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ORIGINAL RESEARCH PAPER

Photocatalytic degradation of methylene blue using ZnO and 2% Fe-ZnO semiconductor nanomaterials synthesized by sol-gel method: A comparative study

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ABSTRACT

ZnO and 2%Fe-ZnO nanomaterials were prepared by using a low-cost sol-gel method. The synthesized nanomaterials were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The XRD and SEM studies reveal that the synthesized nanomaterials have a hexagonal wurtzite structure with average crystalline size ~ 22-23 nm. EDX analysis confirmed the composition and purity of synthesized nanomaterial. The photocatalytic activity of synthesized nanomaterials was monitored using the spectrophotometric method. Also, the photocatalytic removal of methylene blue (MB) dye from its aqueous solution by using ZnO and 2%Fe-ZnO nanopowder under UV light irradiation was studied. The effect of various parameters such as pH of dye solution, dye concentration, contact time and catalyst dose were investigated. Results of the current study demonstrated that, the maximum degradation using ZnO was 86 % and that for 2%Fe-ZnO was 92 % (under the optimum condition initial dye concentration=10 mg/L and pH =2). This study showed that 2%Fe-ZnO is a promising and better photocatalyst than ZnO.

Keywords: *2%Fe-ZnO; Methylene Blue; Photocatalytic Degradation; Semiconductor Nanomaterial; Sol-gel; ZnO*

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INTRODUCTION

Industries such as textile, paper, printing, leather, food, cosmetics, and etc. [1] use synthetic organic compounds in the form of dye to finish their products and release colored effluents in various water bodies like rivers, lakes, and etc. Therefore, it is a crucial task to remove such dyes from the industrial effluent before discharging into various water bodies [2]. Dyes in wastewater directly retard various processes such as photosynthesis and biological activity of various aquatic plants and animals underwater. Also, dyes have a tendency to form a chelate with metal ions and these chelating compounds create toxicity to fishes and other organisms. Some of these dyes have carcinogenic and poisonous behavior; it directly sways its adverse effects on human being [3]. Currently, industries use various dye removal methods but unfortunately, these methods are not so much effective to remove dyes completely from the environment [4]. Therefore, there is a necessity of new methods for the removal of harmful dyes for mankind.

In recent years, one of the attractive research fields is the synthesis of various semiconductor nanomaterials for the removal of textile contaminants from wastewater [5]. Mechanism of advanced oxidation processes (AOPs) contain,

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the formation of a strong oxidizing agent like OH- radical, it has a tendency to eradicate the pollutants from wastewater, shown in Fig. 1. But, due to lack of efficiency of degradation percentage of dyes, as compared to traditional AOPs, the low cost and more efficient AOPs are required and hence the area of research is semiconducting nanomaterial photocatalysis. Semiconductor nanomaterial absorbs greater energy than its bandgap energy which leads to the excitation of electrons from the valence band to the conduction band, subsequently producing electrons and holes. The valence band holes react with the water molecules and hydroxide ions to form hydroxyl radicals whereas the electron reacts with oxygen molecules and form superoxide radicals. These free radicals are powerful oxidizers of organic dyes which can attack organic dyes and degrade them into CO_2 and H_2O [6].

Methylene Blue (MB) is a heterocyclic aromatic compound. MB is a cationic dye, widely used for dying cotton, wool, and silk. This dye is stable and incompatible with the base. The harmful effect of the existence of this dye in wastewater may have arisen from the burn's effect of eye, nausea, vomiting and diarrhea, and etc. It may be poisonous if it is inhaled and in contact with skin. Thus, it is necessary to remove such hazardous dye from industrial effluent before it pollutes the nearby freshwater streams.

ZnO and its doped nanomaterials have been investigated as a potential photocatalyst. Particularly, for dye degradation, nanomaterials were found to be a more efficient catalyst than other semiconductors [7, 8]. Therefore, in this paper instead of traditional materials, synthesized semiconductor nanomaterials were used for the removal of hazardous organic dyes from industrial effluents. The nanocrystalline size of Zinc oxide (ZnO) and Iron doped Zinc oxide (2%Fe-ZnO) has gained much attention because of its physical, chemical, and optical properties which make these materials suitable for heterogeneous catalytic applications, photocatalysis, sensors, ultraviolet (UV) photodetectors, and etc. [9-11]. Till date, various nanomaterial synthesis processes have been reported such as the sol-gel process [12] and hydrothermal process [13], SILAR [14], CVD [15], and etc. But as compared to all such processes sol-gel method is preferred to achieve the higher photocatalytic activity. Likewise, this method of synthesis gives a low-cost eco-friendly solution to industrial wastewater purification problem [16]. Here it has been reported that as compared to ZnO, the 2%Fe-ZnO nanoparticles revealed better photocatalytic activities than ZnO. It was assumed that iron cations could act as shallow traps in the lattice of photocatalyst, which reduced the recombination rate of electron/hole. Best photocatalytic properties could be achieved upon doping iron [17].

Synthesis and photocatalytic studies of ZnO and 2%Fe doped ZnO nanomaterials were reported by researchers but obtained lower degradation of MB dye Many photocatalytic degradation studies had been reported using ZnO and 2%Fe-ZnO nanomaterials; but got lower [18] degradation of MB dye as compared to the present investigation because, in the present work, the optimum condition was achieved at pH 2, which gave the highest percentage degradation, 86% and 92% respectively at λ = 663nm. Therefore, this study concluded that the synthesized 2%Fe-ZnO nanomaterial is a novel, promising and better photocatalyst than ZnO.

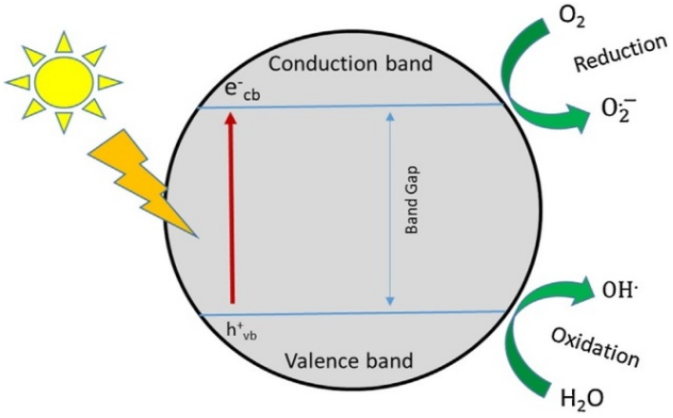
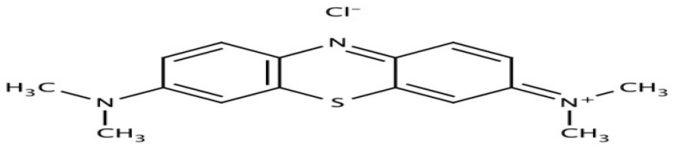


Fig. 1. Mechanism of Photocatalysis

Table 1. Chemical structure and properties of MB

Properties	Description
IUPAC name	{[7-(dimethylamino) phenothiazin-3-ylidene]-dimethylazanium;chloride}
Structure	
Molecular formula	$C_{16}H_{18}C_lN_3S$
Molar mass	319.85 g/mol
Physical state	Solid, Powder
Melting point	Powder 180 ^{0}C
Boiling point	Powder decomposes and solution 100 ^{0}C
Solubility in water	Soluble in water
Dye type	Cationic
Azo bond	1
λmax	663nm

The present work reports a comparative study on photocatalytic activity of pure and doped ZnO nanomaterials. In this investigation, methylene blue (MB) dye has been used as a model pollutant.

EXPERIMENTAL

Materials and methods

All the chemicals used in the present work were of analytical grade and all the solutions were prepared in distilled water. Chemicals used in this synthesis are Zinc Acetate Dihydrate (Zn $(CH_3COO)_2{\cdot}2H_2O$), Sodium Hydroxide (NaOH), Iron Nitrate Nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), Ethanol (C_2H_5OH) and distilled water. For photocatalytic study {[7-(dimethylamino) phenothiazin-3-ylidene]-dimethylazanium;chloride} ($C_{16}H_{18}C_lN_3S$) commonly known as Methylene blue dye was used. The chemical structure and properties of the MB dye were given in Table 1[19].

Synthesis of Photocatalyst

ZnO and 2%Fe-ZnO photocatalytic nanomaterials were synthesized by using the low-cost sol-gel method. Zinc acetate dihydrate (Zn $(CH_3COO)_2.2H_2O$) was used as a precursor and ethanol (C_2H_5OH) was used as a reagent. While sodium hydroxide (NaOH) was used as a source of oxygen. Initially, by dissolving 0.2M zinc acetate dihydrate in ethanol at room temperature and then stirring and mixing this solution using magnetic stirrer. Clear and transparent sol with no precipitate and turbidity was obtained. Then 0.02 M NaOH was gently added to the sol and stirred for 60 minutes. The sol was kept undisturbed till white precipitate settled down at the bottom of the sol. After precipitation, the precipitate was filtered and washed with excess ethanol to remove starting material. Precipitate dried at 500 °C for 15 minutes on a hot plate. Finally, this dry precipitate of ZnO was then annealed at 1000 °C temperature for 24 hours in order to remove impurities if present and to attain suitable crystallinity and properties [20, 21].

The reactions during ZnO formation were presumed to proceed [22] via,

$$Zn(X)_2 + 2NaOH \rightarrow ZnO + 2NaX + H2O \quad (1)$$

Or

$$Zn(X) + 2NaOH \rightarrow ZnO + Na_2X + H2O \quad (2)$$

Where X=acetate group

Also, 2%Fe-ZnO nanomaterial was prepared by using a low-cost sol-gel method. Initially, by dissolving 0.2M zinc acetate dihydrate and 0.2M iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) in ethanol at room temperature with 2% atomic percentage and then stirring and mixing this solution using magnetic stirrer. A transparent and clear sol without any turbidity and precipitate was obtained. After clear sol formation, the rest of the procedure was used as demonstrated above for ZnO synthesis.The detailed scheme of synthesis of ZnO and 2%Fe-ZnO is presented in Fig. 2 (a, b).

Characterizations

The synthesized nanomaterials were characterized by SEM (Hitachi S-4800-Type-II, Hitachi High Technology Corporation), XRD (Rigaku MiniFlex-600), EDX (EDX- Bruker X Flash 5030) techniques and photocatalytic activity was performed by a photocatalytic reactor and UV–Vis spectrophotometer (Systronics 2203 India).

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Photocatalytic degradation experiment

The photocatalytic degradation experiment was performed using a photocatalytic reactor (Lelesil Innovative Systems). The reactor enclosed with a round and hollow Pyrex glass cell with 1.0 L limit, 10 cm breadth, and 15 cm height. For the light source, 150 W mercury light (400-700 nm) was placed in a 5 cm width quartz tube with one end firmly fixed by a Teflon plug. The light and the tube were then submerged in the photoreactor cell with a light way of 3.0 cm. The whole reactor was cooled with water and the temperature was kept at 25 °C. The photocatalytic reactor used for this study and its schematic representation as shown in - Fig. 3 (a, b).

The stock solution for this degradation study was prepared by dissolving MB dye in 100 mL of distilled water. To 10 mL of this stock solution, photocatalyst like ZnO and 2%Fe-ZnO were added. This aqueous solution was magnetically stirred for half an hour and exposed to UV light. In the same way, the next desired concentration of dye solutions (20, 30, 40 and 50 mg/L) was prepared by diluting the stock solution with deionized water. All reactants in the photocatalytic reaction were

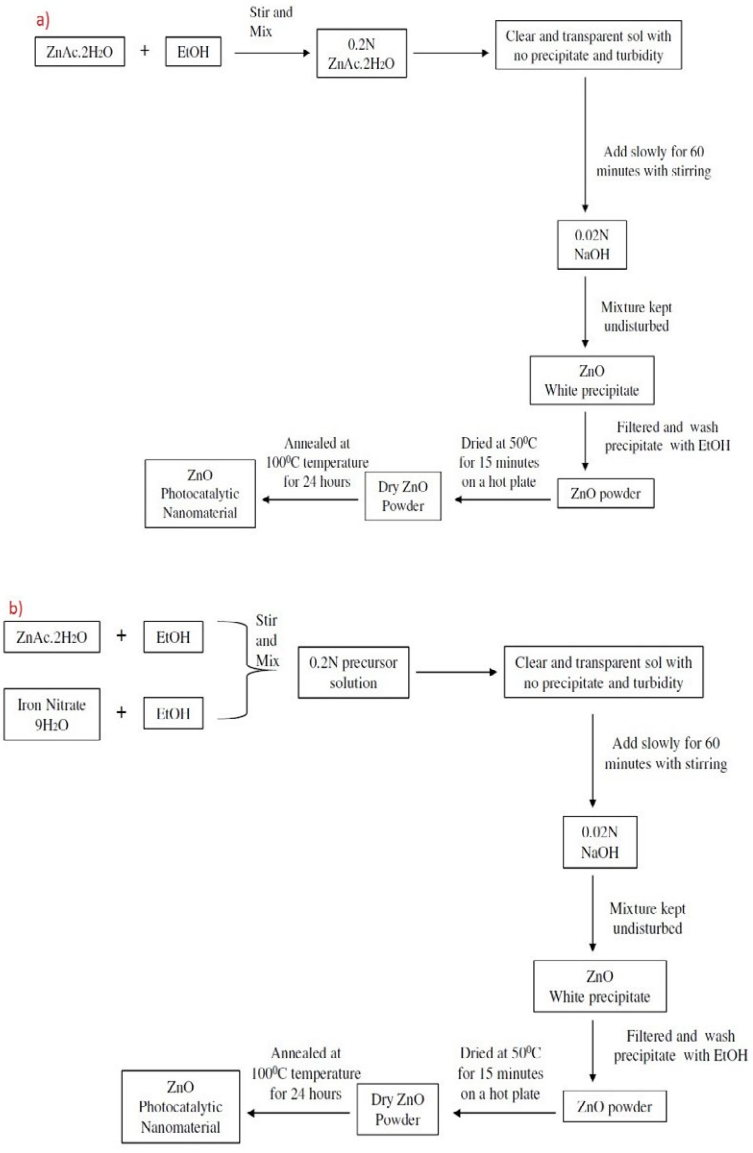

Fig. 2. Scheme of synthesis of a) ZnO b) 2% Fe-ZnO

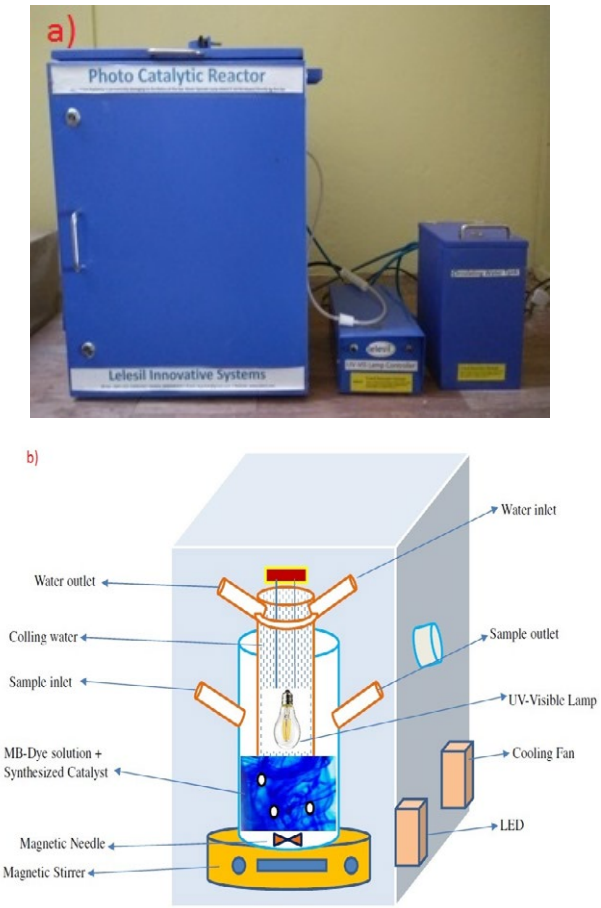

Fig. 3. a) Photocatalytic Reactor used and its b) schematic representation

stirred using a magnetic stirrer situated inside the reactor below the light source, in order to make a uniform suspension of the catalyst throughout the reaction. The photocatalytic activity of the synthesized catalyst was predicted by measuring the residual concentration of MB dye in the solution. The spectrophotometric analysis of dye was used to measure the decolorization efficiency of MB dye. The absorbance of MB dye was measured by using UV–Vis spectrophotometer. The maximum wavelength of absorbance for MB dye is λmax= 663 nm. After the visible light irradiation, the decolorization rate of dye was obtained, by decreasing absorbance of dye at the wavelengths of maximum absorbance. The degradation efficiency of the dye i.e. % adsorption has been calculated using Eq. (1).

$$\%Degradation = \frac{Co - Ct}{Co} \times 100 \quad (1)$$

Where *Co* = initial dye concentration and *Ct* = dye concentration after time t.

RESULTS AND DISCUSSION

XRD analysis

XRD patterns of ZnO and 2%Fe-ZnO nanoparticles were shown in Fig. 4. The XRD spectrum showed three broad peaks for ZnO and 2%Fe-ZnO at the 2θ=31.660, 34.350, 36.155 and 2θ=31.259, 33.949, 35.755 positions. The three diffraction peaks correspond to the (100), (002), and (101) crystalline planes of hexagonal ZnO. Well-defined sharp peaks confirmed the good crystalline quality ofZnO and 2%Fe-ZnO nano photocatalysts. All the peaks in the XRD patterns of ZnO and 2%Fe-ZnO samples could be fitted with the hexagonal wurtzite structure with JCPDS card No.(36-1451) [23,24]. The broadening of the XRD lines is attributed to the nanocrystalline characteristics of the samples, which indicates that the particle size is in the nanometer range.

The average crystalline size of synthesized nanoparticles was calculated by using the Scherer formula as shown in Eq. (2) [25].

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$$D = 0.94\lambda / \beta Cos\theta \quad (2)$$

Where D is the average crystalline size, λ is wavelength in angstrom, β is the FWHM in radian and θ is the diffraction angle in degree.

Based on the Scherrer equation the average crystal size of the ZnO and 2%Fe-ZnO nanoparticles was calculated as 22.01 nm and 23.38 nm respectively.

SEM images of ZnO and 2%Fe-ZnO nanoparticles were shown in Fig. 5 (a, b). The SEM micrograph indicates the morphology of nanomaterials like nanoflakes or nano-flowers [26]. In the present investigation, SEM images showed the crystalline nature of synthesized semiconductor photocatalyst which made that photocatalyst more efficient, as it minimizes electron-hole pair loss owing to the trapping of either charge carriers at defect states as earlier studies were reported [27,28].

EDX spectrum revealed the presence of Zn, Fe and O elements. No other impurity was detected in the sample spectrum, which confirms the purity of the synthesized nanomaterial. The compositional analysis in terms of atomic percentage of the nanomaterial was done by EDX, as shown in Table 2. The presence of Zn, Fe, and O in the EDX analysis is due to the precursors used during the synthesis of nanomaterials.

Photocatalytic studies

Effect of pH of the solution

pH plays an important role in the photocatalytic study, as, it controls the reactions during the degradation of dyes or organic compounds and beside this generation of hydroxyl radicals also

Table 2. EDX analysis of nanomaterials

EDX analysis		
Type of nanoparticles	Elements	at %
ZnO	Zn K	44.99
	O K	54.01
2% Fe-ZnO	Zn K	39.27
	O K	56.72
	Fe K	1.69

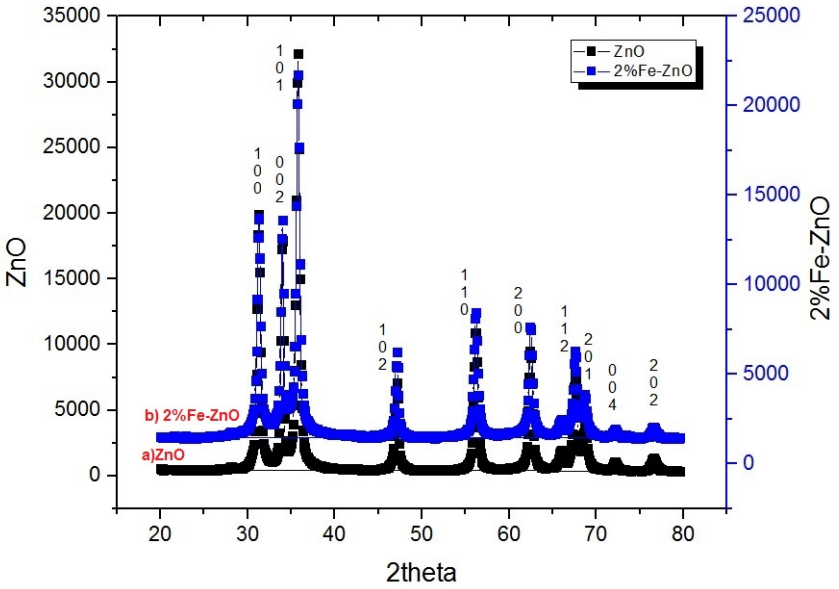

Fig. 4. XRD pattern of nanoparticles ZnO and 2% Fe-ZnO

Table 3. Pseudo-first-order rate constant of MB Photocatalytic degradation

Catalyst	Amount of catalyst in g/L	Conc. of dye in g/L	Rate Const. (k) min^{-1}	Linear regression coefficient (R^2)
ZnO	1 g/L	10	0.01076	0.9824
	1 g/L	20	0.008523	0.9763
	1 g/L	30	0.007135	0.9871
2% Fe-ZnO	1 g/L	10	0.0106	0.9539
	1 g/L	20	0.008421	0.988
	1 g/L	30	0.007505	0.9908

depends on the pH of the solution[29, 30]. Initially, the effect of pH on the photocatalytic degradation of MB dye in the range of pH 1-10 in presence of synthesized photocatalyst was studied under conditions (contact time = 180 minutes, dye concentration = 20 mg/L and catalyst dose = 1 g/L) as shown in Fig. 6. The pH of a solution affects the surface charge properties of the catalyst and indirectly it affects the adsorption behavior [31]. The pHpzc (point of zero charges) of the catalyst was estimated at about (ZnO=8.3 and 2%Fe-ZnO=8.9) using reported method [32]. The surface has net-zero charges at pHpzc and at pH < pHpzc the surface of the catalyst is positively charged while at pH > pHpzc the surface is negatively charged. According to the pHpzc values, the pHpzc of ZnO is 8.3. This means that at pH values below 8.3, the ZnO surface has a net positive charge, while at pH greater than 8.3, the surface has a net negative charge. Similarly, the pHpzc of 2%Fe-ZnO is 8.9. This means that at pH values below 8.9, the 2%Fe-ZnO surface has a net positive charge, while at pH greater than 8.9, the surface has a net negative charge [33].

The percentage of dye removal showed an increase with a decrease in pH value and reached their maximum value in the acidic pH. At low pH value, the surfaces of the catalysts were highly protonated and become positively charged so that the dye cations were electrostatically attracted more towards the catalyst surface as more oxidizing holes increases and thus decoloration of MB dye was enhanced. At acidic pH, the positive holes are considered as the major oxidation species, whereas hydroxyl radicals are considered as the predominant species at neutral or alkaline

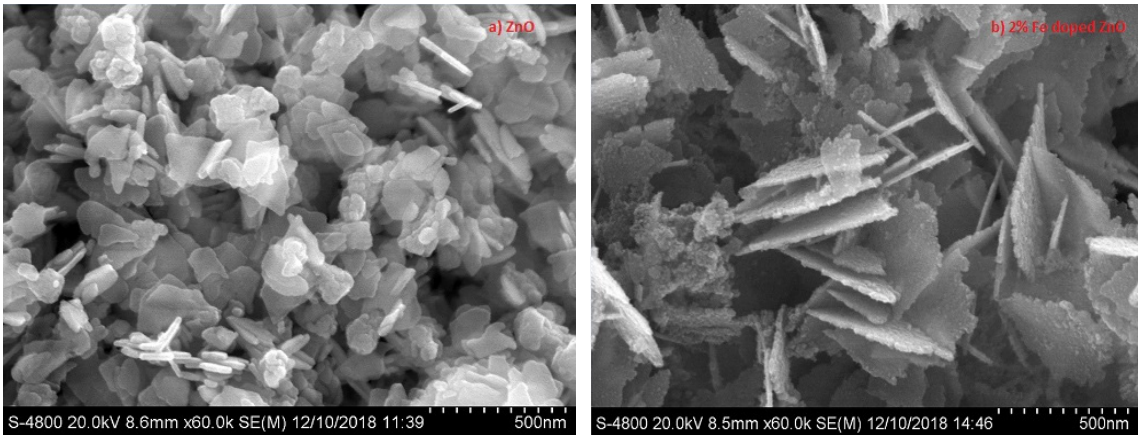

Fig. 5. SEM images of a) ZnO and b) 2% Fe-ZnO nanomaterials

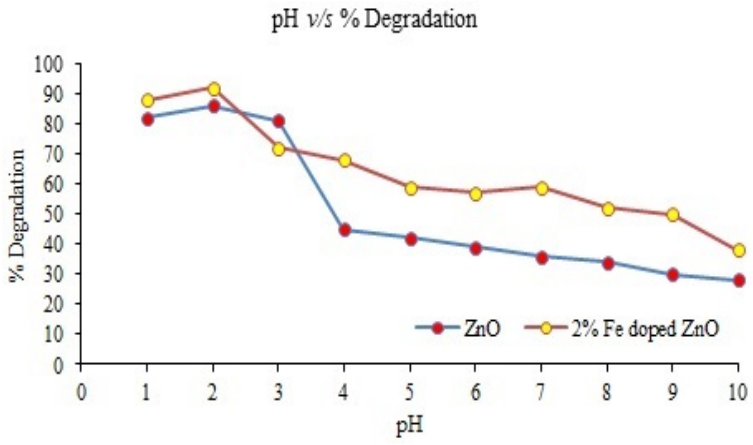

Fig. 6. Effect of pH on photocatalytic degradation of MB dye under conditions: pH= 1-10, dye concentration 20 mg/L and catalyst (ZnO and 2% Fe- ZnO) dose 1 g/L for the irradiation time 180 min.

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pH [34]. Maximum degradation of MB dye at pH 2 using ZnO and 2%Fe-ZnO photocatalysts was demonstrated 86 % and 92 % respectively.

Effect of initial dye concentration

The effect of initial dye concentration on the degradation efficiency was studied at optimized pH= 2 by varying initial dye concentration. Different initial concentrations of MB with a range of 10-50 mg/L were used to assess the photocatalytic activity. Maximum degradation at the initial dye concentration of 10 mg/L as shown in Fig. 7 (a, b).

The degradation efficiency of dye was decreased when the initial concentration of dye increased. This is because; as the initial dye concentration was increased indirectly, the excess of dye molecules will be adsorbed on the catalyst surface, so the active sites of the catalysts will be reduced. As the dye concentration increases, a number of hydroxyl radicals are required for the degradation of dye molecules and while, the formation of hydroxyl radicals on the catalyst surface remains constant for given light intensity, catalyst dose and irradiation time [35]. Therefore the hydroxyl radicals produced are insufficient for the degradation of dye at high concentration. Hence, photodegradation efficiency reduces as the concentration of dye increases.

Effect of contact time

The effect of contact time on photocatalytic degradation of MB dye was examined at an optimum condition (pH=2) and dye concentration of 10 mg/L. The fixed amount of ZnO and 2%Fe-ZnO catalyst was 1 g/L used. The relationships

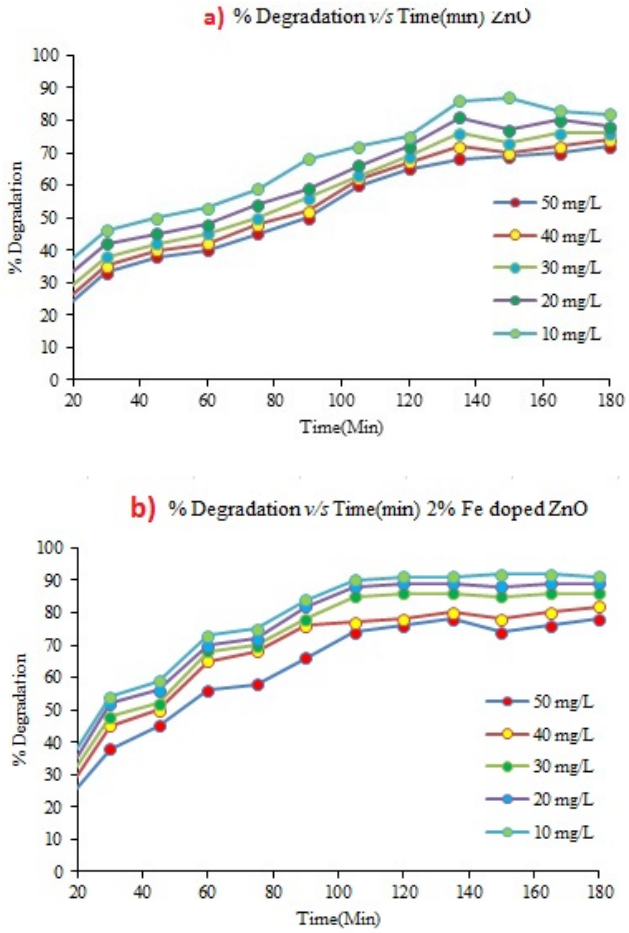

Fig. 7. Effect of initial dye concentration on the photocatalytic degradation (a) MB conditions: pH=2, dye concentration 10, 20, 30, 40, 50 mg/L and (ZnO) catalyst dose 1 g/L for irradiation time 180 min. (b) MB conditions: pH= 2 dye concentration 10, 20, 30, 40, 50 mg/L and (2% Fe-ZnO) catalyst dose 1 g/L for irradiation time 180 min.

between photocatalytic degradation of MB dye and the contact time of catalyst was investigated. The results are shown in Fig. 8. It has been observed that as the irradiation time of catalyst increases, the degradation of MB increases [36].

The graph depicts, initially from zero minutes to 140 minutes due to the availability of a large number of active sites, the degradation rate is faster for the first 140 minutes, and then it attains equilibrium. It means that after these 140 minutes there will be repulsion between dye particles and catalyst surface which lowers the degradation rate.

Effect of catalyst dose

The effect of photocatalyst dose was studied on dye degradation when other experimental conditions (pH=2, dye concentration 10 mg/L and contact time 140 min) were constant. The degradation percentage of MB by different catalyst doses, 0.2–2 g/L for 10 mg/L of dye concentration, was examined. It is observed from the graph; the rate of degradation initially increases rapidly with the increase in catalyst concentration and thereafter decreases as shown in Fig. 9. As the catalyst concentration increases, the agglomeration simply the particle-particle interaction also increases, this is the major factor to reduce light absorption by the photocatalyst. Also, the agglomerations prevent photons from reaching inner layers of the catalyst [37]. Hence, the least amount of catalyst particles gets excited and ultimately less electron/holes and hydroxyl radical were produced. Therefore, the degradation rate tends to decrease as the catalyst dose increases [38].

Kinetics study

The photocatalytic degradation of MB was found to be Pseudo-first order. The ratio ln (C_0/C_t) is directly proportional to contact time. This ratio also indicates that the photocatalytic degradation

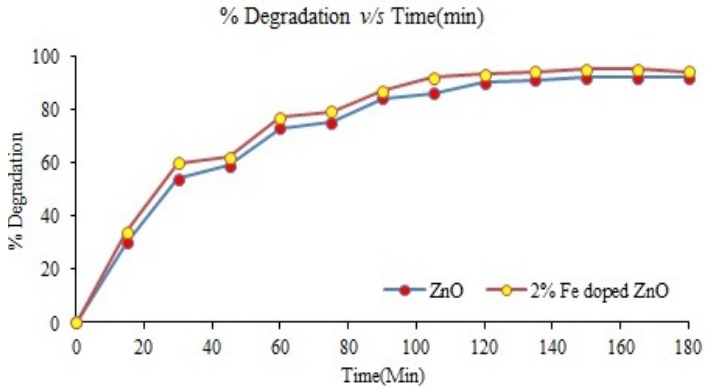

Fig. 8. Effect of contact time on photocatalytic degradation of MB dye under conditions: pH=2, dye concentration 10 mg/L and catalyst (ZnO and 2% Fe-ZnO) dose 1 g/L irradiation time 180 min.

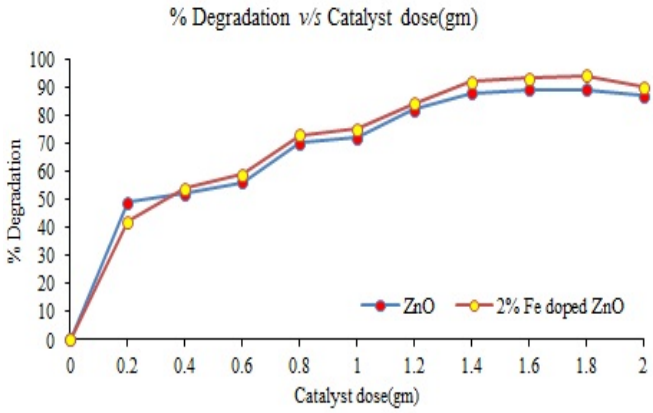

Fig. 9. Effect of catalyst dose on the photocatalytic degradation of MB dye under conditions: pH=2, dye concentration 10 mg/L and catalyst (ZnO and 2% Fe-ZnO) dose 0.2-2 g/L irradiation time 140 min.

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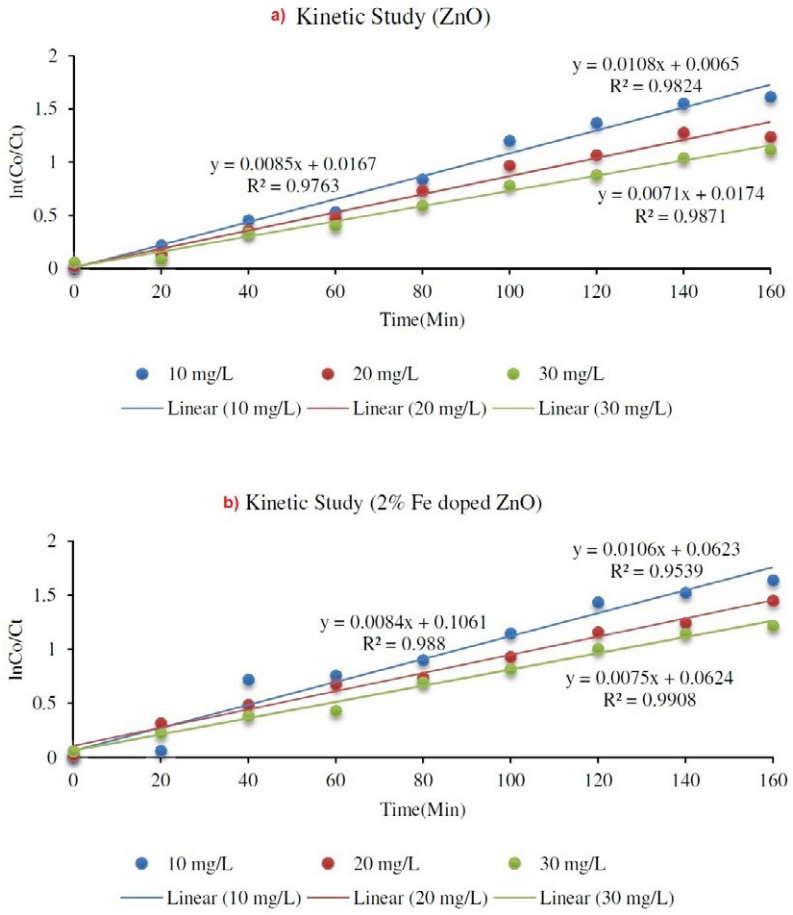

Fig. 10. Pseudo-first-order kinetics for photocatalytic degradation of (a) MB, conditions pH=2, dye concentration. 10, 20, 30 mg/L and catalyst dose 1 g/L irradiation time 140 min. (b) MB, conditions: pH= 2 dye concentration. 10, 20, 30 mg/L and catalyst dose 1 g/L irradiation time 140 min.

of MB solution is directly proportional to the concentration of the MB dye solution. From this we can conclude that the photocatalytic degradation is the pseudo-first-order reaction. The first-order kinetic equation of $\ln (C_0/C_t) = kt$ [39, 40] was used to fit experimental data. Where k is the apparent rate constant, C0 is the initial solution concentration of MB, and Ct is the concentration of MB at time t. The linear transform in $\ln (C_0/C_t)$ as a function of contact time is given in Fig. 10 (a, b). This confirms that the kinetic curves were of pseudo-first-order. The slope of the $\ln (C_0/C_t)$ Vs time plot gives the value of the rate constant k in min^{-1}.

The photocatalytic activity can be compared to k value and linear regression coefficient (R^2) for MB solution with different initial concentrations, this data is summarized in Table 3. The k values, which are obtained by linear fitting from the graph. The rate constant obtained using ZnO nanomaterial are 0.01076, 0.008523, 0.007135 min^{-1} while using 2%Fe-ZnO are 0.0106, 0.008421, 0.007505 min^{-1}.

CONCLUSIONS

ZnO and 2%Fe-ZnO photocatalysts were synthesized using the sol-gel method. This method is simple and low cost. The XRD patterns revealed that the ZnO and 2%Fe-ZnO samples have hexagonal wurtzite structure. The average crystalline size of samples was calculated ~ 22.01 and 23.38 nm respectively. Results of the present study showed, doping of ZnO nanoparticles with iron, improve the photocatalytic properties of ZnO. The degradation efficiency of the photocatalyst directed that the low initial dye concentration and high catalyst dose are more favorable for the degradation of MB dye. Also, follows the pseudo-first-order kinetics with good correlation with linear regression coefficient. This study investigated

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that, the maximum degradation of MB dye was 86% (ZnO) and that of 92% (2%Fe-ZnO). Moreover, this study concluded comparatively from previous reports that 2%Fe-ZnO is a promising and better photocatalyst than ZnO.

ACKNOWLEDGMENTS

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CONFLICTS OF INTEREST

There are no conflicts to declare.

REFERENCES

1. Chebor L.J., (2018), Characterization of synthesized ZnO nanoparticles and their application in photodegradation of methyl orange dye under fluorescent lamp irradiation, *Int. J. Sci. Eng. Sci.* 2:5-8.
2. Hossain A, Rayhan ABMS, Raihan MJ, Nargis A, Ismail IMI, Habib A, et al. Kinetics of Degradation of Eosin Y by One of the Advanced Oxidation Processes (AOPs)—Fenton's Process. American Journal of Analytical Chemistry. 2016;07(12):863-79.
3. Baeissa ES. Photocatalytic degradation of methylene blue dye under visible light irradiation using In/ZnO nanocomposite. Frontiers in Nanoscience and Nanotechnology. 2016;2(5).
4. Mathur N., Bhatnagar P., Sharma P., (2012), Review of the mutagenicity of textile dye products, *Uni. J. Env. Res. Tech.* 2:1-18.
5. Isai K.A., Shrivastava V.S., (2015), Detection and identification of organics and metals from industrial wastewater by ICP-AES, FTIR and GC-MS, *J. Adv. Chem. Sci.* 1:164-166.
6. Assi N., Mehrdad Sharif A. A., Bakhtiari H., Manuchehri N. Q. S., (2014), Photo catalytic property of ZnO and Mn-ZnO nanoparticles in removal of Cibacet Turquoise blue G from aquatic solution, *Int. J.Nano Dimens*. 5: 145-154.
7. Sun L, Yao Y, Wang L, Mao Y, Huang Z, Yao D, et al. Efficient removal of dyes using activated carbon fibers coupled with 8-hydroxyquinoline ferric as a reusable Fenton-like catalyst. Chemical Engineering Journal. 2014;240:413-9.
8. Haydar Mohammad S. Photodegradation of Alizarin Black S Dye Using Zinc Oxide. Journal of Environmental Science and Engineering A. 2015;4(8).
9. Mardani HR, Forouzani M, Ziari M, Biparva P. Visible light photo-degradation of methylene blue over Fe or Cu promoted ZnO nanoparticles. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2015;141:27-33.
10. Shabannia R., (2019), Fast UV detection by Cu-doped ZnO nanorod arrays chemically deposited on PET substrate, *Int. J. Nano Dimens.*, 10: 313-319.
11. Majedi A., Davar F. , Abbasi A. R., (2016), Metal-organic framework materials as nano photocatalyst, *Int. J. Nano Dimens.*, 7: 1-14.
12. Jurablu S., Farahmandjou M., Firoozabadi T. P., (2015), Sol-gel synthesis of zinc oxide (ZnO) nanoparticles: study of structural and optical properties, *J. Sci. Islam. Rep. Iran* 26:281-285.
13. Suresh B. K., Narayanan V., (2013), Hydrothermal synthesis of hydrated zinc oxide nanoparticles and its characterization, *Chem. Sci. Trans.* 2: S33-S36.
14. Isai K.A., Shrivastava V.S., (2017), Optical studies of undoped and doped photocatalytic thin Films, *Asian J. Chem. Env. Res.*10:22-24.
15. Protasova LN, Rebrov EV, Choy KL, Pung SY, Engels V, Cabaj M, et al. ZnO based nanowires grown by chemical vapour deposition for selective hydrogenation of acetylene alcohols. Catalysis Science & Technology. 2011;1(5):768.
16. Balcha A, Yadav OP, Dey T. Photocatalytic degradation of methylene blue dye by zinc oxide nanoparticles obtained from precipitation and sol-gel methods. Environmental Science and Pollution Research. 2016;23(24):25485-93.
17. Lavand AB, Malghe YS. Synthesis, characterization and visible light photocatalytic activity of carbon and iron modified ZnO. Journal of King Saud University - Science. 2018;30(1):65-74.
18. Oliveira APA, Hochepied J-F, Grillon F, Berger M-H. Controlled Precipitation of Zinc Oxide Particles at Room Temperature. Chemistry of Materials. 2003;15(16):3202-7.
19. Yu X, Meng D, Liu C, Xu K, Chen J, Lu C, et al. Enhanced photocatalytic activity of Fe-doped ZnO nanoparticles synthesized via a two-step sol–gel method. Journal of Materials Science: Materials in Electronics. 2014;25(9):3920-3.
20. Sivashankar R., Susheeba O.K., Sivasubramanian V., (2015), Adsorption of organic dye on to novel magnetic biocomposite: kinetics and equilibrium studies, *Res. J. Chem. Env.* 19:48-57.
21. Isai K.A., Shrivastava V.S., (2018), Synthesis and characterization of ZnO and Fe doped ZnO photocatalytic nanomaterial using sol-gel method, *J. Appl. Sci. Comp.* 5:73-81.
22. Yang L-Y, Dong S-Y, Sun J-H, Feng J-L, Wu Q-H, Sun S-P. Microwave-assisted preparation, characterization and photocatalytic properties of a dumbbell-shaped ZnO photocatalyst. Journal of Hazardous Materials. 2010;179(1-3):438-43.
23. N. Singh, Mehra R.M., Kapoor A., (2011), Synthesis and characterization of ZnO nanoparticles, *J. Nano-Electron. Phys.* 3: 132-139.
24. Pourrahimi AM, Liu D, Pallon LKH, Andersson RL, Martínez Abad A, Lagarón JM, et al. Water-based synthesis and cleaning methods for high purity ZnO nanoparticles – comparing acetate, chloride, sulphate and nitrate zinc salt precursors. RSC Adv. 2014;4(67):35568-77.
25. Shokri A, Rabiee F, Mahanpoor K. Employing a novel nanocatalyst (Mn/Iranian hematite) for oxidation of SO2 pollutant in aqueous environment. International Journal of Environmental Science and Technology. 2017;14(11):2485-94.
26. Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental Applications of Semiconductor Photocatalysis. Chemical Reviews. 1995;95(1):69-96.
27. Beydoun D., Amal R., Low G., McEvoy S., (1999), Role of nanoparticles in photocatalysis, *J. Nanopart. Res.* 1:439-458.
28. Shokri A, Joshagani AH. Using microwave along with TiO2

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for degradation of 4-chloro-2-nitrophenol in aqueous environment. Russian Journal of Applied Chemistry. 2016;89(12):1985-90.
29. Shanthi M., Kuzhalosai V.,(2012), Photocatalytic degradation of an azo dye, Acid Red 27, in aqueous solution using nano ZnO, *Ind. J. Chem.* 51:428-434.
30. Mohammadzadeh S, Olya ME, Arabi AM, Shariati A, Khosravi Nikou MR. Synthesis, characterization and application of ZnO-Ag as a nanophotocatalyst for organic compounds degradation, mechanism and economic study. Journal of Environmental Sciences. 2015;35:194-207.
31. Fatehah MO, Aziz HA, Stoll S. Stability of ZnO Nanoparticles in Solution. Influence of pH, Dissolution, Aggregation and Disaggregation Effects. Journal of Colloid Science and Biotechnology. 2014;3(1):75-84.
32. Farrokhi M, Hosseini S-C, Yang J-K, Shirzad-Siboni M. Application of ZnO–Fe3O4 Nanocomposite on the Removal of Azo Dye from Aqueous Solutions: Kinetics and Equilibrium Studies. Water, Air, & Soil Pollution. 2014;225(9).
33. Akpan UG, Hameed BH. Parameters affecting the photocatalytic degradation of dyes using TiO2-based photocatalysts: A review. Journal of Hazardous Materials. 2009;170(2-3):520-9.
34. Khairnar S. D., Patil M. R., Shrivastava V. S., (2018), Hydrothermally synthesized nanocrystalline Nb_2O_5 and its visible-light photocatalytic activity for the degradation of congo red and methylene blue, *Iran. J. Catal.* 8:143-150.
35. Marathe YV, Ramanna MMV, Shrivastava VS. Synthesis and characterization of nanocrystalline CdS thin films grown by chemical bath deposition at different molarities for removal of methylene blue. Desalination and Water Treatment. 2013;51(28-30):5813-20.
36. Farzi G. A., Tayebee R., Naghibinasab S., (2015), Surface modification of ZnO nanoparticles with Trimetoxyvinyl Silane and Oleic Acid and studying their dispersion in organic media, *Int. J.Nano Dimens.* 6: 67-75.
37. Ajoudanian N, Nezamzadeh-Ejhieh A. Enhanced photocatalytic activity of nickel oxide supported on clinoptilolite nanoparticles for the photodegradation of aqueous cephalexin. Materials Science in Semiconductor Processing. 2015;36:162-9.
38. Sadiq M.M., Nesaraj A.S., (2014), Reflux condensation synthesis and characterization of Co_3O_4 nanoparticles for photocatalytic applications, *Iran. J. Catal.* 4:219- 226.
39. Nezamzadeh-Ejhieh A., Banan Z., (2012), Kinetic investigation of photocatalytic degradation of dimethyl disulfide by zeolite a containing nano CdS, *Iran. J. Catal.* 2:79-83.
40. Benmaamar Z., Hamitouche H., Boutoumi H., Benmaamar H., Ould Baba Ali S., Benmaamar A., Aggoun A. (2017), A batch study of adsorption equilibrium and kinetic for methylene blue onto synthesized zeolite, *J. Mat.Environ.* Sci., 8:539-550.

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