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Utilization of solar energy for photodegradation of basic violet 10 using tin oxide doped ZnO

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In this study, the Tin oxide doped Zinc Oxide (TZO) photo catalyst was fabricated using drop by drop method, an effective route to produce novel nano TZO which will enhance the photocatalytic decolorization of Basic Violet 10 dye. The structural and surface morphology were investigated using techniques such as XRD, SEM, and EDAX. In this study, the degradation of basic violet 10 dye had been carried out in the presence of sunlight. It was observed that the prepared TZO photocatalyst was very effective in degrading the dye entirely within a short period (120 minutes). The influence of operating parameters on basic violet 10 including the amount of photocatalyst, dye concentration, H_2O_2 concentration and temperature were thoroughly examined. The kinetic study revealed that the degradation of photocatalytic reaction showed pseudo-first-order kinetics.

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Keywords: Basic Violet 10, Tin oxide, ZnO, Photo catalyst, Dye degradation, Solar light

1. Introduction

The developing industries, growing population and spillage of poisonous gases have brought about increase of the natural contamination which is a disturbing threat to biological system. For environment protection, identification of hazardous gases and exclusion of non biodegradable dye is required. Enormous amount of water is devoured by chemical processes and products involving dyes. Presence of tinted compounds in water and wastewater causes light penetration being frustrated in water, therefore upsetting the biological treatment process. A vast amount of dyes, approximately 5–10% of the annual global production (ca.107 kg), is discharged as effluent mainly by paint and textile manufacturing industries. (Nikos et al. 2010). These effluents cause environmental problems and public health concerns if improperly disposed. Basic Violet 10 is one among the dyes. Fig.1 shows the structure of the dye.

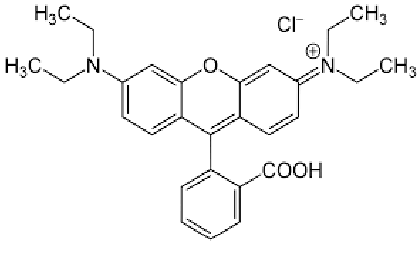

Fig.1.Basic Violet 10 Structure

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Numerous conventional methods have been applied for this purpose, such as adsorption, biological treatment, oxidation, coagulation, and flocculation. These methods have been widely applied, they have some disadvantages. For example, adsorbents are usually difficult to regenerate [1]. Heterogeneous photocatalyst is considered as a major key function in solar powered vitality helped natural remediation. It can use solar energy to decompose unsafe natural contaminants existing in water, air and soil which coordinating to the feasible clean world future [2]. Hetero- generous photocatalysis is based on the use of a wide-band-hole semiconductor and irradiation with UV–Visible light (Fig. 1), which produces electron in the conduction band (CB) and holes. This process is of special interest since sunlight can be used for it. The photo-excited nanoparticles can generate electron-hole pairs by absorbing the sun light. These photo-excited electrons and holes are capable to activate the redox reactions among pollutants [3]. Few of the transition metal oxides like ZnO, In_2O_3, SnO_2 and TiO_2 were noteworthy in optoelectronic, sensors and catalytic applications [4]. Various analysts demonstrated that ZnO, TiO_2 and SnO_2 were the successful catalysts in the degradation of pesticides, phenols, dyes and in gas sensor also [5]. So applications could be improved through the use of catalysis and solar energy.

1.1. Solar Photocatalysis

The heterogeneous solar photocatalytic detoxification process comprises of utilizing the solar energy illumination (visible and near-bright) band of the sun based spectrum to photo excite a semi-conductor catalyst in the presence of oxygen. Under these circumstances, oxidizing species, either bound HO^- or free holes, which attack oxidizable contaminants, are generated producing a progressive break-up of molecules yielding CO_2, H_2O and diluted inorganic acids [6, 7]. The publications regarding the photo catalytic process rose continuously over the last years surpassing meanwhile a total number of more than 8000 peer-reviewed publications per year in 2014. Fig. 2 likewise illustrates that much of the literature takes into account the possibility of driving the process with solar radiation.

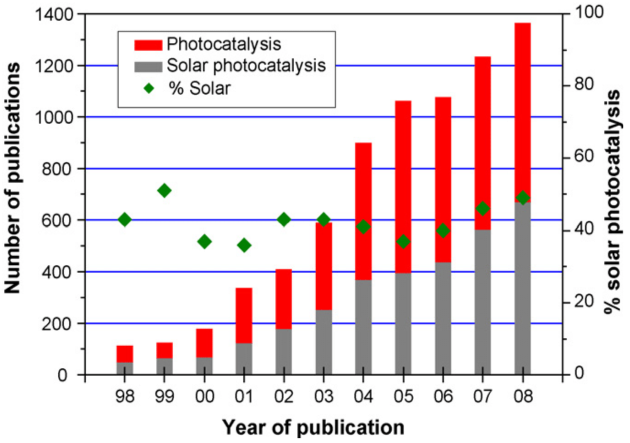


Fig.2. Publications treating photocatalysis and the share treating solar-driven photocatalysis (source: http://www.scopus.com, 2009)

In the present work, we have synthesized TZO nanoparticles and the obtained product was characterized by XRD, EDAX and SEM. It was observed that the use of TZO photocatalyst had better photocatalytic activity for degradation of Basic Violet 10 in the presence of solar light. The effect of dye variation, catalyst loading, pH, oxidizing agent variation was studied and the optimum conditions were found out.

2. Materials and Methods

2.1. Reagents

All chemicals were purchased from Merck, India (GR) and used without any additional purification.

2.2. Synthesis of Tin oxide Doped Zinc Oxide:

Tin oxide doped Zinc oxide were prepared by drop by drop method. Synthesis of tin oxide doped nanosized ZnO particles was accomplished by instant mixing of 10 mmol of $SnCl_2.2H_2O$, 50 ml of 0.1M $ZnSO_4.7H_2O$, 50 ml of 0.4 M NaOH were added into the 30 ml of pure ethanol and 10 ml distilled water stirred continuously. Tin oxide, zinc oxide was accomplished by 1:5 ratios. The white precipitate formed was washed with deionized water and calcined at 150°C in a furnace for 2 hours at temperature ramp rate of 5°C min^{-1}

2.3. Photocatalytic Activity Assessments

The photo catalytic experiments were carried out in the presence of sunlight. In all the experiments, 50ml of Basic Violet 10 was taken and the absorbance was measured. The maximum absorbance of Basic Violet 10 was 555 nm. Prior to irradiation, the photo catalyst suspension was blended well in dark to ensure the adsorption equilibrium. The suspension was kept under sunlight for photo degradation. The suspension sample was taken at steady interval of 30 minutes, centrifuged at 2500 rpm for 10 minutes to remove photo catalyst particles from the suspension. The absorbance was measured at 555 nm. From the data, the percentage of decolourization is calculated as

$$\mathbf{D = [(A_o - A_t) \div A_o] \times 100}$$

where A_o - is the initial absorbance and
A_t - is absorbance of dye solution at time't'.

3. Results and Discussion

3.1. Characterization of Prepared Tin Oxide Doped ZnO (TZO)

3.1.1. XRD Analysis

From Fig. 3 the diffraction peaks of as synthesized tin oxide doped zinc oxide corresponds to the hexagonal wurtzite structure with the space group of (100), (002), (101), (102), (110), (103), (200), (112), (201) (JCPDS No. 36-1451). The sharp peaks at 31.78°, 47.59°, 56.64°, 62.86° and 67.91° are indexed with (100), (102), (110), (103), (004), (104), planes of ZnO [8]. The diffraction peaks of tin oxide were also observed at the 2θ value of 26.5°, 33.7° and 51.7° which can be attributed to the (110), (101) and (211) planes of SnO_2. No other impurities were observed. The average crystallite size of TZO calculated using Debye-Scherrer equation is 55 nm.

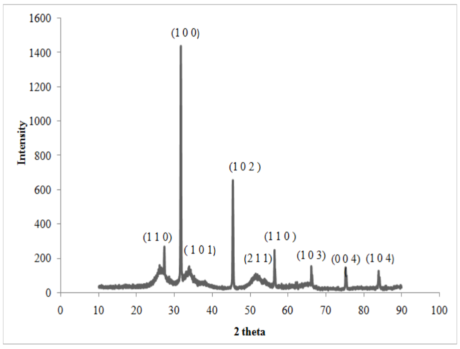
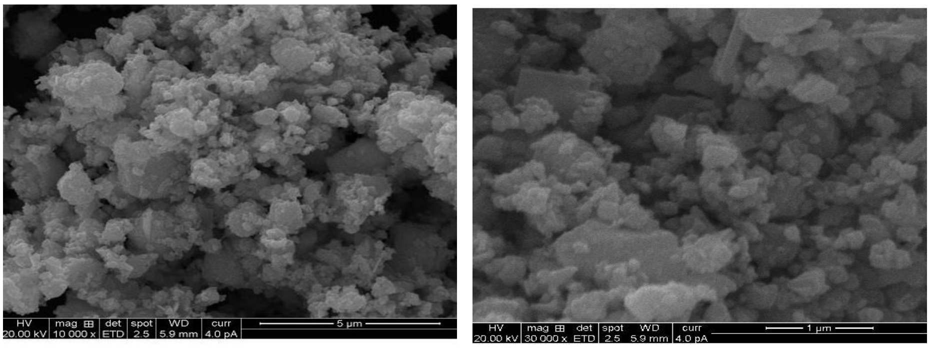


Fig. 3.XRD pattern of TZO.

3.1.2. SEM Analysis

Fig. 4 shows SEM images of synthesized TZO nanoparticles. They were reasonably uniform in size, well dispersed, granular and flower like (three dimensional) structure



a) *b)*

Fig. 4. SEM images of TZO:
a) Granular like TZO nanoparticles, b) Flower like TZO nanoparticles

3.1.3. EDAX Analysis

Fig. 5 shows the energy dispersion X-ray analysis spectra of TZO. It was mainly composed of zinc, tin and oxygen elements. This suggested that tin is incorporated into the ZnO nanoparticles.

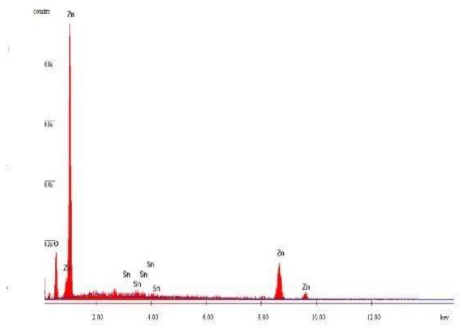


Fig. 5. EDAX analysis of TZO.

3.1.4. UV Analysis

The UV-Vis spectra of TZO and ZnO nanomaterials were depicted in Fig. 6 The as-synthesised photocatalysts were subjected to UV-Vis analysis to ascertain the visible light activity of the photocatalyst. The results indicated that TZO nanomaterials absorbed both UV and visible light region of the spectrum with a sharp peak at 380 and a very strong absorption in the visible region which may be due to strong absorption capability in the entire UV and visible region, resulting from the interactions between tin oxide and ZnO. Therefore, TZO can act as a photosensitizer, which was probable to improve the photocatalytic activity of TZO nanocomposite under visible light irridation.

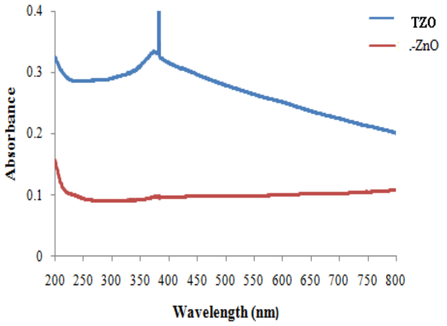


Fig. 6.UV analysis of TZO.

3.2. Photocatalytic Degradation of Basic Violet 10

3.2.1. Effect of Doped Catalyst

Fig. 7 depicted the effect of undoped and doped catalyst zinc oxide on the decolourization of Basic Violet 10. It was observed that 40% of decolourization occurs in the presence of ZnO in 120 minutes whereas 71.66% decolourization was observed in the presence of tin oxide doped ZnO (TZO) under solar light irridation. Under solarlight irradiation, the photocatalyst generated free radicals which serves as powerful oxidizing agents and degraded the dye molecules.

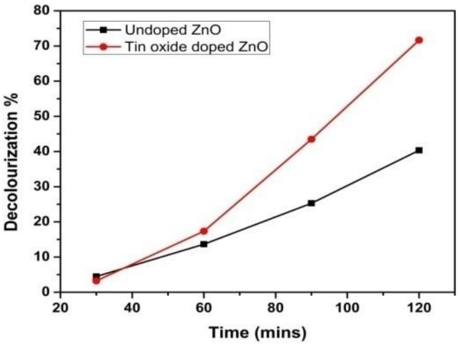


Fig.7. Effect of undoped and doped catalyst TZO.

3.2.2. Effect of Photocatalyst

The effect of concentration of TZO photocatalyst (10-50 mg/L) on the degradation of Basic Violet 10 was shown in fig. 8. The photocatalyst was added to the dye solution and it was mixed well to enhance the diffusion of the catalyst. The above solution was kept in solar light for degradation. Fig. 8 shows that 58.53% target compounds were decolourised in the presence of sunlight. The decolourization was maximum in 10 mg/L within the short time of 30-120 minutes. The results indicated that the degradation decreased on incremental addition of photocatalyst. The decrease of degradation may be due of deactivation of activated molecules by collision with ground state molecules [9]. Higher amount of catalyst loading deactivates the activated molecules by collision with ground-state molecules which results in the lower rate of reaction (Neppolian et al. 2002; Lu et al. 2009; Wong and Yu 1999; Banate et al. 1996 ;). Thus, an optimum catalytic dose of 10mg/L was selected.

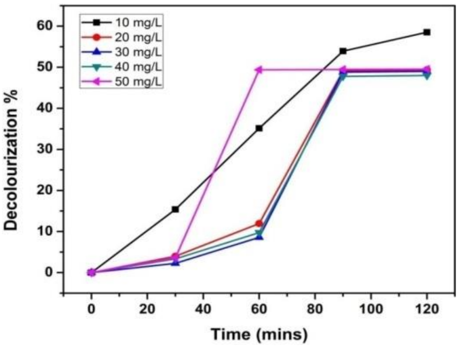


Fig. 8.Effect of Catalytic dose.

3.2.3. Effect of H_2O_2 Dosage

It was an essential parameter that the degradation of Basic Violet 10 was influenced by the amount of hydrogen peroxide. The variation of initial H_2O_2 concentration on the decolourization of dye was observed by irradiating the dye solution containing different H_2O_2 dosage (0.10, 0.12, 0.14, 0.16, 0.18 and 0.20 M).The percentage degradation ranges from 95.56 to 58.97(Fig 7).

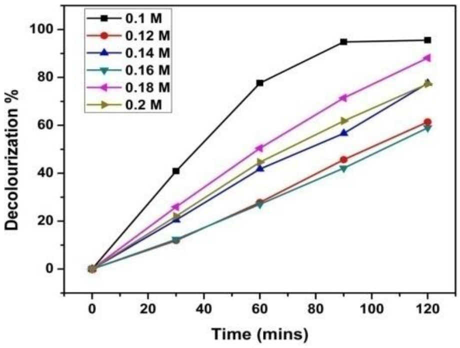


Fig. 9.Effect of H_2O_2 Concentration.

The percentage degradation decrease with increase in H_2O_2 dosage. In fact, H_2O_2 absorbed solar radiation and O–O bond ruptured leading to the production of activated OH• [10] as shown in the following equation:

$$H_2O_2 \ +h\nu \ \rightarrow 2OH\bullet$$

It was known that at higher concentrations of H_2O_2, scavenging of hydroxyl radicals will occur [11] which can be expressed by the following equations:

$$H_2O_2 + OH\bullet \rightarrow HO_2\bullet + H_2O$$

$$HO_2\bullet + OH\bullet \rightarrow H_2O + O_2$$

Since $HO_2\bullet$ is less reactive than OH•, increased amount of hydrogen peroxide has a diminishing effect on the reaction rate [12]. Therefore, it was important to optimize the H_2O_2 concentration in order to maximize the performance of degradation. As shown by Fig. 9 0.1M dosage was found to have complete decolourisation on irradiation for 120 minutes. Hence 0.1M H_2O_2 dose was selected as optimum H_2O_2 dose.

3.2.4. Effect of Dye Concentration

The effect of dye concentration was also an important parameter and it was optimized. Fig. 10 shows the percentage of dye degradation on various dye concentrations. It was noticed that by increasing the initial dye concentration the percentage degradation progressively decreased (97.03 to 87.67%). This may due to the fact that the dye concentration increases; the colour becomes more intense, which may prevent the light penetration on the photocatalyst surface.

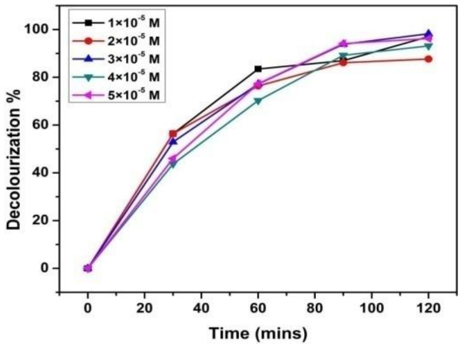


Fig. 10.Effect of Dye Concentration.

Therefore, the generation of relative amount of •OH (hydroxyl) and O_2─• (peroxide) on the photocatalyst surface did not increase [13]. In such cases, the •OH and O_2─• formed on the surface of the photocatalyst are also constant, so the strength of •OH and O_2─•Vs increasing concentration of dyes become less; hence, the photodegradation efficiency decreases, whereas the generation of •OH radicals on the surface of the catalyst is reduced at high dye concentrations, since active sites are covered by dye ions (Neppolian et al. 2002; Lu et al. 2009; Wong and Yu 1999; Banate et al. 1996; Namasivayam et al. 2001; Chatterjee et al.2005; Engenidou et al. 2005).

3.2.5. Effect of pH

The generation of hydroxyl radicals is also a function of pH. Thus, pH plays an important role in the characteristics of the dye. The pH of solution modified the surface charge of the photocatalyst, its reactivity and reaction rate. The photocatalytic degradation of the dye was observed in the pH range 2-12. Fig. 11 showed the degradation of the dyes at various pH values.

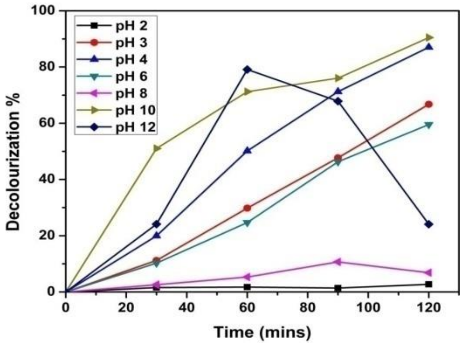


Fig. 11. - Effect of pH.

The surface of photocatalyst was positively charged in acidic medium, where as it was negatively charged in alkaline medium [14]. The results showed that the dye removal was carried out effectively at pH 4 and at pH 10. It was observed that at low pH, surface adsorption of photocatalyst was more effective in photocatalytic degradation of dyes. In acidic medium, the photodegradation of dyes was probably due to the formation of hydroxyl radicals. In the alkaline solutions, the presence of large quantities of OH^- ions on the particle surface as well as in the reaction medium favors the formation of OH^- radical. (D. Naresh Yadav et al.2017) Hence the efficiency of photodegradation decreases in the pH range 5-10 which was due to the formation of hydroxyl radicals in large quantities. These hydroxyl radicals would enhance the photodegradation of azo dyes which was known to be primary oxidizing species responsible resultant in the enhancement of the efficiency of the process.

3.2.6. Effect of Temperature

The observed reaction rates was not much influenced by temperatures in the range of 30-45°C and photo catalytic process could be carried out effectively at room temperature.

3.2.7. Photo Degradation Kinetics

Fig. 12 depicts the relationship between $\log(C/C_0)$ and reaction time of Basic Violet 10 degradation with varying amounts of photo catalyst.

$$C = C_0 \exp(-kt) \text{ or } \log(C/C_0) = -kt$$

C - Initial concentration of Basic Violet 10 (mole/L)
C_0 - concentration of the dye at various interval times (mole/L)
t - Illumination time (min)
k -reaction rate constant.

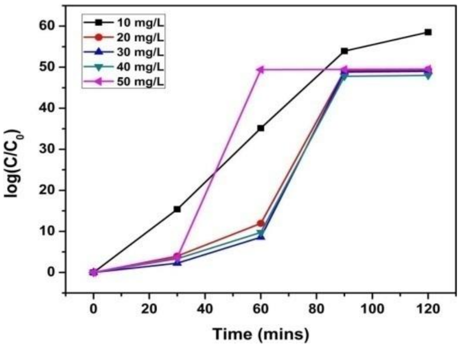


Fig. 12.Hinshelhood Plot for Dye variation.

The linear relationship between $\log(C/C_0)$ and T indicated that the photo catalytic degradation reaction followed the pseudo first-order reaction the apparent constants were calculated to be (0.003,0.003,0.003,0.003 and 0.003) min^{-1} for 10mg, 20mg, 30mg, 40mg and 50mg catalysts, respectively.

Fig.13 Relationship between $\log(C/C_0)$ and reaction time of Basic Violet 10 degradation with varying amounts dye

$$C = C_0 \exp(-kt) \text{ or } \log(C/C_0) = -kt$$

The linear relationship between $\log(C/C_0)$ and T indicates that the photocatalytic degradation reaction followed the pseudo first-order reaction, [15] the apparent constants were calculated to be (0.012, 0.006, 0.016, 0.010 and 0.013) min^{-1} for$1x10^{-5}$, $2x10^{-5}$, $3x10^{-5}$, $4x10^{-5}$ and $5x10^{-5}$ respectively.

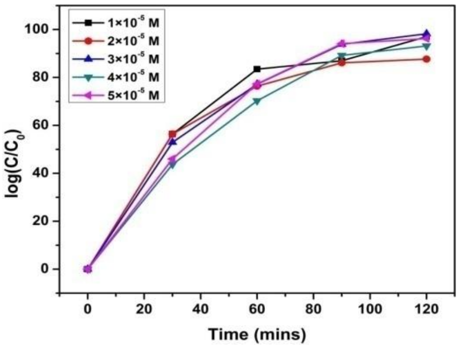


Fig. 13.Hinshelhood Plot for catalyst variation.

3.2.8. COD Removal (Chemical Oxygen Demand)

Fig. 14 showed that the COD decreases slower than the degradation of the photocatalytic solution. This is due to the fact that the dyes are not directly mineralized, however changed into intermediate photoproducts. The formed photoproducts may submit other cycle for degradation to complete the mineralization process.

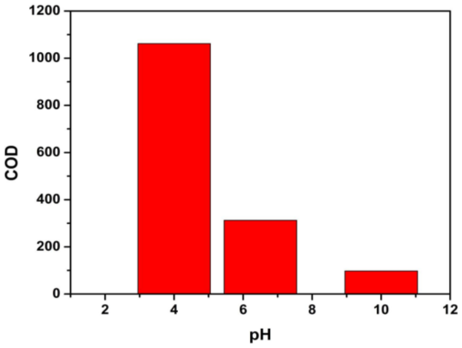


Fig. 14.COD removal at different pH values.

3.3. Reusability of Photocatalyst

Reusability of the TZO photocatalyst for photocatalytic degradation of Basic Violet 10 was studied. After each experiment of degradation, the photocatalyst was washed with water and reused for degradation process. After four catalytic cycles, the degradation performance of TZO was decreased from 97% to 88%. Fig.15 showed SEM image of reused TZO catalyst and indicating that the catalyst can be reused again whereas; the decrease in percentage dye degradation may be due to the loss of catalyst in the process of recycling.

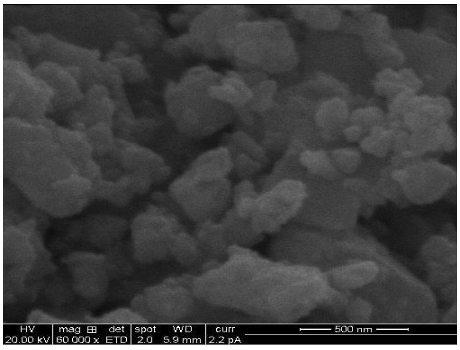


Fig.15. SEM image of reused TZO.

3.4. Mechanism

The mechanism of photocatalytic activity of TZO nanoparticle is shown in Fig.16. Under sunlight irradiation TZO molecules get excited and transfer electron from valence band to the conduction band. Electron in the conduction band of TZO can reduce molecular oxygen and produce the super oxide radical. These excited electrons react with water to produce OH- and hydrogen peroxide radicals. These OH- and hydrogen peroxide react with the dye and subsequently transfer the organic pollutants into less toxic material.

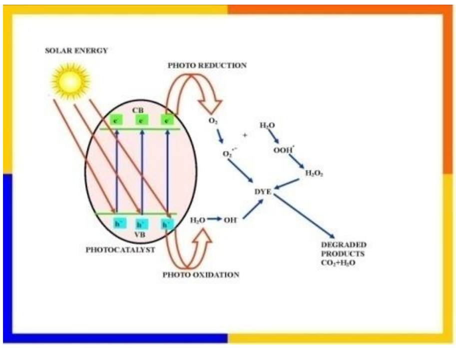


Fig. 16.Mechanism of Basic Violet 10 degradation.

Dye Degradation: Several photocatalysts are reported for Basic Violet 10 degradation. ZnO is one of the photocatalyst which degrades the dye under UV radiation at various conditions 95% degradation was achieved at 70 min [16]. The dye degradation was achieved 75.94% by heterogeneous sono-Fenton process using magnetite nanoparticles after the reaction time of 120 min [17]. It was observed that Bi_2O_3-bentonite as photocatalyst, the dye degradation percentage was observed 97.6% under visible light irradiation within 80 minutes [18]. The removal efficiency of basic violet 10 was found to be greater than 87% with Si-MCM-48 and 81% with Si-MCM-41 mesoporous materials, respectively, at room temperature [19]. The basic violet 10 dye was degraded by the BiOCl–NiFe–LDH composite and BiOCl, respectively. The degradation percentage was about 93.3% and 97.1%BiOCl–NiFe–LDH composite and BiOCl [20].

4. Conclusion

Tin Oxide doped Zinc Oxide (TZO) nanoparticles were synthesized and characterized by the XRD, SEM & EDAX studies. It was observed that the prepared TZO photocatalyst were very effective in degrading selected azo dye completely in a short interval of time (120 minutes). The degradability of Basic Violet 10 under sunlight with H_2O_2/Photocatalyst condition was also examined. Surprisingly 97% decolurization was observed. So H_2O_2/photocatalyst in the presence of sunlight was capable of the complete degradation of the Basic Violet 10 dye solution. So it can be concluded that the prepared tin oxide doped ZnO photocatalyst (TZO) can efficiently degrade the Basic Violet 10 dye solution in the presence of sunlight.

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