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Research Article

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Fabrication of ZnO nanocatalyst as an excellent heterogeneous catalyst applicant for Methyl Orange dye degradation in aqueous medium.

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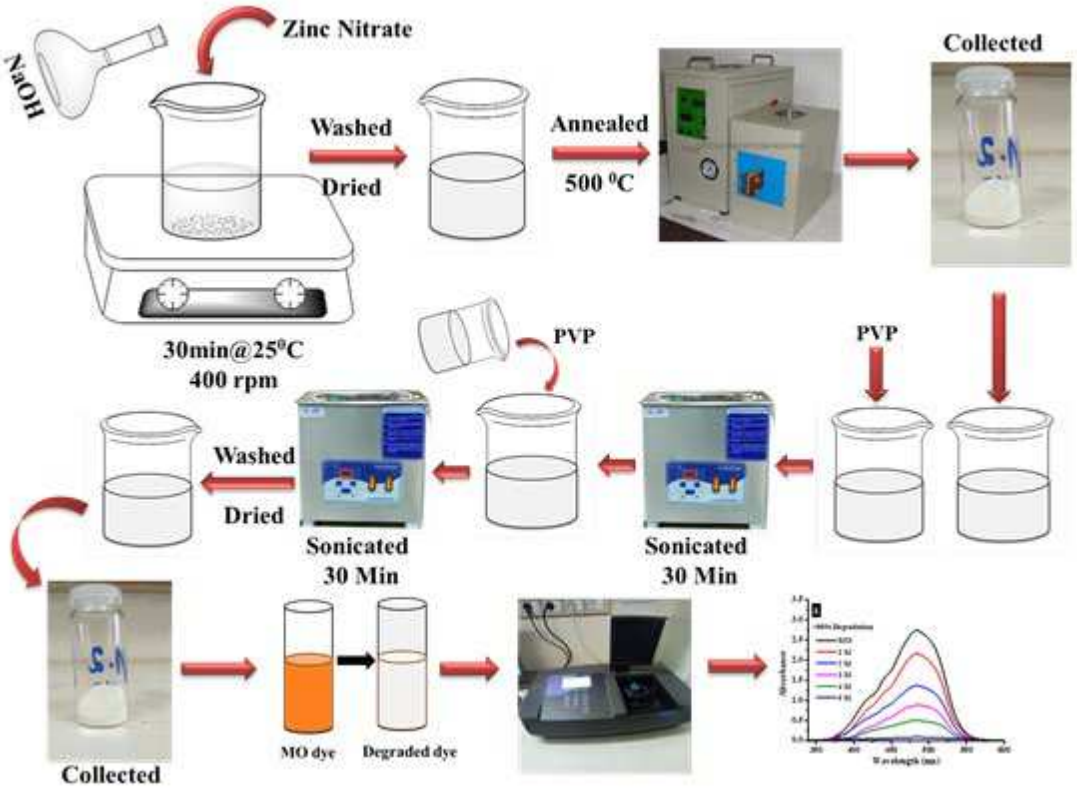
Abstract

The current paper describes the fabrication of an excellent and economical heterogeneous nanocatalyst for the degradation of methyl orange dye in aqueous medium. ZnO/PVP nanocatalyst has been successfully synthesized by the chemical degradation route, followed by ultrasonication. The size, shape and crystalline structure of synthesized ZnO/PVP nano composite was characterized by UV-visible spectroscopy, X-ray diffractometry, Dynamic Scattering Light, Zeta Potential, Fourier transform infrared spectroscopy, Scanning Electron Microscope, Energy Dispersive X-ray and X-ray photoelectron spectroscopy. To authenticate the catalytic efficiency of nanocatalyst, the fabricated ZnO/PVP nanocompoiste was screened for methyl orange dye degradation. Finally, synthesized nanocatalyst exhibited an admirable catalytic efficiency, above 98% of methyl orange degradation observed just in 90 seconds using least catalyst dose (150µg) in aqueous medium. The engineered ZnO/PVA nanocomposite shows several advantages over traditional methods for the degradation of hazard and toxic dyes, such as high percentage degradation, short time and minimum dose of nano catalyst and excellent reusability. It is suggested that this rare nanocatalyst may be used successfully on commercial level for degradation toxic pollutants.

Keywords: ZnO/PVP nanocomposites, heterogeneous Catalysis, Chemical Degradation method, Methyl Orange.

Graphical Abstract



***Scheme 1**: Synthesis layout of ZnO/PVP nanocatalyst and Methyl orange degradation mechanism.*

Introduction

The world's population is increasing globally day by day and the demand for fresh water will increase in the future. As per reports of WHO, 80% of diseases are associated with water in the developing countries. Polluted water causes diseases. Bacterial and viral pathogens are responsible for approximately 3.3 million deaths (Ali et al., 2020). Anthropogenic activities waste a lot of water with many impurities. These impurities come out from fertilizers, pesticides, dyes, Heavy metal, germs, etc. These produce heavy effects and some of them may be carcinogenic. These pollutants persist in colloidal, suspended or soluble form in water. Dyes are being widely used by textile, leather, pharmaceuticals, and food, photography and cosmetics industries. These industries have high-colored effects that can lead to water pollution. Over ten thousand dyes are available commercially in the world. A dye has complex structure and it creates problems in its degradation. Most of dyes are toxic and are carcinogenic to both aquatic and to humans lives (Kumar et al., 2014a, Kumar et al., 2014b). Dyes are responsible for lung, skin and respiratory disorders. Even a minor amount of dyes can be readily noticed and could be the source for embarrassment of photosynthesis. Dyes are extremely stable to the traditional methods for the entire color removal and degradation. Several methods and techniques like reverse osmosis, coagulation-fluorescence, membrane filtration and biological degradation, electrochemical and solvent extrusion processes are used for cleaning dye waste. The increasing cost of these given methods requires alternative methods that are reliable in combination with the green nature. These methods for treating water are quaint. In these methods, only pollution is transferred from one stage to another. This is why they face different types of pollutants that demand more treatment. The chromophore setting of the dye is the traditionally homogeneous arrangement. Therefore, adsorption is accepted in place to treat water containing dyes. The Adsorption technique is simple, highly effective and reusable so that it is more applicable (Pinky et al., 2015, Kumar et al., 2014c, Gupta et al., 2012, Ameta et al., 2013).

Nano materials undergo revolutionary changes in nano-technology. Nano materials are used to treat water because of their attractive physico chemicals. They can be specially specific and reusable legends for poisonous ions in molecules, inorganic and organic solutes in aqueous media. Using new materials to purify water can create huge opportunities, as they create large surface areas. Numerous properties of ZnO NPs, including electric and catalytic, depend on the shape and size. Different methods can be used to produce ZnO nanoparticles like thermal conduction, homogeneous precipitation, spray pyrolysis, sol-gel processing, and

mechanical milling, hydrothermal, microwave, reflux and chemical synthesis. ZnO is an environmentally friendly material. It is used in practical applications as an effective photo catalyst which is sensitive to UV light. Chemical reactions are also created by catalyst, the generated electron/hole pairs. The structure of relatively harmless end products represents one of the more attractive features of this method (Chen et al., 2011, Roy and Mondal, 2014). Methyl orange ($C_{14}H_{14}N_3NaO_3S$) belongs to an anionic azo dye family. Methyl orange has been widely used in innumerable industries including printing, paper, textile, food, leather, pharmaceutical as well as photography. Conversely, methyl orange (MO) dye causes environmental serious pollution, known as carcinogenic (Chen et al., 2008). MO dye is soluble in water and has good stability and possesses distinct color. Photocatalytic degradation of dyes containing wastes has also been extensively described (Al-Qaradawi and Salman, 2002, Wang et al., 2004, Liu et al., 2006, Baiocchi et al., 2002, Kansal et al., 2007, Prevot et al., 2004, Liu et al., 2005). Maximum absorption of methyl orange was reported in the range of 460-470 nm. This compound is orange and red in the basic and acidic medium respectively. MO belongs to group of azo dyes that are widely used for colorization in many industries. ZnO/PVP nano composite were incorporated in the precipitation and ultra-sonication method, and used to remove Methyl orange dye from water medium. There are a large number of studied reported for the degradation of Methyl Orange by various scholars in which they used cheap metal oxides as catalyst. Photo degradation of methyl orange (10 ppm), Congo red (10 ppm), and Eosin Y (20 ppm), dyes in existence of H_2O_2 using $Fe_2Mo_3O_{12}$ catalyst with excess MoO_3 was carried out by Suresh P et al. Around 97.4%, 100, and 96.6, degradation was observed within 45, 45 and 120 min, respectively (Suresh et al., 2014). Additionally, Zhang & Oh (2009) investigated decomposition effect of dyes underneath several circumstances. They selected non-biodegradable dyes such as Methyl Blue (MB), Rhodamine B (Rh B) Methyl Orange (MO) using Fe-ACF/TiO_2 catalyst in the existence of H_2O_2 as a reducing agent (Zhang and Oh, 2009). Wang et al. synthesized ZnO NPs via thermal evaporation method and chemical deposition method with numerous size scales; MO degradation was investigated and results revealed 80% degradation in 120 mints (Wang et al., 2007). Hong et al. reported the synthesis of Fe3O4/ZnO nanoparticles via precipitation method and observed 83% de-colorization of methyl orange dye in 360 mints (Hong et al., 2008). Fu et al. prepared ZnO-Cu NPs and 88% degradation of MO was noticed in 240 mints (Fu et al., 2011). Substrate of Indium-Tin capped ZnO Nano rods was prepared and investigated for the degradation of MO dye and 71% dye was degraded observed in 2.5 h (Zheng et al., 2011). J Dhanalakshmi et al. reported the bromophenol blue and methyl orange

dyes degradation by TiO_2 catalyst, about 85.51%and 67.12% degradation was achieved in 240 mins using 10 mg catalyst and 10 ppm dye (Dhanalakshmi and Padiyan, 2017). Eyasu et al. fabricated Cr capped ZnS NPs and reported 65% and 74.28% degradation of MO dye under UV and visible radiation after at 5, respectively (Eyasu et al., 2013).

Catalytic degradation of Methyl Orange by ZnO/PVP nano-catalyst was carried out**.** Conversely, the ZnO/PVP nano-catalyst has infrequently been fabricated. Upon the above fact, here we proposed a simple and effective process for the photocatalytic degradation of methyl orange by $NaBH_4$. Because of ultrafine handling, intense recycling and cost-effective preparation route, low water solubility, low short-term rates and an abnormal decrease in the potential for decomposition, the proposed nano-catalyst is extremely effective. Above the recorded protocols, which mark the best trademarks, the nano-catalyst presented here is more defined and realistic.

Experimental work

Reagents

Zinc nitrate hexahydrate salt ($Zn(NO_3)_2.6H_2O$), poly vinylpyrrolidone (PVP) and sodium hydroxide (NaOH), Methyl orange dye ($C_{14}H_{14}N_3NaO_3S$) and sodium borohydrate ($NaBH_4$) were acquired from Sigma Aldrich company and used as conventional deprived of an additional sanitization. All samples using Milli Q water were prepared in aqueous medium.

Fabrication of ZnO Catalyst

Previously reported pattern was followed for the fabrication of Zinc Oxide NPs with slight modification (Chen et al.)**.** In experimental way, 7.1g of Zn(NO3)2.6H2O was liquefied in 150mL twice purified water and 4g of NaOH was thawed in 50mL of Double purified water independently to prepare homogenous solutions. Solution of NaOH was mixed with zinc nitrate hexahydrate solution with continuous stirrer at room temperature. The impurities were removed by washing particles more than one time with Double distilled and ethanol, then dehydrated was performed at 70^oC for 20h in furnace. Further, synthesized NPs were strengthened at 550^0C for 90 mints to get crystal-like particles. The obtained precipitate was grinded to make particles fine. White pulverized nanoparticles was obtained and applied for additional characterisation. The complete chemical reaction is given as below;

$$\mathbf{Zn(NO_3)_2.6H_2O_{(aq)} + \mathit{2}\ NaOH_{(s)} \rightarrow ZnO_{(s)} + 2NaNO_{3(aq)} + \mathit{6}H_2O_{(l)}} \quad (1)$$

Fabrication of ZnO nanostructure by PVP

ZnO/PVP nano-composite was prepared by means of ultra-sonication routine. In this respect, 1.5g of synthesized ZnO nanoparticles was circulated in 100mL of Double distilled water and 0.2g of PVP were liquefied in 100mL of Double distilled and standardized in an ultra-sonication bath at 30◦C for 30minutes, separately. Both solutions were mixed and reserved in an ultra-sonic bath for 2h to homogenies the solutions. Acquired precipitate was splashed many times with double purified water and dryied at 85^0C for 24h.

Methyl Orange dye degradation

Commercial Methyl Orange dye ($C_{14}H_{14}N_3NaO_3S$, MW = 327.38g/mol) is chosen as the typical pollutant to evaluate the ZnO/PVP degradation. In experimental routine, Initially, the solution of MO dye and catalyst were prepared than 10 mL Methyl orange dye having 0.1 mM solution along with $NaBH_4$ (0.5 mM) was reserved in the glass vessel, and a piece of ZnO/PVA was implanted in the reaction mixture sendoff for 15 seconds so as to attain adsorption-desorption symmetry. 4 mL of the reaction mixture was engaged as a reference, and its UV-Visible spectrum was recorded over UV-Visible spectrophotometer. Additionally, different factors were optimized such as catalyst dose, reducing agent, Sun light effect, and irradiation time and microwave power. Gradual degradation in the color of mixture indicated methyl orange dye degraded. The percentage degradation was calculated by equation as assumed under:

$$\% \textbf{Degradation} = (\mathbf{Xi} - \mathbf{Xf})/\mathbf{Xi} \times \mathbf{100} \quad (2)$$

Here, X_i is initial and X_f is final absorbance of dyes.

Characterizations techniques

Fistly, UV–visible spectroscopy (Biochrom Libra S-22) were used to confirm the synthesized ZnO nanostructure. Dynamic Light scattering and Zeta sizer Nano (ZS90, Malvern, UK) were used to examine stability and size distribution of synthesized ZnO nanocatalyst. SEM (JSM-5410LV, JEOL) technique was used to study morphology of the fabricated Zinc Oxide NPS. Functional groups of prepared nanocompoiste were confirmed by FTIR spectra. In this regards, Thermo Nicolet 5700, Thermo Fisher Scientific Inc. USA, FTIR Spectrophotometer was used in the assortment of 4000–400cm^{-1}. Elemental ananlysis was supported out by EDX technique. XPS analysis (AXIS ultra by Shimadzu equipped with dual-anode X-ray source

Al/Mg and the HAS hemispherical sector analyzer detector) was performed to investigate the chemical bonding and composition of fabricated nanocatalyst. X-ray diffractometer (D/max-IIB, Rigaku) was used to investigate the nanometric size, crystal-like nature and phase purity with a Kα1 Cu (λ = 1.5406 nm) at a tube voltage of 40 KV and 20 mA current.

Results and Discussion

Characterisation of synthesized catalyst

Nanocomposite Peak, Stability and Band Gap study

Catalyst was confirmed by utilizing UV-Visible technique. As shown in figure 1A, the ZnO/PVP nanocomposite reveals the absorbance peak at 302 nm. While insect displayed the band gap measurement of fabricated nanocomposite via Tauc's relation. About, 3.38 eV direct band gap energy was calculated. Moreover, stability of prepared nanomaterial was checked by interlinking the spectra of fresh and two month later recorded spectra of similar nanoparticles. As shown in figure 1B, insignificant change in the peak intensity was detected with the passage of time. It indicates that the fabricated catalyst is highly stable.

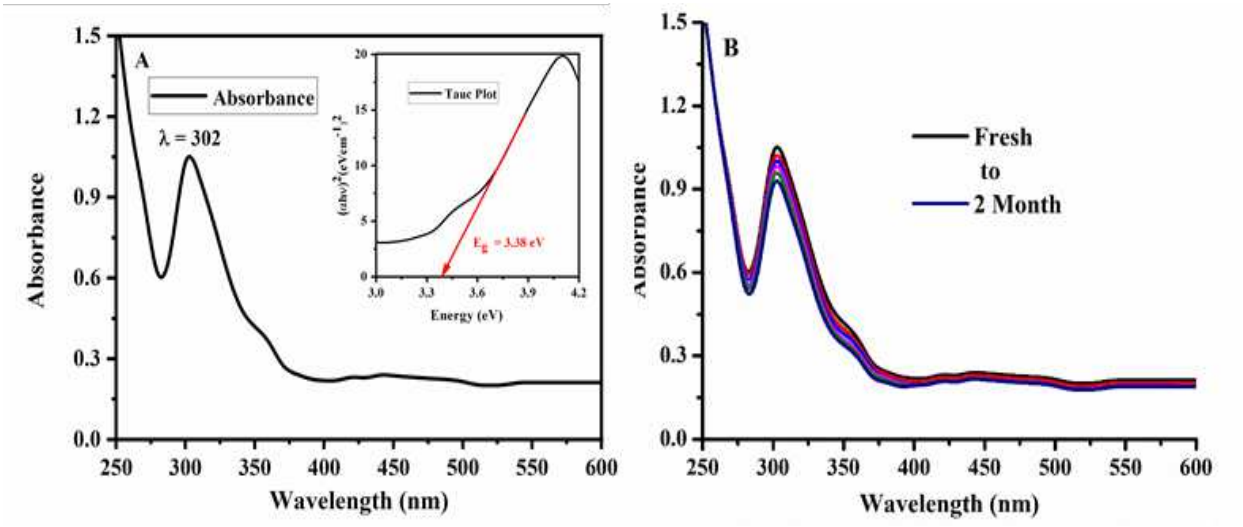


Figure 1: (A) ZnONPs UV–V spectrum, insect shows Tauc plot (B) stability of nanocatalyst

XRD analysis

The XRD array of prepared nanocatalyst is shown in Figure 2. The peaks are more exhaustive and thinner suggesting a worthy crystalline nature of the prepared ZnO/ PVP nanocatlyst. The corresponding pattern of nanocomposite appear at the distinctive points of crystals at 2θ = 31.79, 34.56, 36.33, 47.64, 56.74°, 63.06, 66.39, 68.05 and 69.05 in accordance with planes

(100), (002), (101), (102), (110), (103), (200), (112), and (201) as reported in JCPDS card (NO.36-1451) that indicates the hexagonal wurtzite assembly of Zinc Oxide NPS (Krishna Reddy et al., 2017). In XRD pattern peaks of impurities were not observed indicating that synthesized nanocomposite are highly crystalline in nature. The Debye-Scherrer principle was used to calculate the average crystalline size (L) of the nano-composite as given below (Chen et al., 2007):

$$D = \frac{k\lambda}{\beta cos\theta}$$

Here D represents the crystalline size (nm), λ the wavelength (nm), K crystal shape factor, θ (°) the Bragg diffraction angle (°) and β FWHM (radian). The average crystalline size of fabricated nano composite was calculated about 41.2 nm.

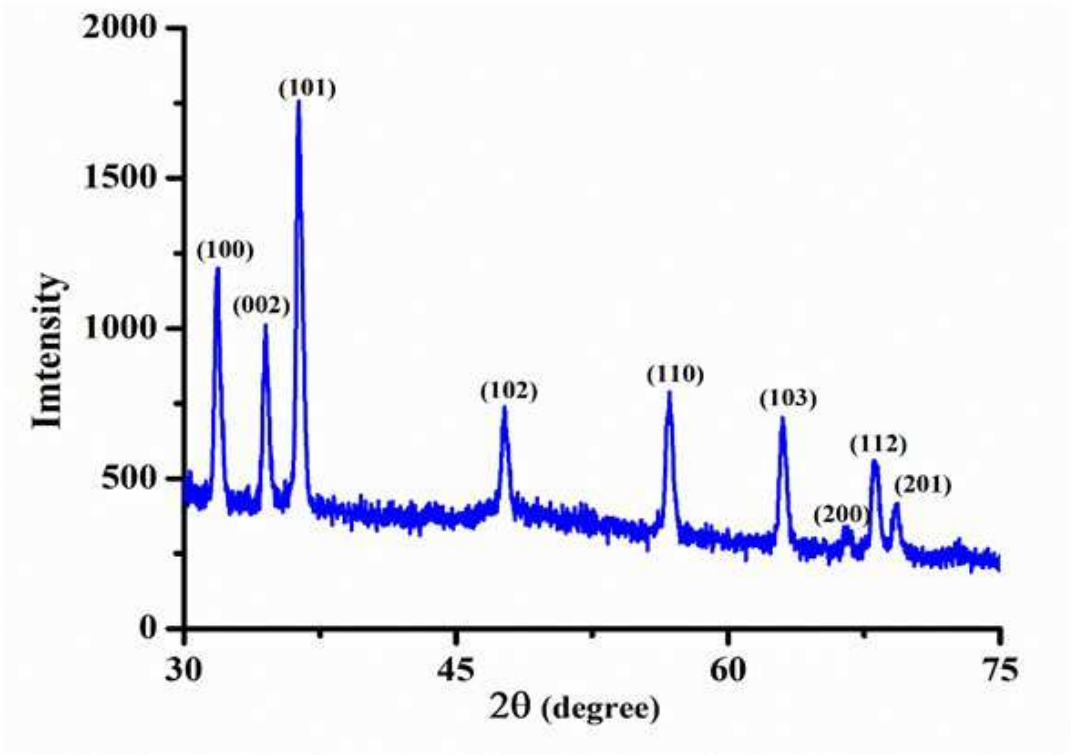


Figure 2: XRD pattern of catalyst

Functional group of catalyst

Chemical configuration of synthesized ZnO/PVP Nano composite was investigated by FTIR as demonstrated in Figure 3. The change in oure ZnO nanoparticles spectra was observed when PVP solution added that revealsthe fabrication of ZnO/PVP nanostructure. The band at 3435cm^{-1} and 2846cm^{-1} entrusted the stretching vibration OH ion of water adsorbed at the

particle's surface and of C-H bond respectively. The peaks near to 2846cm^{-1}, 1781cm^{-1} and 1451cm^{-1} are assigned to stretching vibration of C-H, C=O and C–N bonds correspondingly. The characteristic of peak at 1390 cm^{-1} is belongs to the bond of C–H in PVP. The absorption band near at 471 cm^{-1} and 678 cm^{-1} assigned to stretching vibrations of Zn–O bond (Hong et al., 2009). Consequently, FTIR Spectra indicates that chemical reaction occur among ZnO NPs and polymeric preservative, by synchronization of ZnO NPs with oxygen and nitrogen in PVP (Ilegbusi and Trakhtenberg, 2013).

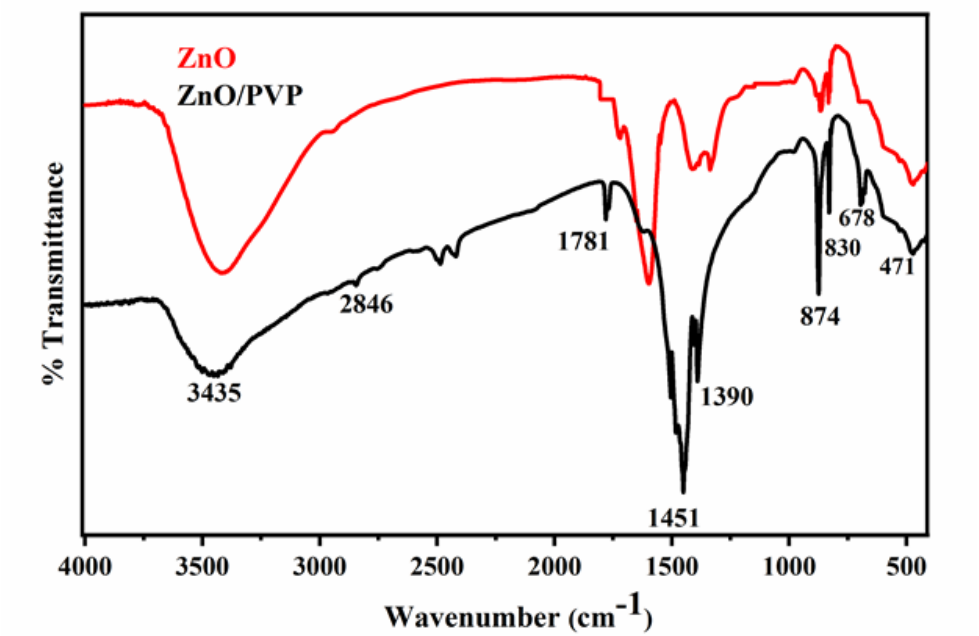


Figure 3: FTIR spectra of catalyst

Size and charge determination of catalyst

For the operative usage of metal oxide nanomaterial, the ZnO/ PVP nanocomposite must be in the range of small size. The nanocomposite can be successfully obtained with properties at the nanoscale and effectively applied in photocatalytic applications. The average size f prepared nanocatalyst, and PDI calculated as 280 nm and 0.253 by using the DLS technology (Fig: 4). On the bases of these outcomes, it is recommended that the formed nanocomposite are mono dispersions and the combined size distribution of nanoparticles. In addition, ZP was analyzed to uncover the surface charges obtained by Zinc oxide nanoparticles, which have been used to determine the stability of the fabricated ZnO/PVP nanocatalyst. It is reported in literature that the particles possess the ZP value more than + 30 mV or −30 mV have the greater stability (Gautam et al., 2018). Nanoparticles have the electrostatic repulsion force that depends on the surface charge of nanoparticle. The negative charge of nanoparticles

provide collective resistance and long-term stability. In current composition, the potential value of additional negative zeta supports the movement of repulsion among nanoparticles and thus improves the stability of synthetic particles. As shown in Figure 5, The Zeta potential value of the prepared ZnO/PVP NCs was detected at −22.8 mV. On the behalf of these outcomes it is summarized that the prepared PVP capped ZnO nanocatalyst is particularly stable.

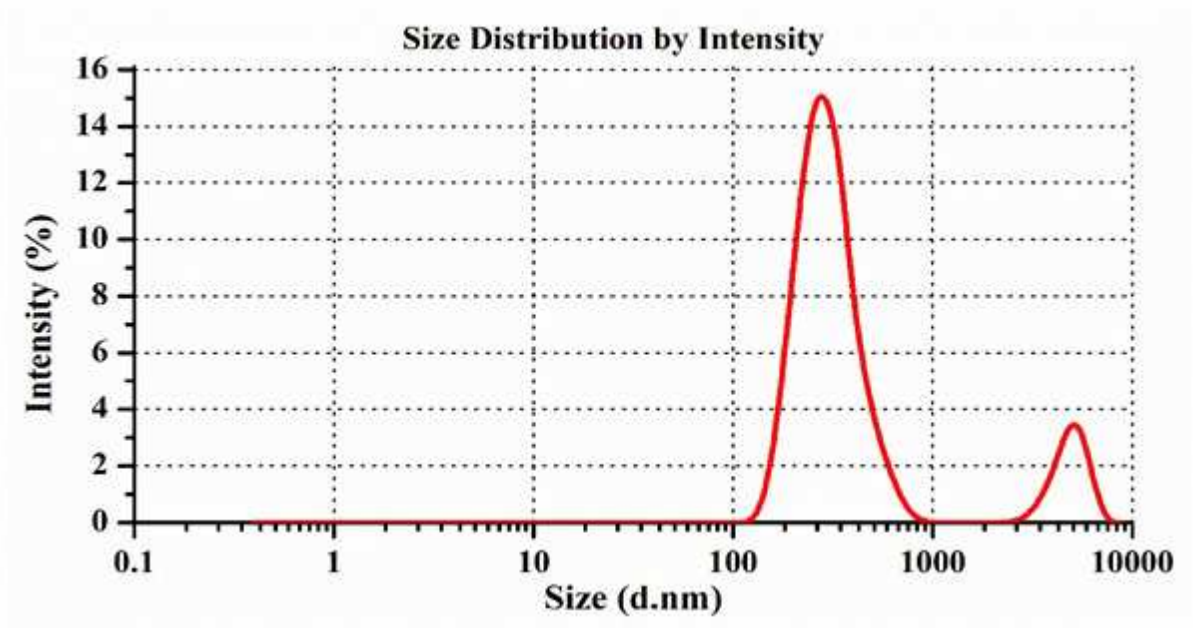


Figure 4: DSL of ZnO/PVP catalyst

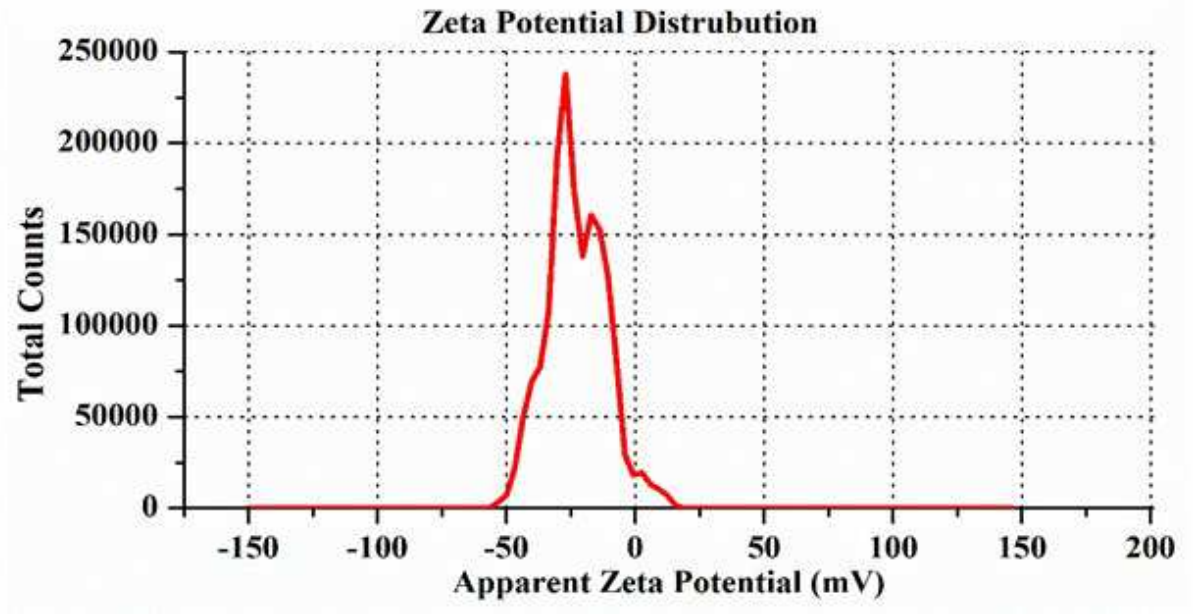


Figure 5: ZP of ZnO/PVP catalyst

Surface morphology and elemental anaylysis of catalyst

The morphology of the material fabricated at the nanoscale may show a significant character in the catalytic reaction. In quest to investigate the geographical evaluation of a jointly designed ZnO/PVP nanocomposite, SEM was performed effectively. Figure 6 (A&B) shows the SEM images of synthesized ZnO/PVP nanomaterial. The synthesized nano sheets smoothness proved to be a reliable and effective preparation of PVP capped ZnO on the nanoscale. However, the similarity in texture shows that the synthesized particles can be used for a catalytic reaction. Additionally, Elemental structure of ZnO/PVP nanocatalyst was inspected via EDX study. Figure 7 exposes the presence of Zn, O and C as the main elements of fabricated nanocatalyst. Resultantly, the prepared nanocomposites were found pure.

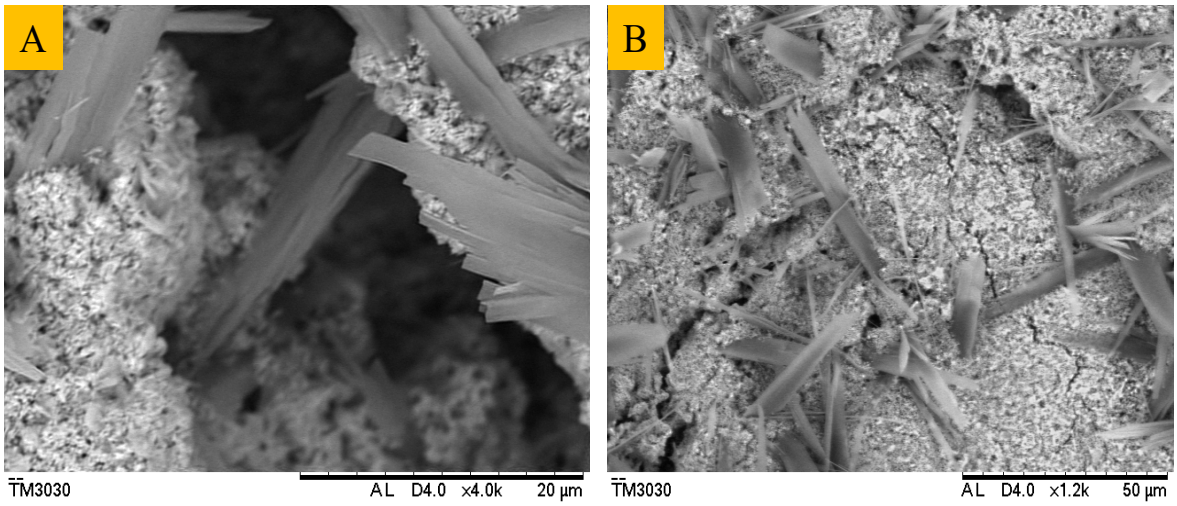


Figure 6: SEM descriptions of catalyst A. low resolution B. High resolution

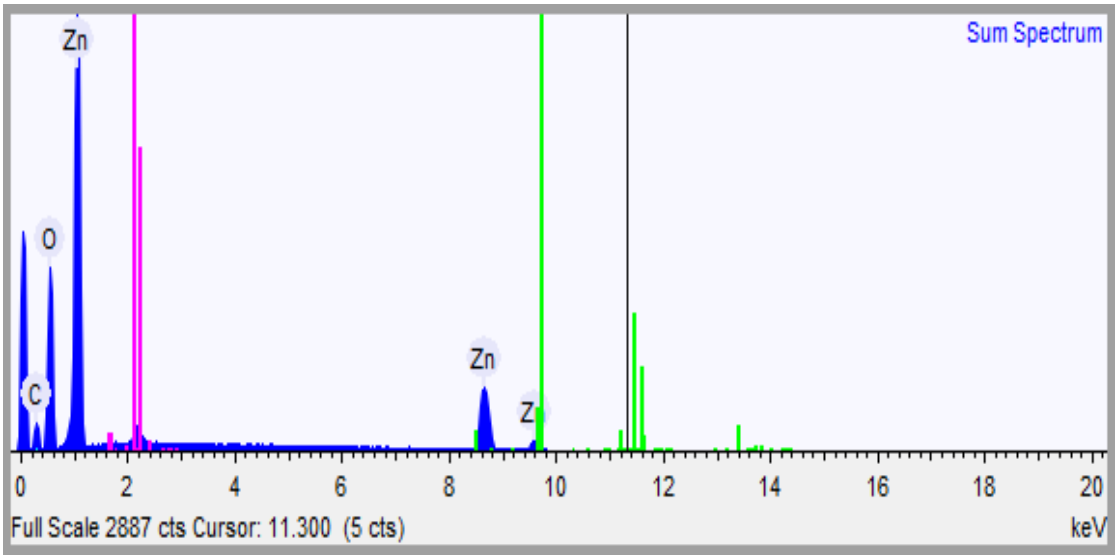


Figure 7: EDX pattern of catalyst

X-ray Photoelectron Spectroscopy Study

Synthesized ZnO nanocatslyst were further investigated by XPS technique (Figure 8). The Binding Energy of nanocomposites at 1021.98 and 1044.95eV would assigned to Zn $2p_{3/2}$ and $Zn2p_{1/2}$, respectively as displayed in Figure 8B. The Binding Energy at 285eV and 532eV are linked to C1s and O1s of ZnO, respectively as exposed in Figure 8 (C&D) (Morozov et al., 2015, Saáedi et al., 2016).

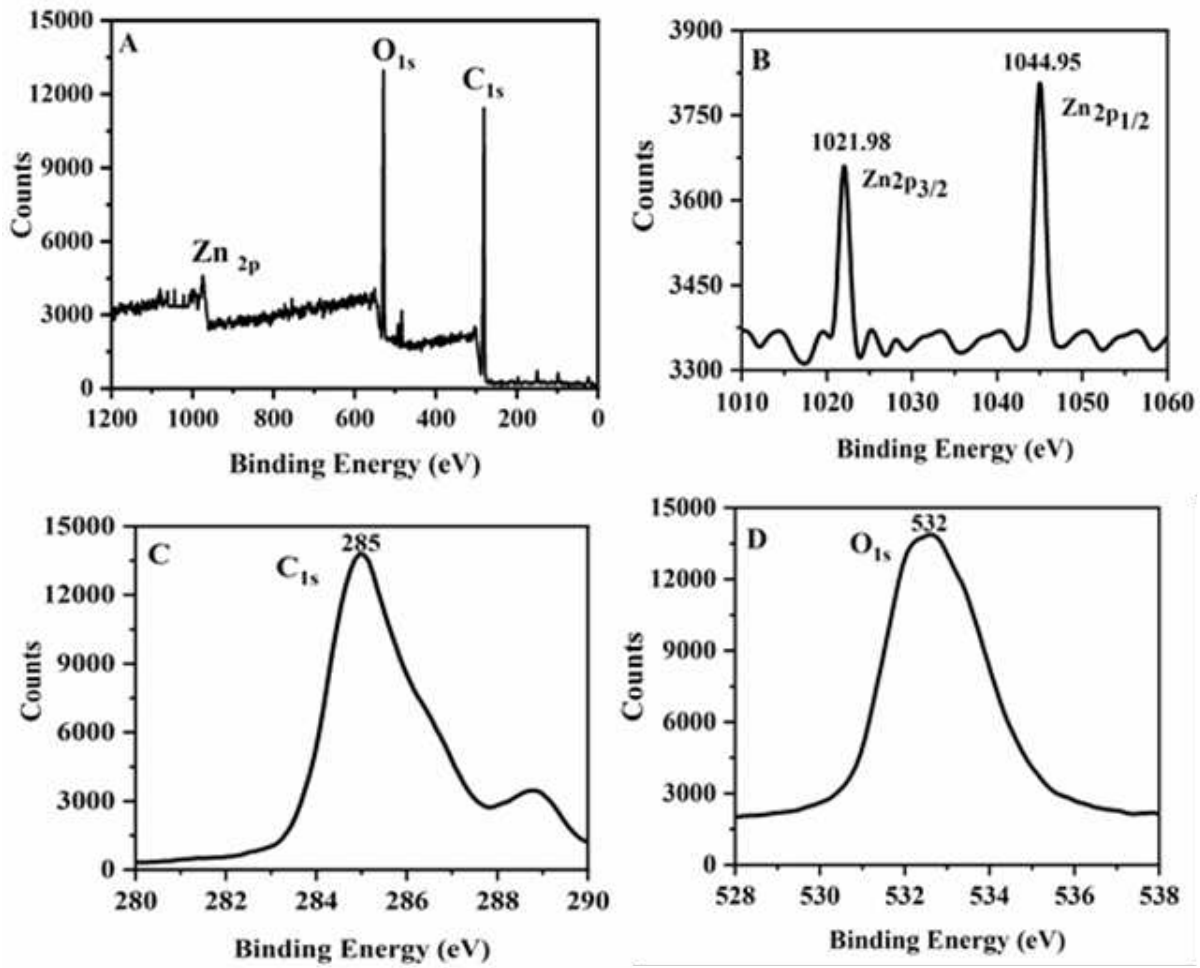


Figure 8: (A) Full XPS spectrum of ZnO/PVP nanocatalyst, (B) Zn2p (C) C1s (D) O1s

Catalytic investigation of synthesized ZnO nanocatalyst.

Methyl orange (MO) dye nominated as a contaminant to assess the catalytic potency of synthesized ZnO/PVP nanocomposite in presence and absence of sodium borohydare ($NaBH_4$) as reducing agent under different circumstances. Experiment was carried out after optimizing all the parameters such as reducing agent, Sun light effect, catalyst dose, irradiation time and microwave power. UV-V Spectrometer was used to monitor the degradation. Absorbance peak of MO dye was perceived at 464 nm (λ-max) (Radini et al., 2018). During process, gradual degradation of absorption intensity with passage of reaction

and color of methyl orange dye become less intensive because of MO oxidation in the presence of synthesized nanocatalyst.

Parameters Optimization study

Effect of reducing agent

Sodium borohydrate is a crucial component which is very supportive to boost the degradation ability of suggested nanocatalyst. The sources of the proposed proton from $NaBH_4$ and supporting factors have been evaluated to check the performance of the proposed nanocatalyst. Initially, the $NaBH_4$ effect was examined by adding different volumes (25–200 µL of 0.5 mM), at fix concentration of Methyl orange dye (0.1 mM). By increasing the volume of reducing agent a significant variation was noticed in peak degradation (figure 9A). Approximately, 21% the degradation in MO was detected, while no significant decrease in intensity was observed upon the addition of NaBH4. Only 1-2% degradation was observed as shown in figure 9B. Additionally, it was observed that the extensive dose of $NaBH_4$ didn't deliver better outcomes, because of the certain boundaries that could be due to the absence of any support to adsorb/capture of hydride ions. The problem was subsequently resolved by adding the surface modified ZnO/PVP nanocatalyst. This assisted as a durable support for the impressive deposition of hydride ions that severely degrade the MO molecule to significant point.

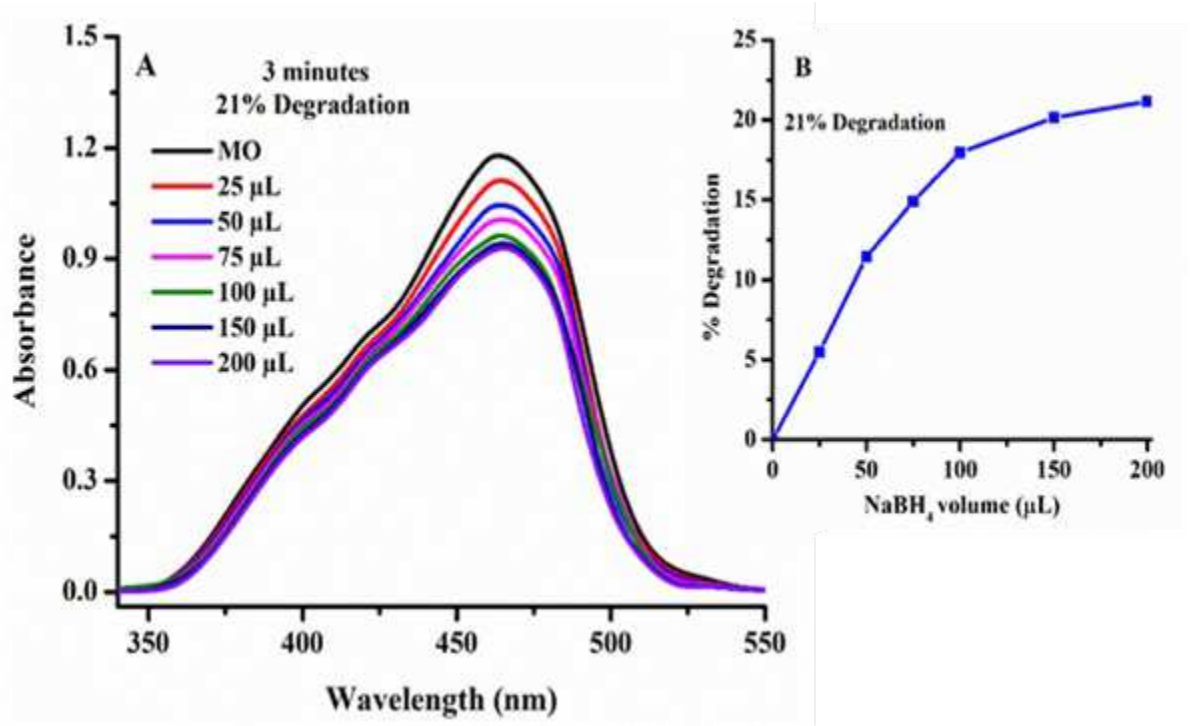


Figure 9: UV-Vis spectral for (A) Effect of reducing agent (0.5 mM, 25–200 µL) on the degradation of Methyl orange dye (0.1 mM) in without of catalyzed, utilizing 3 minutes B. % degradation at different volume of reducing agent

Sunlight effect

Secondly, the effect of sunlight was adjusted without nanocatalyst, after the reducing agent optimization (0.5 mM $NaBH_4$, 200 µL). In peak intensity of Methyl orange (0.1 mmol L^{-1}) notable deviation was observed. The organized solution was taken under the sun for 1 to 50 minutes and noteworthy variation in peak was noticed as shown in Figure 10 (A&B). Nearly, 40% methyl orange dye reduced, although no noticeable variation was detected up on succeeding additional the energy of sun on the solution; merely 3% noted. It was obviouses that putting the solution below sunlight for more period no significant variation could be spotted. Subsequently, certain additional aspects could be optimized like as nanocatalyst doseage and time with the purpose of make the work more economical.

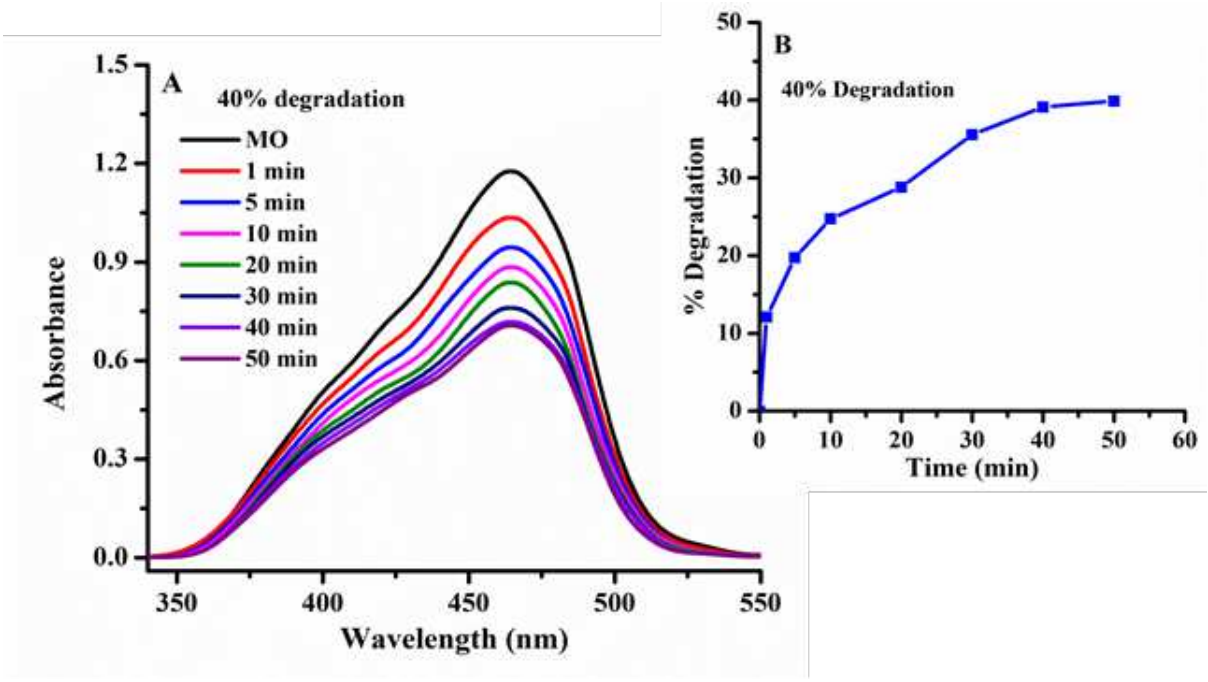


Figure 10: UV-Vis spectral for A. Effect of sunlight on the degradation of Methyl orange dye (0.1 mM) utilizing using 0.5 mM NaBH4, 200µL B. % degradation at different volume of reducing agent

Effect of nanocatalyst without sodium borohydride in the existence of sunlight

After the optimization of above factors, effect of nanocatalyst was inspected in the nonexistence of $NaBH_4$. A noteworthy deviation was noticed in the peak intensity of methyl orange dye when arranged solution was incubated at 25–200µg of ZnO/PVP nanostructure and appropriate quantity of methyl orange (0.1 mM) was retained in sun irradiation for almost 20 minutes in the deficiency of $NaBH_4$. Approximately 85% of methyl orange dye degraded, that is fairly sufficient but time ingesting procedure (Fig.11 A&B). In order to make the work more operative and sufficient, reducing agent must be applied to acquire more degradation and to decrease the time ingesting.

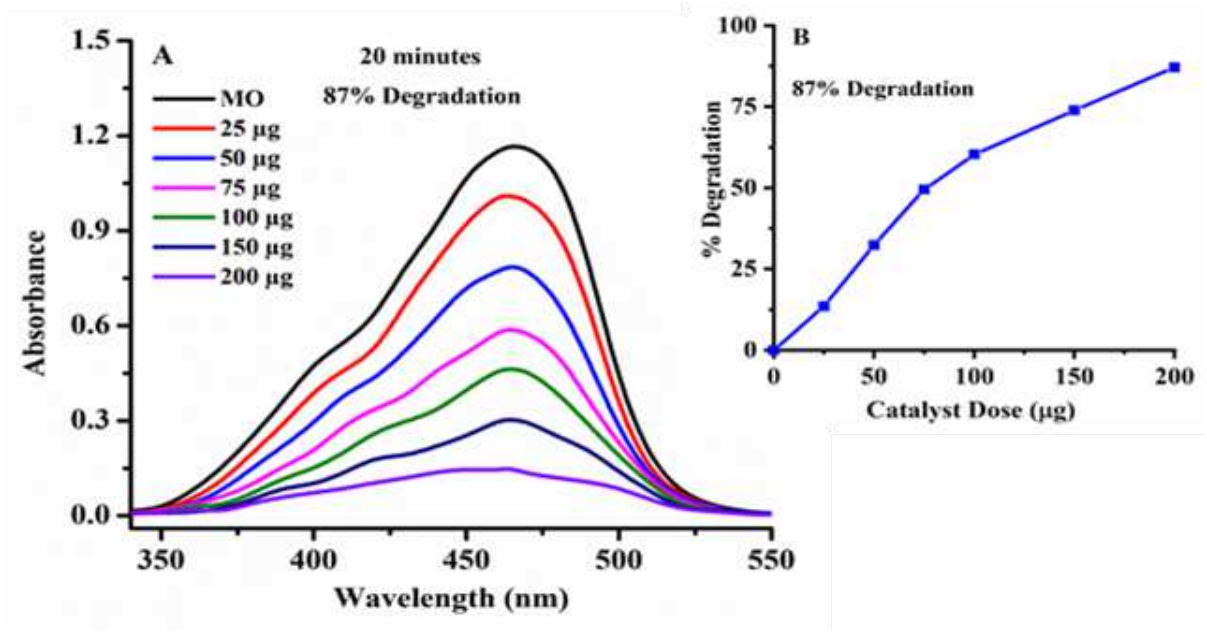


Figure 11: A. Catalyst dose effect (25-200µg) in the absence of NaBH4 on the degradation of methyl orange dye (0.1 mM) B. showing % degradation graph at different catalyst dosage in 20 min.

Effect of Nanocatalyst with sodium borohydride in the existence of sunlight

After elevating various factors mentioned above, the catalyst dose effect (25-150µg) was investigated in the presence of $NaBH_4$ (0.5 mM, 200µL) at fix concentration of methyl orange (0.1 mM). Approximately, 92% degradation was observed in peak intensity of the methyl orange dye (Figure 12 A&B). Typically Sodium borohydrate is attached to the ZnO/PVP surface, thereby increasing the activity of the nano-catalyst due to the release of proton (H^+). Lastly, more than 90% degradation was attained by utilizing 150µg and 200µL of ZnO/PVP nanocatalyst and $NaBH_4$, respectively, only employing 2 minutes in every catalytic trial.

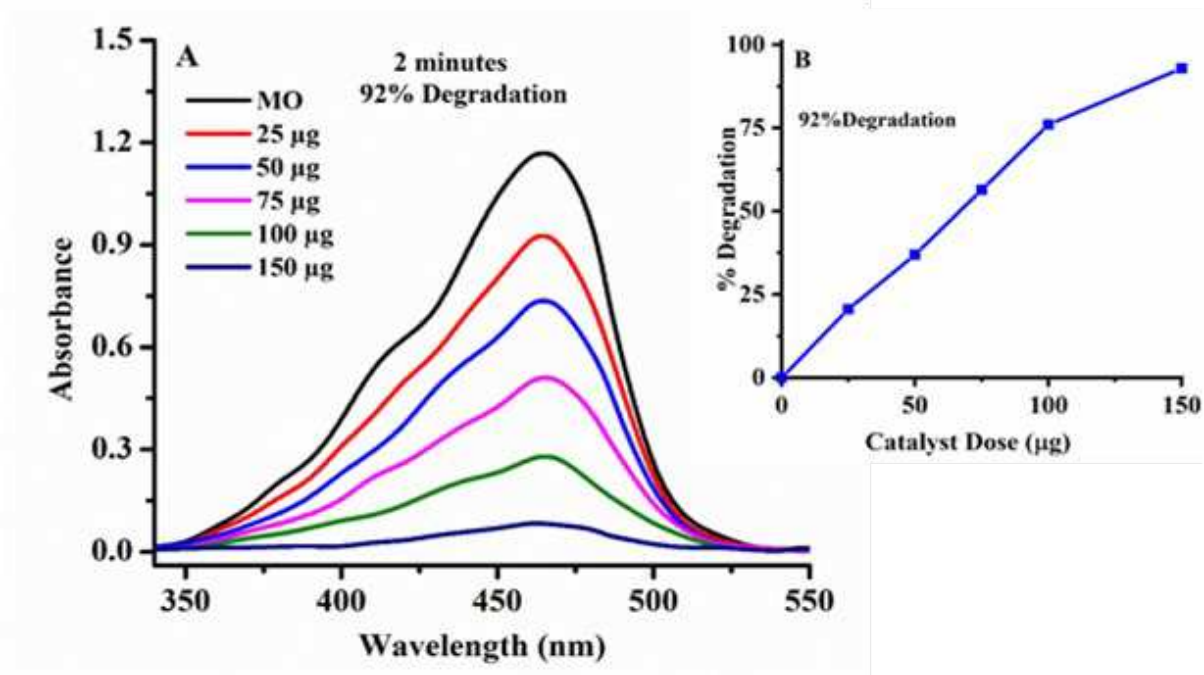


Figure 12: A. Catalyst dose effect (25-150µg) in the presence of NaBH4 (0.5 mM, 200µL) on the degradation of methyl orange dye (0.1 mM) B. % degradation graph in 2 min.

Microwave effect study

It is a critical factor that is helpful in increasing the catalytic competence of the suggested nanocomposite. Consequently, by examining all above mentioned factors, eventually the microwave power upshot desires to be inspected to make research worthy. To assess this important effect, a fixed power rate was employed (110 W) using a 150µg nano-catalyst dose and 200µL, 0.5 mM $NaBH_4$ volume using 0.1 mM MO dye in the nonexistence of sunlight. The effect of microwave power was monitored by increasing the sample contact duration as shown in Figure 13 (A&B). By increasing time exposure (15-90 seconds) the degradation was increased. This may be due to more energy MW power or rise in temperature. Finally, 97.8% degradation was succeeded with 150µg ZnO/PVP nanocatalyst, 200µL of $NaBH_4$ within 90 seconds microwave power.

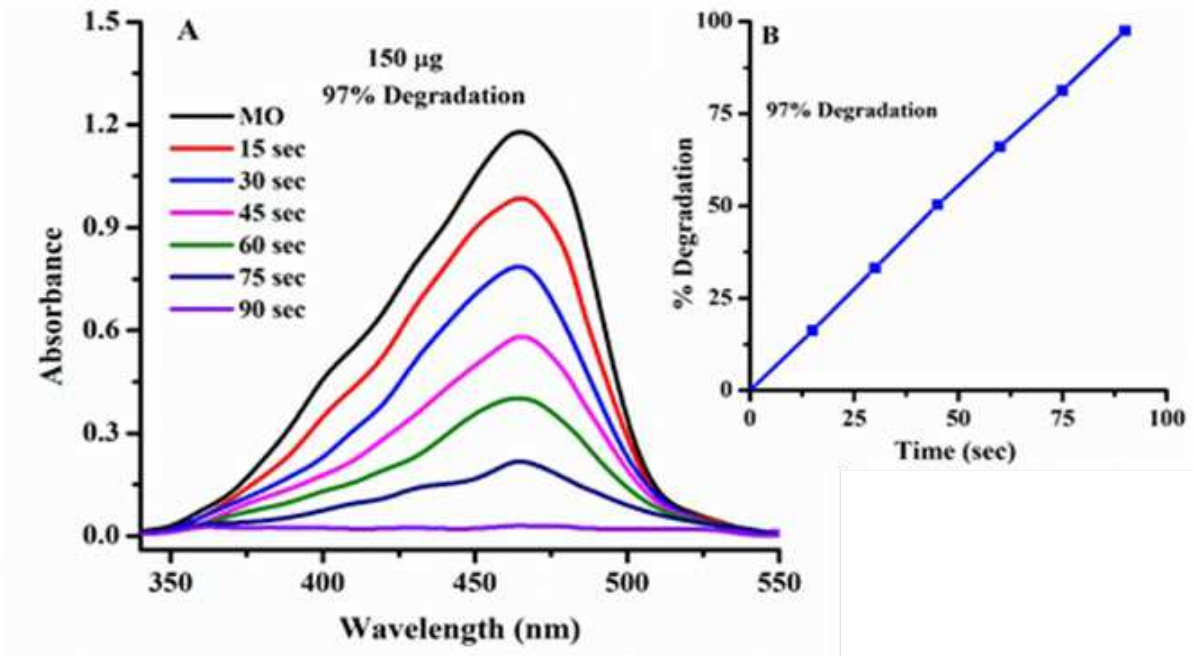


Figure 13 A. Effect of MW power (110 W) on the degradation of MO dye (0.1 mM) using 0.5 mM NaBH4, 200µL and 150µg ZnO/PVP nanocatalyst, B. showing % degradation graph.

Kinetic Study

In order to inspect the order of the reaction, degradation abilities and rate constant, the Lagergren kinetic model was successfully applied to examine the 1st and 2nd pseudo order reaction.

1st pseudo order:

$$(qe - qt) = \ln qe - \frac{k_1 t}{2.303} \qquad (8)$$

2nd pseudo order:

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{1}{qe} t \qquad (9)$$

Where, k1 and k2 are rate constants for 1st and 2nd orders, respectively, and qe, qt and *t* demonstrate the equilibrium adsorbed Methyl Orange concentration (mg/g), and dye absorbed (mg/g) over nano catalyst surface at time.

The graph was plotted among the equation ln (qe−qt) in contradiction of time (*t*) to investigate the adsorption potential (qe), correlation coefficient (*R*) and rate constant (*k*) for pseudo 1st and 2nd order reaction as revealed in Figure 14 A&B. It was presumed that using the Lagergren model, the degradation reaction shadows the second order kinetics in compression of first order as exposed in Table 1.

***Table 1**: kinetic study for the degradation of Methyl Orange dye*

Pseudo first order			Pseudo second order		
K_1	qe (mg g^{-1})	R^2	K_2	qe (mg g^{-1})	R^2
0.09851	0.04891	0.9598	0.28109	0.1238	0.9679

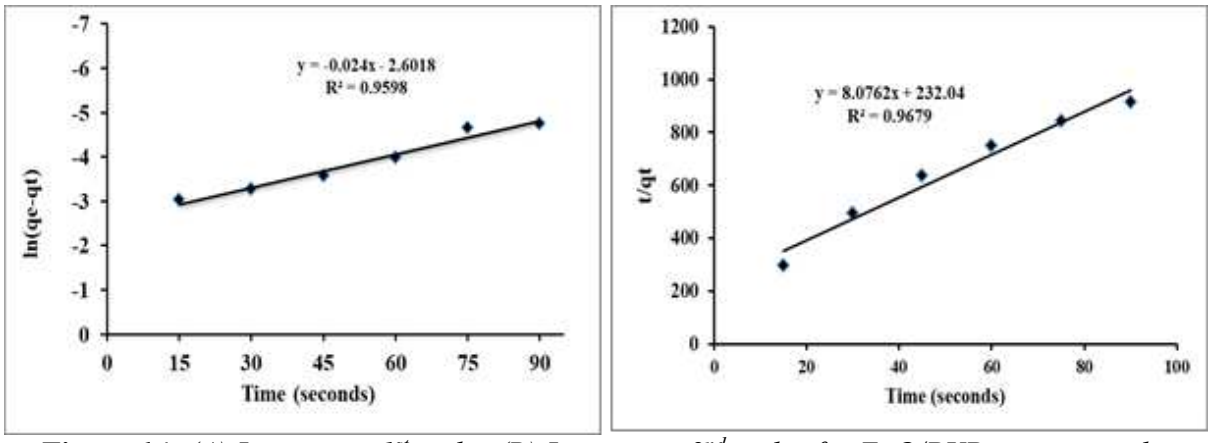


***Figure 14:** (A) Lagergren 1st order (B) Lagergren 2nd order for ZnO/PVP nano particles*

Reusability investigation

The reusability and restoration of the CuO/PVA nanocatalyst is examined for the degradation of dye by execution of recycling investigates using $NaBH_4$. As exposed in Figure 15, there is no substantial variation in the catalytic activity of nanocatalyst after five successive phases. It demonstrates the great stability of the synthesized catalyst.

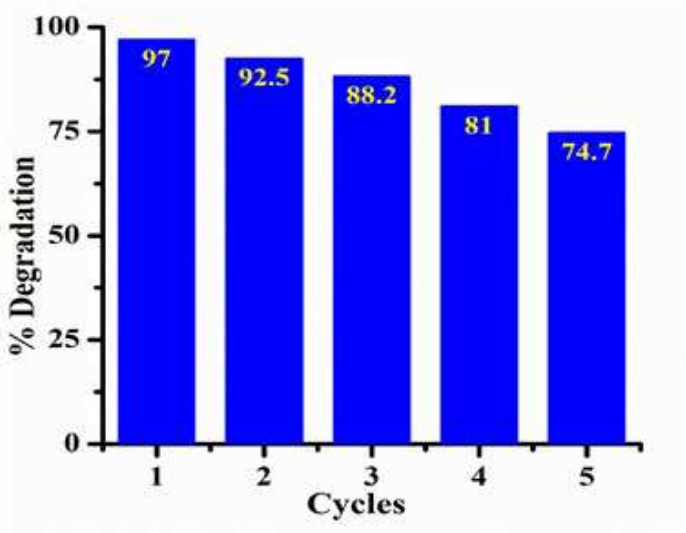


***Figure 15:** Reusability cycle of catalyst*

Methyl Orange dye degradation nechanism

The degradation mechanism of dyes in the presence of catalysts was proposed by the earlier reported (Veerakumar et al., 2015). The degradation mechanism of methyl orange with ZnO/PVP nanocatalyst is revealed in Figure 16. The process comprises the transfer of electron through the surface of catalyst from the valence to conduction band with Microwave/Sunlight. These electrons separately can interact or recombine with other molecules. On the surface of catalyst, the H_2O molecules and holes created can interact and produces the hydroxide ions although superoxide anion formed when electrons are captured by adsorbed oxygen. The resultant ions may generates more peroxide in the presence of strong oxidizing scavenger. Being a strong oxidizing agent hydroxyl radical attack on the molecules of dye and forms oxidized product as exposed in figure 16. The summary of reaction is described below and possible fragmentation of methyl orange dye is similarly assumed in Fig. 17

$$\text{Catalyst} + h\nu \rightarrow h^+ + e^- \quad (3)$$

$$h^+ + e^- \rightarrow \text{heat} \quad (4)$$

$$h^+ + H_2O \rightarrow OH^{\bullet} + {}^+H \quad (5)$$

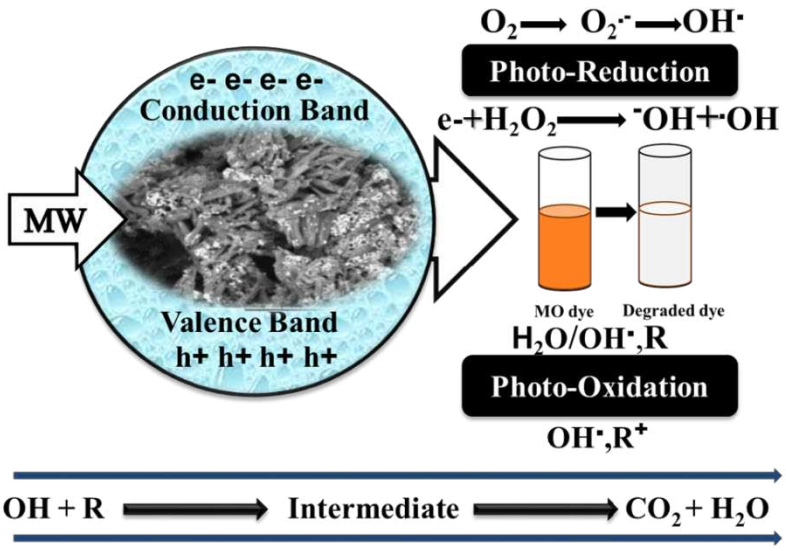
$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (6)$$

$$O_2^{\bullet -} + {}^+H \rightarrow OH^{\bullet}{}_2 \quad (7)$$

$$OH^{\bullet}{}_2 + OH^{\bullet}{}_2 \rightarrow O_2 + H_2O_2 \quad (8)$$

$$H_2O_2 + \rightarrow 2^{\bullet}OH \quad (9)$$

$$^{\bullet}OH + MO \rightarrow \text{Oxidized product} \quad (10)$$



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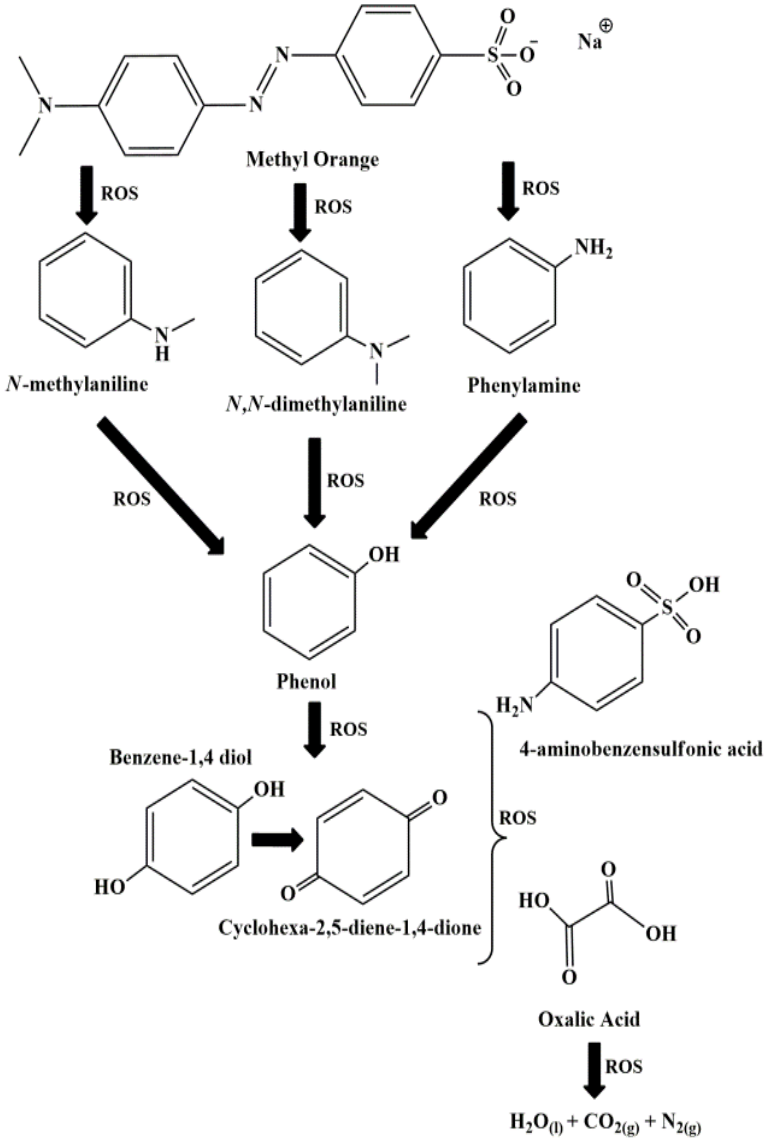
398 ***Figure16:*** *Schematic diagram for the degradation mechanism of MO dye*



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400 ***Figure 17:*** *Fragments of methyl orange dye*

Evaluation of ZnO/ PVP nanocatalyst with testified work

Eventually, amongst numerous nanocomposite ZnO/PVP nanocatalyst has excellent catalytic activity for degradation/degradation of MO dye than the earlier conveyed work as table 2 shows. Examination of the reported anomalous literature proves that our recommended nanocatalyst is very effective and discriminating postulant in relations of maximal % degradation of methyl orange below infinitesimal catalyst dose and reducing agent dose in just 90 seconds. Various types of nanocatalyst were synthesized and their catalytic degradation was investigated under different conditions. However, the reported work couldn't reach the 85% degradation. On the other side, we have oppressed the simplest ZnO/ PVP nanocomposite and more than 97.8% degradation was observed in just 90 seconds. Based on the above facts we have proposed the prepared ZnO/PVP nanocomposite and it could be a major aspirant for the de-colorization of MO dye and other pollutants.

Table 2: Evaluation of ZnO/ PVP nanocatalyst with testified work

Catalyst	Catalyst Dose	Dye Conc:	% Degradation	Time	Reference
Fe3O4/ZnO	0.075 g	20 ppm	83	360 min	(Hong et al., 2008)
TiO_2 NPs	10 mg	10 ppm	67.12	240 min	(Dhanalakshmi and Padiyan, 2017)
ZnO NPs	0.3 g/L	20 mg/L	80	120 min	(Wang et al., 2007)
Cr-ZnS NPs	0.5g/100ml	2.5 × 10-4 M	74.28	300 min	(Eyasu et al., 2013)
ZnO/PVP	**150 µg**	**0.1 mM**	**97.8**	**90 sec**	**Present study**

Conclusion

In summary, simple, low-cost and reliable method is adopted to synthesize the ZnO/PVP nanocatalysts with an excellent catalytic performance in current study, and catalyst was characterized via different techniques. The synthesized catalyst was screened for the degradation of MO dye an aqueous medium in the existence of sodium borohydate at optimized conditions. In the prearranged circumstances, more than 97.8% of degradation was attained just in 90 seconds of reaction. According to our best knowledge its first analysis of methyl orange dye photocatalytic degradation by ZnO/PVP nanocomposite as nanocatalyst.

The proposed method is best in terms of simple, operative cost and favored economically, reproducible and excellent in reusability. On the bases of above facts, the synthesized PVP capped ZnO nano-composite is suggested for degradation of toxic contaminates at commercial level.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests

Data Availability

All data that support the findings of this work are contained within the article.

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Contributions

Zaheer Ahmed Mahar: Performed Experimental work and also took part in writing portion, Ghulam Qadir Shar: Supervisor help in manuscript designing and revision and Aamna Blouch: Co-Supervisor gave a placement at laboratory and facilitate with chemicals and glassware. And also help in manuscript and experimental designing. All authors read and approved the final manuscript.

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