization of metal oxide semiconductor nanomaterials, like ZrO_2 , ZnO , TiO_2 , and, SnO_2 , as gas sensors, photocatalysts, and heterogeneous catalyst has drawn much attention because of the ability of these nanomaterials to detect pollutant gases at comparatively low temperature, to degrade the organic pollutant under UV radiation, and catalysed the variety of organic reactions [13–16]. Despite of TiO_2 , ZrO_2 is a popular and widely employed nanomaterial in gas sensing, photocatalysis, and heterogeneous catalysis, researchers were motivated to explore the properties of ZnO in different areas of research like gas sensors, photocatalytic reactions, and organic transformations [17–20]. The suitable alternative to the ZrO_2 , TiO_2 and other nanocatalyst is ZnO because of its significant surface properties, similar band gap energy, inexpensive and exhibits extraordinary performance in gas sensing, it detects a wide range of gasses, it shows good performance in all ranges of pH (acidic, basic) for the degradation of organic dyes, and with suitable dopants, it is highly efficient in catalysing certain organic reactions[21–26].

Several methods such as chemical vapour deposition sol-gel, mechanochemical, hydrothermal, microwave assisted; [27–32] etc. methods have been proposed to prepare ZnO nanocatalyst in different structures and morphologies. Still more promising, the co-precipitation (CPT) method is applied for the synthesis of ZnO nanostructure due to its cost-effective nature, easy way of synthesis, and does not require harsh experimental conditions [33–35]. Additionally, this method can produce ZnO nanoparticles with different sizes, morphologies, and surface areas [36, 37]. Moreover, the gas sensing performance, photocatalytic activity, and catalyst efficiency strongly depend on the surface areas, and shape of the ZnO nanocatalyst, because the controlled morphology can tune the properties of the ZnO nanocatalyst [38, 39]. Hence the adsorption-desorption rate of the gas molecules on the surface of nanocatalyst, rate of oxidation-reduction in the photocatalytic activity, and reactant adsorption-desorption rate on the surface while, organic transformations could be enhanced [40–42].

To enhance the photocatalytic efficiency, performance the gas sensors and catalytic activity of the ZnO nanocatalyst, the rapid recombination of electron-hole have to reduce, decline the band gap, enhancement in the surface areas. With this purpose the transition metal ions like Ni, Fe, Cr, Mn, [43–47] etc. doped with zinc oxide appears very effective, could produce material with superior physical and chemical properties like declined band gap, high surface area, material that easily activated with UV-visible light, having good thermal and chemical stability [48, 49]. Also, these modified nanomaterial shows enhanced photocatalytic performance in the degradation of organic pollutant, good sensing response in the detection of several gasses at trace amount and comparatively low temperature, further it proves efficient as heterogeneous catalyst in catalysing different organic reactions [50–52].

Fe/ZnO nanocatalyst has fabulous characterization so that up to today, many researcher groups have been studied their properties and applications. Fe ions after doping in to the crystal lattice of ZnO have been seen in Fe^{2+} , Fe^{3+} chemical states which influence the electrical properties and band gap [53, 54]. In the present work, the successful fabrication of 5% Fe doped ZnO nanocatalyst was proposed by the economical co-precipitation method. The effect of Fe doping on electrical, optical, structural, and

photocatalytic performance in the degradation of methylene blue dye, gas sensing properties to ethanol, also the heterocatalytic performance in the organic synthesis of dihydropyrimidinones were studied.

2. Materials And Methods

The chemicals utilized in the present research are of analytical grade (AR) reagents and purchased from sigma-Aldrich limited, Mumbai and SD fine chemicals, Mumbai. The chemicals purchased were 99.99 % of purity and used without further any refinement. The Chemicals used are $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, sodium hydroxide (NaOH) and Deionized water. The general characteristics of the dye crystal violet used in the present are as depicted in **Figure 1**.

2.1 Synthesis of undoped ZnO nanoparticles by co-precipitation method

The zinc oxide nanoparticles were fabricated by conventional co-precipitation method. The zinc nitrate and sodium hydroxide was used as precursors. During the preparation of zinc oxide, 0.01 M aqueous zinc nitrate solution was prepared in deionised water in 100 ml of water. To, the zinc precursor solution, 0.01 M NaOH solution was added drop wise over the magnetic stirrer at 80 °C till the complete 50 ml addition of NaOH to reach the pH of the reaction up to 12. After complete addition of sodium hydroxide, the white coloured precipitate of zinc hydroxide was obtained, which was centrifuged at 3000 rpm for 15 minutes. The resultant solution was filtered off through whatman filter paper number 41. The obtained residue was washed two to three times with hot water to dissolve any impurities present. The zinc hydroxide precipitate dried at 110 °C under IR lamp and finally dried residue was transferred to silica crucible and calcined in muffle furnace at 600 °C for 3 hours. The white coloured zinc oxide nanoparticles were recovered from muffle furnace on the next day. The prepared ZnO nanoparticles were used for characterization and further study.

2.2 Synthesis of 5% -ZnO nanoparticles by co-precipitation method

The iron modified zinc oxide nanoparticles also synthesized by co-precipitation method. The overall procedure for the fabrication of Fe^{3+} modified ZnO was same as discuss in section 2.1, except addition of ferric nitrate as dopant during the synthesis of zinc oxide nanoparticles. The ferric nitrate salt added as dopant in the form of Fe^{3+} during the synthesis of ZnO nanoparticles. The atomic weight Percent of 5% of Fe^{3+} was added during synthesis of ZnO nanoparticles. After, following complete procedure as discuss in section in 2.1, with addition of 5% Fe, the grey coloured Fe^{3+} modified ZnO nanoparticles were synthesized.

2.3 Fabrication of thick films of undoped ZnO by screen printing strategy

The prepared catalysts viz. undoped ZnO and 5% Fe^{3+} doped ZnO investigated as a sensor material. Hence, to study gas sensing applications, the fabricated catalysts were utilized to prepare sensor material by screen printing strategy. For, this preparation the prepared nanoparticles and binders ratio was 70:30. Initially, the thick films of undoped ZnO were prepared. For this purpose nearly 0.7 g of ZnO

nanoparticles were weighed and transfer to mortar pestle, to these nanoparticles pinch of ethyl cellulose (EC) binder powder was added into mortar pestle and this mixture was grinded for 30 minutes and mixed homogeneously. After this mixing binder butyl carbitol acetate (BCA) 2-3 drops was added to the above mixture and mixed thoroughly till the formation of thixotropic paste. The prepared paste of this this overall composition was applied over previously cut glass substrate having 1.5 * 3 cm dimensions (length and breadth) by standard photolithographic technique. The fabricated film sensors of undoped ZnO material then kept under IR lamp for drying purpose for 20 minutes, the dried films then fired under muffle furnace at 400 °C for 3 hours.

2.4 Fabrication of thick films of 5% Fe³⁺ doped ZnO by screen printing strategy

The thick film sensor of 5% Fe³⁺doped ZnO prepared using same screen printing. Only the material 5% Fe³⁺doped ZnO was added to mortar pestle for grinding. The overall procedure remains same as discussed in section 2.3. The prepared 5% Fe³⁺doped ZnO sensor was utilized for further gas sensing study.

3. Results And Discussions

3.1 X-Ray diffraction study

The XRD pattern for the materials undoped ZnO and 5% Fe-modified ZnO fabricated by co-precipitation route is as depicted in **Figure 2**. The XRD instrument has Braggs scanning angle varying from 10-90°, while for generating the X-rays, CuKα₁ radiations with wavelength 1.54 Å. The ZnO material belongs to two typical crystal lattices viz. hexagonal and Wurtzite structures. As per the data obtained from XRD analysis, confirms that the fabricated materials belong to the typical Hexagonal wurtzite ZnO lattice. The Braggs' reflection peaks attributed to the formation of Hexagonal wurtzite ZnO lattice. From the analysis the 2θ values of diffraction peaks for the ZnO material are 31.89°, 34.42°, 36.28°, 47.59°, 56.66°, 62.96°, 68.02°, 69.18°, 72.66°. The 2θ values are attributed for the characteristic hkl planes reflection such as (100), (002), (100), (102), (110), (103), (200), (112), (201) planes. The hkl planes and two theta values mentioned above confirms the formation of ZnO hexagonal Wurtzite material [55, 56]. The average grain size was calculated by using Debye- Scherer's formula. $[D = K\lambda/\beta \cos \theta]$, here D is the average grain size, K is constant ranges between 0.9 to 1, while β is full-width half maxima (FWHM) for diffracted peak and θ is the angle of diffraction between two planes. From the calculations using Debye- Scherer's formula the average grain size for undoped ZnO was 25.93 nm, and average grain size for 5% Fe doped ZnO was calculated as 23.46 nm. The formation of hexagonal wurthzite ZnO nanoparticle formation matches with match scan data of JCPDS card number 00-036-1451.

3.2 Scanning Electron Microscopy (SEM) study

The material undoped ZnO and 5% Fe- doped ZnO, prepared by co-precipitation method. Both these materials were characterized by scanning electron microscopy (SEM). Since SEM is useful feature to

investigate the surface properties of the prepared material such as texture, pores, size of the pores, appearance of the crystals, grains and particles over the surface lattice of the material under investigation. The SEM micrographs of the prepared material 5% Fe- doped ZnO is as depicted in **Figure 3 a-f**. From the SEM images it can be seen that the prepared material has homogeneous surface area, with varied size pores over the lattice; grains of the different size are closely agglomerated together. From the SEM images the material is observed to be porous in nature. Since, the material is consists of various size of pore or interstitial cavities throughout the surface lattice. Thus, the fabricated material has excellent porosity, which is essential in the catalytic applications. The fabricated material is applied in the photocatalytic applications. Thus, the porosity of the material is prime parameter for holding the dye molecules so that the effective redox mechanism might be possible between host and guest lattice i.e. Fe/ZnO and tested dye methylene blue. The interstitial cavities hold up the dye fragments for effective redox process and the ease dye degradation will be occur with the rapid rate. Thus, the prepared catalyst is found to be efficient at the photocatalytic route in faster diminishing the MB dye fragments over the porous surface of catalyst.

3.3 High resolution transmission electron microscopy (HR-TEM) study

The fabricated catalyst materials viz. undoped ZnO and 5% Fe-doped ZnO were investigated by means of high resolution transmission electron microscopy (HR-TEM). The **Figure 4 a-d** shows HR-TEM images of the prepared material ZnO and 5% Fe-doped ZnO. While **Figure 4 e-f** represents the selected area electron diffraction (SAED) pattern for the prepared materials. The images a,c as represented in **Figure 4** shows HR –TEM images undoped ZnO material and images b,d depicts the HR-TEM images for 5% Fe-doped ZnO. The HR-TEM images of both these materials depict the various size grains of the fabricated material. The material ZnO belongs to the wurtzite according to the XRD data analysis. The HR-TEM images shows the topology of the fabricated material ZnO with the different grains with nearly spherical in case undoped ZnO and roughly rod shaped arrangement for the iron modified ZnO material implying some structural, grain changes in case of modified ZnO material. As per the TEM data obtained for the prepared material shows the typical formation of wurtzite ZnO material [57, 58]. From the characteristics plane distance data of 2.78, 2.55 and 2.40 Å⁰, the selected area diffraction pattern data correlated with (100), (002), 101 planes are the typical planes for the wurtzite ZnO material. Moreover, the SAED pattern of both the prepared material shows the bright spots appear in the continuous ring form suggest that the prepared material belongs to the typical polycrystalline type material.

3.4 Energy dispersive spectroscopy (EDS) study

The prepared catalysts were investigated by energy dispersive spectroscopy (EDS) for chemical composition analysis. The EDS spectrum for both these materials is as depicted in **Figure 5 a-b** for undoped ZnO and Fe³⁺ modified ZnO. Since the zinc oxide material doped with iron hence the doping percentage was confirmed from EDS. The EDS spectrum as represented in **Figure 5-b** for Fe³⁺ modified ZnO. The peaks for iron and zinc can be easily seen from spectrum. The elemental zinc resolved at 9.0 KeV, whereas elemental iron resolved at 6.4 KeV. The chemical composition of iron modified ZnO is

represented in the inset image of figure 3-b. The elemental composition is found in stoichiometric ratio as expected. The undoped ZnO EDS spectrum is represented in figure 4-a. The EDS results for both the materials undoped ZnO and Fe³⁺ modified ZnO is in good agreement with the reported ZnO data.

3.5 Optical properties studies

The UV–vis absorption spectra of ZnO and 5% Fe/ZnO nanomaterials were recorded in diffuse reflectance spectral (DRS) mode. **Figure 6 a-d** shows the absorption spectra of produced synthesized ZnO and 5% Fe/ZnO nanomaterials recorded at room temperature. The current study's improved visible light absorption of MB dye is due to the generation of more photo-excited electrons in the 5% Fe/ZnO nanomaterial, which has the potential to improve MB dye degradation efficiency. In compared to the undoped ZnO nanostructure, the UV–Vis spectral findings clearly demonstrated that a substantial red shift had occurred in the 5% Fe/ZnO nanomaterial. The presence of ferric ion doping is thought to be the cause of the red shift. The **Figure 6 c-d** shows the direct optical band gap (E_g) of synthesized ZnO and 5% Fe/ZnO nanomaterials obtained from the relation, $\alpha h\nu = A(h\nu - E_g)^{1/2}$ where A is a constant, α is the absorption coefficient and $h\nu$ is the energy of the incident photon. Tauc's plot was drawn between $(\alpha h\nu)^2$ and $h\nu$ and the value of E_g was obtained by extrapolating the linear region of the plot to $\alpha=0$. For ZnO and 5% Fe/ZnO nanoparticles, E_g was determined to be 3.30 eV and 3.09 eV, respectively. The reduced band gap indicates an unavoidable electron transfer process, which leads to easy photocatalysis of MB dye and ethanol gas sensing behaviour.

3.6 Brunner- Emmet and Taylor (BET) study for surface area

Both the prepared catalysts have been utilized as photocatalyst, which is a surface phenomenon. Since for photocatalysis reaction surface area provided by the catalyst is crucial parameter for redox mechanism between adsorbed dyes over the catalyst surface. Hence, the prepared catalysts were analysed by Brunner- Emmet and Taylor (BET) adsorption isotherm for investigating the surface area of both photocatalysts. The BET analysis mainly was carried out to investigate pore volume, pore radius, porosity and overall surface area of the fabricated materials. As per data obtained from nitrogen adsorption-desorption experiment regarding the important characteristics of the prepared materials are as represented in **Table 1**. The nitrogen adsorption-desorption curves plotted between parameters relative pressure and adsorbed volume of nitrogen gas for both materials undoped ZnO and Fe³⁺ modified ZnO depicted in **Figure 7**. As per the data obtained it was observed that the adsorption isotherm for both catalysts belongs to type IV out of six categories of BDDT related to isotherm adsorption. The type adsorption isotherm is typical category of porous material. The total surface area calculated from BET(S_{BET}), pore volume (V_p), pore diameter (D_p), correlation coefficient (R^2) characteristics are as shown on **Table 1**.

Table 1 BET surface area, pore volume and pore diameter of Undoped ZnO and 5% Fe³⁺ doped ZnO

Prepared Material	Surface Area (m ² /g)	Pore volume (cc/g)	Pore radius (Å)	R ²
Undoped ZnO	46.50	0.357	70.54	0.9889
5% Fe ³⁺ doped ZnO	60.65	0.391	75.12	0.9998

3.7 Photocatalysis study

The prepared materials undoped ZnO and iron modified ZnO were investigated for photocatalysis study over methylene blue (MB) dye. The photocatalytic degradation of MB dye was investigated by means of photocatalytic reactor equipped with mercury lamp possessing power of 260 Watts. The reactor additionally consists of magnetic stirrer, chiller for water circulation, safety cabinet along with control panel, double jacket quartz immersion well. During the experiment there are plenty of changes in overall dye concentration. The changes in MB dye concentration were recorded by means of double beam UV-spectrophotometer possessing the UV range of 200-800 nm. The pH is another prime parameter which decides degradation of dye in acidic or basic condition. The pH was monitored with digital pH meter make lab India possessing glass electrode. Before using the pH meter it was standardise by buffer solution of pH 3, 9 and 12. Final absorbance for supernatant dye liquid was recorded after centrifugation to avoid the interference of catalysts molecules.

The photocatalytic degradation of MB dye was calculated from **Equation 1**

$$\% D = (C_0 - C_t) / C_0 * 100 \quad \text{———— Equation 1}$$

C_0 is initial concentration of MB dye and C_t is the concentration of MB dye at time t.

3.8 Parameter optimization for photocatalytic degradation of MB dye

The photocatalytic degradation of methylene blue dye was estimated at λ max 664 nm. After complete investigation of all the parameters for MB dye degradation at undoped ZnO and Fe³⁺ modified ZnO the important degradation parameters were fixed. The optimised dye concentration was 30 ppm, pH = 8.0 (for undoped ZnO and Fe³⁺ modified ZnO photocatalysts), catalysts concentration of 0.8 g/L. The overall results obtained from photocatalytic degradation of MB dye are presented in following parameters.

3.9 Effect of Catalyst concentration

Catalyst dose optimization is an important parameter for catalytic activity. Hence, the optimum catalyst dose for catalytic activity is essential parameter. In the present experiment undoped ZnO and Fe³⁺ doped ZnO both catalyst were optimised for concise quantity required for photodegradation of MB dye. The catalyst dose optimization was done in batch experiment. The catalyst concentration was monitored from 0.2 g to 0.8 g for both of the catalyst for different dye concentration of MB dye from 30 ppm to 90 ppm. In case of undoped ZnO catalyst, with increase catalyst loading from 0.2 g L⁻¹ – 0.8 g L⁻¹ for

lower MB dye concentration, the optimum degradation from 70.12% to 90.5 % was obtained. The same batch experiment was repeated for Fe^{3+} doped ZnO catalyst to compare the photocatalytic activity of both prepared catalysts. In case of Fe^{3+} doped ZnO for catalyst dose of 0.2 g L^{-1} – 0.8 g L^{-1} the optimum degradation of 81.20 % to 96.40 % was achieved. From the observation of degradation study it was observed that in case Fe^{3+} doped ZnO catalyst at higher dose i.e. 0.8 g L^{-1} the highest degradation was obtained in comparison to the undoped ZnO. The doped ZnO is found more rapid and efficient at MB dye degradation. Since, enhancement of catalyst dose leads generates more active sites which generate more electron hole pairs in contact with water and atmospheric oxygen. The declined band gap of Fe^{3+} doped ZnO ($E_g = 3.09 \text{ eV}$) is another worth factor in contrast to undoped ZnO. Because declined band will provide easy platform to transfer the electrons from valence band to conduction band, these electron in combination with water and oxygen generates reactive species like superoxide radicals, hydroxide radicals and hydrogen peroxide radicals. These reactive oxygen species (ROS) are the main keys for effective degradation of MB dye, which mineralizes the MB molecules to smaller molecules. This effective redox mechanism is somewhat delayed in case of undoped ZnO hence in comparison to doped ZnO the photocatalytic activity for undoped ZnO is observed to be sluggish. The effects of catalyst dose are represented in **Figure 8 a-b**.

3.10 Effect of change in pH over MB degradation

The reaction pH is another prime parameter in catalytic applications. Since, surface catalysis greatly affected by change in pH. Most of reactive oxygen species (ROS) and reaction equilibrium is controlled by variation in pH. Before starting the experimental set of for pH the zero point charge (ZPC) of the material was estimated by standard ZPC determination method. Here 0.1 M HCl and 0.1 M NaOH solutions were used to set pH range from 0 to 12 with addition of fix catalyst amount 0.1 g to each reaction vessel consists of pH 0 to 12. Then with the addition of catalyst the reaction vessels were kept for 24 hours and next pH was measured of each reaction vessel. The graph was plotted between fixed pH and pH after 24 hours. The intercepting point is the ZPC for each catalyst. The pH_{ZPC} estimated was 7.5. After adding the catalyst undoped ZnO and Fe^{3+} doped ZnO separately from pH 1- 12 reaction vessels, the reaction mixture was stirred for 30 minutes to attain the adsorption-desorption equilibrium and then each reaction vessels were subjected for UV-irradiation to measure absorbance of each reaction vessel. The graphs of variation in pH for both catalysts are as represented in **Figure 9 a-b**. Now as per generalise thumps rule the $\text{pH} < \text{pH}_{\text{ZPC}}$ the catalyst surface is positively and hence it attracts the negative dye species. Hence the dyes carries net negative charge would attracted between this ranges their degradation is expected within pH_{ZPC} value. But, in this investigation MB dye being basic in nature has net positive charge and expected to be attracted in the $\text{pH} > \text{pH}_{\text{ZPC}}$, i.e in the basic range from 7.5 onwards. As per the results obtained the % degradation of MB dye is very slow from 1 to 7 pH as represented in **Figure 8 a-b**. But with increment in pH beyond 7.5 the rapid degradation from 7.5 to 8.0 pH was observed and almost all the dye concentration was degraded around pH 9.0 The lower degradation of MB dye below ZPC is attributed to the positive surface. The repulsion between positive surface of ZnO, Fe^{3+} doped ZnO and positively charge MB dye creates electrostatic repulsive force. Hence MB dye

particles not forms the constructive bonding between positively charge catalyst surface and MB dye. Ultimately this repulsive force is responsible to lower degradation at $\text{pH} < \text{pH}_{\text{ZPC}}$.

3.11 Effect of Initial dye concentration

To set optimum degradation parameter the dye concentration examination is important aspect in photocatalysis study. This parameter is useful to determine overall contact time and rate of the reaction under study. In the present investigation MB dye concentration was altered from 30 mg L^{-1} to 90 mg L^{-1} (30 ppm to 90 ppm) with optimum catalyst dose of 0.8 g fixed for all MB dye concentration. From the overall study of dye concentration it was found that with enhanced concentration of MB dye from 30 ppm to 90 ppm, the rate of degradation by the tested catalyst for MB was declined. The photocatalytic degradation of MB dye for concentration of 30 ppm to 90 ppm at undoped ZnO was observed to be 90.5% to 65.40 % with fixed catalyst dose of 0.8 g L^{-1} . In case Fe^{3+} modified ZnO, for MB dye concentration of 30 to 90 ppm, the rate of Photocatalytic degradation was found to be 96.40% to 80.20 %. With rise in concentration of MB dye the accumulation of MB dye over the catalysts surface observed to increase which is in turn quenching between the upper energy state MB molecules also increases and due to this the photocatalytic degradation of MB dye decreases with increase in concentration. In addition to that rise in concentration of MB dye restrict the photons from irradiated light to come into direct contact with catalyst surface due to accumulation of dye particles over catalysts surface. The presence of more dyes particles on the surface of catalysts will also abate the active sites of catalysts. Due to inactivity of catalyst with increase in MB dye concentration the photocatalytic degradation is found to be decrease. The diagrammatic presentation of effect of initial dye concentration is as depicted in **Figure 10**. Inset diagram showing the variation of MB dye from 10 mg L^{-1} to 100 mg L^{-1}

3.12 Contact time study

The contact time investigation is a prime parameter, which gives the actual time required for the photocatalytic degradation of dyes at the various concentrations of tested dyes. The effect of contact time for various concentration of MB dye from 30 mg L^{-1} to 90 mg L^{-1} is as depicted in **Figure 11 a-b**. The dye degradation initially occurs very faster and almost 80 % of MB dye is degraded in 90 minutes and reach to equilibrium, while the 20% of MB dye concentration degraded in next 10 minutes with sluggish rate. In the initial stage the degradation of MB dye occur at the faster rate, because availability of more surface active site of the undoped and doped ZnO catalyst, these surface active sites promotes the catalyst for degradation at the faster rate. As the photocatalysis proceeds there is accumulation of dye particle or molecules over the catalyst surface, which restrict the effective photon striking with catalyst surface. In case of higher concentration of MB dye the available active sites and effective photon interaction even more decreases and hence with increase in concentration of MB dye and time the photocatalytic degradation of MB dye decreases. The parameters set required for effective degradation of overall concentration of MB dye are catalyst dose 0.8 g L^{-1} , $\text{pH} = 8.0$, MB dye concentration of 30 mg L^{-1} . By keeping all these parameters constant the overall contact time for the reaction is observed to be 100 minutes. With this time there is overall mineralization of MB dye is observed.

3.13 Detection of ROS by scavenging study

During the course of photocatalysis, the reactive oxygen species (ROS) are formed which play a vital role in the dye degradation process. The ROS generated mainly are hydroxide radicals ($\text{OH}^\cdot$), $\text{O}_2^\cdot$, h^+ etc. The scavengers are mainly used to capture the ROS to confirm the generation of these species. Most commonly used species for capturing these ROS species are ethylene diamine tetra acetic acid (EDTA), Benzoquinone (BQ = $\text{O}_2^\cdot$ scavenger), isopropyl alcohol (IPA = $\text{OH}^\cdot$ scavenger) etc. In the present research scavenging study was performed for the prepared catalyst 5% Fe^{3+} doped ZnO catalyst. The overall scavenging study result is as depicted in **Figure 12**. Initially for the scavenger IPA rate of photocatalytic degradation found to be decline to 10%, when it was added to the reaction vessel containing the 5% Fe^{3+} doped catalyst with specific MB dye concentration. Simultaneously when Benzoquinone and ethylene diamine tetra acetic acid scavengers were added to the same parametric conditions the rate of MB dye degradation was further found to be decrease with 16.10 % for BQ and 20.80% for EDTA scavenger. From the overall experiment it can be concluded the generation of ROS are trapped by scavengers and hence there is decrease in the photocatalytic degradation of MB dye for 5% Fe^{3+} doped ZnO catalyst. EDTA has more scavenging effect in comparison to the other scavengers tested in the present research, implying that the scavengers have potential impact to trap the ROS generated in the photocatalytic mechanisms.

3.14 Reusability performance of prepared photocatalysts

The reusability test is important parameter to confirm the repeatability of the tested results for the fabricated catalyst. The prepared catalyst in this study i.e. 5% Fe^{3+} doped ZnO catalyst was utilized for reusability study as per the optimized parameter such as tested (MB) concentration was 30 ppm, pH= 8.0 and catalyst dose of 0.8 g/L under UV –Visible illumination consists of 260 watt voltage. Initially, the catalyst was recovered from the reaction vessel which is left after contact time study. The 5% Fe^{3+} doped ZnO catalyst was firstly filtered with Whatmann filter paper 41, then washed with acetone and hot water and then dried under IR lamp for 30 minutes. The dried catalyst was utilized for further reusability test. The reusability test was performed in four runs to make the firm conclusion of the obtained results. In the first run for 5% Fe^{3+} doped ZnO catalyst the MB dye degradation was observed to be 96.70 %. Before starting second run the catalyst was recovered from reaction vessel and same procedure was followed as explain earlier to dry the catalyst and further use. In the second run after optimizing the reaction parameters the MB dye degradation was found to be 94.10 %. In the third and fourth run the % degradation of MB dye for same recovered catalyst was found to be 92.50 % and 91.80 %. From the overall degradation study it was observed that the fabricated catalysts 5% Fe^{3+} doped ZnO is very stable and firm catalyst at the degradation of MB dye with negligible % degradation variation of MB dye. The decrease in MB dye at every run is accredited to decrease in surface activity of catalyst with the multiple uses of catalyst, decrease in surface area, as well as decrease in catalyst concentration during the filtration process. From the overall test of reusability test it can be concluded that 5% Fe^{3+} doped ZnO catalysts is highly effective, accessible and stable catalyst for MB dye degradation. The reusability results over MB dye are as represented in **Figure 13**.

3.15 Comparison of the prepared catalyst

The ZnO based materials are extensively utilized for different catalytic processes, as well as the ZnO based nanocomposites are also used for photocatalytic degradation of different dyes, azo dyes, pesticides, herbicides, colour shades, effluent from pharmaceutical and chemical waste and industrial effluents. The comparison of the photocatalysis is made on the basis of similar types of ZnO based materials used as photocatalysis for degradation of various contaminants and dyes reported by researchers so far. The prepared catalyst utilized as photocatalyst for the deterioration of MB dye. The results are quite successful for the degradation of MB dye, in 30 ppm dye concentration with slightly alkaline condition with the contact time of 100 minutes and catalyst dose of 0.8 g L⁻¹. The comparative study for photocatalytic degradation of various dyes against the ZnO based materials is as represented in **Table 2**.

Table 2 Comparative study of Fe³⁺ doped ZnO catalyst against the ZnO based materials for the reported photocatalytic degradation of different dyes

ZnO Based catalysts	Method of preparation	% D	Radiation source	Dye	Irradiation time (min.)	Year	Ref
S-doped ZnO	Co-precipitation	97.0	Halogen light	Rhodamine B	150	2020	59
ZnO	Sol-gel	99.70	Hg-vapour lamp	Azo dyes	110	2017	60
Fe/ZnO	Sol-gel	92.0	Hg-vapour lamp	Methylene blue	140	2019	61
Cu/ZnO/rGO	Hydrothermal	90.30	Sunlight	Aq.NH ₃	-	2018	62
Ag/ZnO	Co-precipitation	96.0	Hg-vapour lamp	Methylene blue	80	2020	63
Ag/ZnO	Sol-gel	96.50	Xenon lamp	Methylene blue	120	2021	64
ZnO/TiO ₂	Surfactant method	36.5	Hg-vapour lamp	Phenol	180	2018	65
Cu-Ag/ZnO	Precipitation	95.0	Hg-vapour lamp	Methylene blue	180	2021	66
5% Fe doped ZnO	Co-precipitation	96.70	Hg-vapour lamp	Methylene blue	100	Present Research	

3.16 Gas sensing study of undoped ZnO and Fe³⁺ modified ZnO sensors

The prepared material i.e. 5% Fe³⁺ doped ZnO was utilized as a gas sensor for the detection of ethanol vapors. Gas sensing properties of the fabricated film sensor of 5% Fe³⁺ doped ZnO was investigated at elevated temperature from 250 °C to 30 °C with the time interval of 20 °C in cooling cycle. The gas sensing study was operated at each optimum temperature to get optimum response of the gas sensor. The gas sensing study of the fabricated sensor was executed in home built static gas sensor device as depicted in **Figure 14**. The electrical resistance of the sensor was measured in presence of air (R_a) and gas (R_g). The circuit diagram consists of glass chamber, inside the chamber there is sample compartment at which the film sensor is mounted. The thermocouple is fixed around sensor which is able to sense the temperature across the sensor film material recorded by digital temperature controller unit. The digital multimeter with model number CIE-705 was utilized to record voltage output given by the sensor material. The calculated gas concentration in ppm concentration was allowed to pass through the glass chamber at the particular temperature; the response was recorded by computerized multimeter. After recording the reading the gas residue was removed for further readings. After overall study gas response was calculated by using **Equation 2**.

$$S\% = \frac{R_a - R_g}{R_a} \times 100 \text{-----Equation 2.}$$

The fabricated sensor 5% Fe³⁺ doped ZnO was utilized as a gas sensor for ethanol vapors (AR grade ethanol was gently heated over magnetic stirrer, the vapors were collected and utilized in the present research). The gas sensing results obtained for ethanol vapors against 5% Fe³⁺ doped ZnO sensor is as depicted in **Figure 15-a**. The ethanol vapors were investigated from 100 to 1000 ppm concentration. The highest response (88.90 %) of the sensor was recorded at 600 ppm gas concentration for tested sensor at 120 °C. From figure 14-a it can be observed that, with every increment of the ethanol gas concentration from 100 ppm to 600 ppm there is gradual enhancement of gas response. But, there is steady decrease of the gas response is observed from 700 to 1000 ppm of ethanol gas vapours for the tested sensor 5% Fe³⁺ doped ZnO. The decrease in the gas response by the sensor with increase in gas concentration is attributed to the tendency of the sensor towards the saturation point for the tested gases, as well as with increment in the gas concentration no successful quenching between adsorbate ethanol gas vapours and adsorbent 5% Fe³⁺ doped ZnO sensor this behavior is also responsible for unperceptive redox mechanism over the sensor surface. The sensor was also tested at the lower ethanol gas concentration from 10-100 ppm to check the gas response at lower concentration. **Figure 15-b** depicts gas response for ethanol vapors at elevated gas concentration for the fabricated sensor. From figure it can be seen that the gradual increase in the gas response for 10-100 ppm ethanol vapors.

For the effective working of the sensor, the gas sensing parameters must be reproduced by the sensor to draw firm conclusion of the designed sensor against tested gases. The reusability experiment was performed for the fabricated sensor at optimum conditions like gas concentration of 600 ppm, temperature 120 °C and identical experimental setup etc. The reusability results for the tested sensor is

as depicted in **Figure 15-c**, the results are recorded with the time interval of days in four cycles. From the results obtained over reusability testing, the sensor shows slight variation in the gas response over the ethanol vapors tested as 600 ppm. Because, when these sensors were repeatedly tested for reusability, it was discovered that the covering surface activity had decreased due to gas vapour exposure. Each run causes the adsorption characteristics of the sensor surface to decrease. As a result, a modest decrease in sensitivity response was observed throughout the study for every recycling.

Additionally, the fabricated sensor was also examined for gas sensing response at various operating temperature range from 210 °C to 30 °C. The data obtained from the study is as depicted in **Figure 15-d**. From figure it can be seen that the sensor shows good response from 30 °C to 120 °C, the highest response is recorded at 120 °C with 88.90 % at 500 ppm ethanol gas vapour concentration. The sensor tested to higher temperature and it was observed that the sensor is not much sensitive to ethanol vapors and gas response graph is observed to be declined after 120 °C.

The fabricated sensor material 5% Fe³⁺ doped ZnO was also investigated under humidity environment. The relative humidity plays an important role in the food industries, research and development fields, moisture sensitive units and apparatus etc. Hence humidity effects over the prepared sensor are prime topic of investigation due the various impacts of humidity on gas response. In the present investigation the fabricated sensor 5% Fe³⁺ doped ZnO was exclusively utilized as sensor for ethanol vapours. **Figure 16-a** depicts the effect of humidity on the gas response of ethanol for fabricated sensor 5% Fe³⁺ doped ZnO. In the overall observations it was observed that with rise in humidity the gas response for the fabricated sensor was found to be increased up to 70% relative humidity. Thereafter there is continuous declined the gas response for the sensor was observed. In most of the cases the relative humidity and resistance of metal oxide semiconductor are inversely proportional to each other i.e. resistance of the film sensor declines with rise in relative humidity as depicted in Figure 16-b. According to direct mechanism proposed by Heiland and Kohl proven that increase in surface conductivity in the presence and water vapours (RH) imparted due to decline in resistance in presence of humidity. This is due the fact that there is quantitative effect of adsorbed water molecule over the sensor surface responsible for charge carrier concentration. It can be simplified that the presence water in the form of humidity enhances the background of free charge carriers generated in presence of adsorbed oxygen in the vicinity of sensor surface responsible to alter the output signal of the sensor material. In overall conclusions it can be stated that the water vapors in the form relative humidity acts as ideal conditions for adsorption of O₂, free electrons and various vacancies. Thus, in final extent the water adsorption certainly speed up adsorption over the sensor surface which is in turn responsible to tune the output signal of the sensor material.

The response and recovery is another prime investigation for the developed sensor. Here the fabricated sensor was investigated for these two parameters under the optimized conditions like 500 ppm ethanol vapors concentration, definite temperature etc. The sensor showed very quick response and recovery for the ethanol gas vapors against the fabricated sensor material 5% Fe³⁺ doped ZnO implying that the

fabricated sensor fits to sense the moderate concentration of ethanol vapors with rapid response and recovery parameters. The response and recovery curves for the fabricated sensor is as depicted in figure 16-c.

Conclusions

In the summary for the portrayed work for the multifaceted material 5% Fe³⁺ doped ZnO used here for environmental remedial applications. The iron modified ZnO material with improved surface area demonstrated by BET and tuned band gap, with higher porosity material was fabricated by simple and cost effective co-precipitation method. Whereas the thick film sensor was design by lithographic technique via screen printing methodology. The higher porosity possessing Fe³⁺ modified ZnO material is found to be very excellent towards the degradation organic dye methylene blue. As the data obtained from present investigation the material aims to degrade the MB dye with high efficacy and minimum time span, which is good step towards environmental remedy applications in the small scale laboratory batch processes. The excellent Photocatalytic activity towards the MB dye is attributed to the numerous virtues like plenty of voids over catalyst surface, concise photoelectric conductivity, sufficient active sites and high surface area, implying that the material has excellent potential in actual contaminated water purification. Additionally the fabricated sensor material has excellent sensing performance for ethanol vapors at moderate gas concentration. The humidity experiment demonstrates that the material has good ability to sense ethanol vapors in humid atmospheres also. Thus iron modification over ZnO is found to be successful for the material and it can be used as multifaceted material over the environmental based applications.

Declarations

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Conflict of Interest

Authors declared that they have no conflict of interest for the present research

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Figures

Figure 1

General characteristics of methylene blue dye used in present research

Figure 2

XRD pattern of undoped ZnO and 5% Fe modified ZnO material

Figure 3
 (a-c) SEM micrographs of undoped ZnO; (d-f) 5% Fe modified ZnO material

Figure 4

(a-b) HR- TEM images of undoped ZnO; (c-d) 5% Fe modified ZnO material, (e) SAED pattern for undoped ZnO, (f) SAED pattern for 5% Fe doped ZnO

Figure 5

(a) EDS spectrum of undoped ZnO material, (b) 5% Fe modified ZnO material

Figure 6

(a) UV-Visible absorption spectrum of undoped ZnO (b) Tauc plot of $(Abs-h\nu)^2$ versus $h\nu$ to calculate E_g of undoped ZnO, (c) UV-Visible absorption spectrum of 5% Fe doped ZnO, (d) Tauc plot of $(Abs-h\nu)^2$ versus $h\nu$ to calculate E_g of 5% Fe doped ZnO

Figure 7

Brunauer-Emmett-Teller (BET) N_2 adsorption-desorption curves for (a) undoped ZnO (b) 5% Fe^{3+} /modified ZnO

Figure 8

(a) Effect of ZnO catalyst dose on % degradation of MB dye for different MB dye concentrations, (b) Effect of Fe^{3+} doped ZnO catalyst dose on % degradation of MB dye for different MB dye concentrations

Figure 9

Effect of pH on degradation of MB dye for undoped ZnO and Fe³⁺ doped ZnO

Figure 10

Effect of initial dye concentration for degradation MB dye for undoped ZnO and Fe³⁺ modified ZnO at 0.8 g L⁻¹ and pH 8.0

Figure 11

(a) Contact time study for MB dye degradation at undoped ZnO, (b) Contact time study for MB dye degradation at Fe³⁺ doped ZnO at pH= 8.0, catalyst dose 0.8 g/L

Figure 12

Radical scavenging studies for MB dye at 5% Fe³⁺ doped ZnO photocatalyst

Figure 13

Reusability study of 5% Fe³⁺ doped ZnO at MB dye in multiple runs

Figure 14

Static gas sensing circuit diagram used in present research

Figure 15

(a) Gas response of 5% Fe³⁺ doped ZnO sensor for various gas concentration of ethanol, (b) PPM variation of ethanol gas vapours from 10-100 PPM, (c) reusability study for 5% Fe³⁺ doped ZnO sensor at ethanol vapors, (d) effect of temperature on gas response for ethanol vapors.

Figure 16

(a) Effect of relative humidity on gas response of 5% Fe³⁺ doped ZnO sensor, (b) Effect of relative humidity on electrical resistance of 5% Fe³⁺ doped ZnO sensor, (c) Response and recovery study for ethanol vapours,

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