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The Study of the Photocatalytic Degradation of Methyl Orange in the Presence of Zinc Oxide (ZnO) Suspension

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Authors' contributions

This work was carried out in collaboration among all authors. Author MMR designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors TAP and DCM managed the analyses of the study. Authors MA and MMH managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Photodegradation of methyl orange spectrum in aqueous ZnO suspension by UV irradiation has shown time-dependent UV photodegradation. Methyl orange shows absorption peaks at 463 nm in the visible region. The rate of decolourization was recorded with respect to the change in the intensity of absorption peaks at 463 nm. The absorbance decreased with time and finally disappeared as the irradiation was scattered with time. It is seen that about 40% of dye was degraded after 30 minutes whereas about 60% of dye degraded after hours. The effect of photocatalyst concentration on the photo-degradation rate of the methyl orange dye was investigated by employing different concentrations of ZnO from 0.2 to 2.0 g/100 mL with dye concentration of methyl orange solution was observed for the ZnO of 1.4 g/mL during 60 minutes of irradiation. After optimizing the catalyst concentration of ZnO suspension (1.4g/100mL), the photocatalytic

degradation methyl orange solution was carried out by varying the initial concentration of dye from 6mg/100mL to 10mg/100mL in order to assess the appropriate concentration of the dye required for maximum degradation. The percentage of degradation of methyl orange is scattered with an increase in dye concentration. In the case of 7mg/100mL of MO solution about 68% of degradation was found after 60 minutes. The highest degradation of methyl orange is 64.458 which were obtained at pH 7.

Keywords: Methyl orange; ZnO; photo-degradation; dye.

1. INTRODUCTION

A dye may be a coloured substance that has an affinity to the substrate to that it's being applied. The dye is usually applied in a solution and needs a mordant to enhance the fastness of the dye on the fibre. Each dye and pigments seem to be coloured as a result of they absorb some wavelengths of sunshine over others [1]. In distinction with a dye, a pigment usually is insoluble and has no affinity for the substrate. Some dyes will be precipitated with an inert salt to supply a lake pigment and supported the salt used they may be atomic number 13 lake, atomic number 20 lake or atomic number 56 lake pigments. Coloured flax fibres are found within the republic of Georgia in a very prehistoric cave dated to 36,000 BP [2-6]. Archaeological proof shows that, notably in the republic of India and geographic area, colouring has been wide allotted for over 5,000 years [7].

The dyes were obtained from animal, vegetable or mineral origin with none too little or no process out and away the best supply of dyes has been from the kingdom Plantae, notably roots, berries, bark, leaves and wood however solely many have ever been used on an ad scale [8]. The primary human-made organic dyestuff was discovered serendipitously by Henry Perkin in 1856, the results of an unsuccessful try at the full synthesis of antimalarial drug. Alternative aminobenzine dyes followed, like fuchsine, safranine, and induline. Several thousands of artificial dyes have since been ready [9-11]. Artificial dyes quickly replaced the standard natural dyes. They valueless, they offered a colossal vary of the latest colours, and that they imparted higher properties to the coloured materials. [12-14] Dyes square measure currently classified in step with however they're employed in the colouring method.

It is one in every of the foremost necessary dyes, that is usually employed in the textile trade. The acid-base indicator may be a pH indicator often employed in titrations due to its clear and distinct colour amendment [15-18]. As a result of it changes colour at the pH of a mid-strength acid, it's typicallyemployed in titrations for acids. Not like a universal indicator, the acid-base indicator doesn't have the full spectrum of the colour amendment; however, it features a swindler finish purpose. An acid-base indicator shows red change acidic medium and it shows yellow change basic medium [19].

In a solution turning into less acidic, the acidbase indicator moves from red to orange and at last to yellow with the reverse occurring for an answer increasing in acidity [20]. The whole colour amendment happens in acidic conditions. In an acid, it's blood-red and in alkali, it's yellow. The acid-base indicator features a pKa of 3.47 in the water at 25° C (77°F) [21-22].

2. MATERIALS AND METHODS

2.1 Preparation of Solution and Suspension

All liquid solutions were ready with deionized water. The ZnO suspension was ready by taking 2.0 g of ZnO in a very 100 mL beaker and 5 mL of deionized water was supplemental to that. The suspension was coated and unbroken long. The quantity of ZnO was modified once the diluted suspension was necessary.

2.2 Stock Solution of Methyl Orange

The stock solution of the acid-base indicator was ready by dissolving 0.585 g of acid-base the indicator in a thousand millilitre of deionized water. Thus 585.0 mg/mL of the stock resolution was obtained having molar concentration a pair of 0.5×10^{-5} M more dilution was created once necessary [23]. The concentration varies used for experiment was 2mg/100ml to 10mg/100ml.

2.3 Uv-spectrochemical Analysis

2.3.1 Spectrum of methyl orange and ZnO suspension

The spectrum of methyl orange and ZnO suspension were recorded by using UV-Visible spectrophotometer.



Scheme 1. Molecular structure of methyl orange

2.3.2 Determination of working wavelength and molar absorption coefficient of methyl orange

The spectrum of sensible acid-base indicator in solution the height at 463 nm is that the most intense that falls within the visible region. This peak has been taken because the operating wavelength to follow the concentration of acid-base indicator [24-25]. The standardization Curve was made by plotting absorbance of resolution versus concentration of acid-base indicator among the vary 2mg/100mL to 10mg/100mL. The Experimental knowledge and therefore the corresponding customary curve are shown in Table 1 the worth of molar coefficient was calculated from this standardization curve.

2.4 Photodegradation of Methyl Orange under Different Conditions

Experiments to look at photodegradation of acidbase indicator were carried in ZnO suspension below totally different experimental conditions to analyze the subsequent factors. 2.6.1 Impact of the various quantity of ZnO needed for photodegradation of acid-base indicator. 2.6.2 Impact of the various initial concentration of acidbase indicator on the photodegradation in the presence of ZnO suspension. 2.6.3 Impact of the various pH on the photodegradation of acid-base the indicator in the presence of ZnO suspension [26-27].

3. EXPERIMENTAL SECTIONS

3.1 Determination of Optimum Concentration of ZnO Suspemsion Required for Photodegradation of Methyl Orange

Derived data from section and experimental condition of section are given to obtain the optimum amount of ZnO:

Determination of optimum concentration of methyl orange for photodegradation of MO in presence of ZnO suspension.

4. RESULTS AND DISCUSSION

4.1 Photodegradation of Methyl Orange in the Presence of ZnO Suspension

Results of photodegradation of methyl orange in aqueous ZnO suspension by UV irradiation has shown in section 3.1.

Methyl orange shows absorption peaks at 463 nm in the visible region. The rate of decolourization was recorded in order to the change in the intensity of absorption peaks at 463 nm [28-30.]

Fig. 1 shows the time-dependent UV-Visible spectrum photodegradation.

Fig. 1 shows fitting the polynomial curve for the plot of absorbance vs. concentration of MO solution. Table 1 shows that the absorbance decreased gradually with increasing the time.

Fig. 1 shows the change of absorption of the degraded solution with time using different amount of ZnO suspensions. The degraded solutions were found to be different colours at different time. It is seen that the absorbance gradually decreased with increasing in time.

Fig. 2(a) shows the % degradation is increased with an increase in time at the experiment no. 7 during 60 minutes of irradiation. From Table 2 and Fig. 3, it is seen that about 40% of dye was degraded after 30 minutes whereas about 60% of dye degraded after an hour. The change of decolourization was also monitored by centrifuging to obtain clear solutions.

4.2 Effect of Photocatalyst Concentration on the Degradation Rate

It is necessary from each the mechanistic and application points of reading to analyze the dependence of the photocatalytic reaction rate on the concentration of ZnO suspension. Hence, the impact of photocatalyst concentration on the photodegradation rate of the azo dye was investigated by using completely different concentration of ZnO from 0.2 to 2.0 g/100 cc with dye concentration 2mg/100ml at the traditional pH scale is 6.4 of methyl orange solution. [31]

4.3 Determination of Optimum Concentration of ZnO Suspension Required for Photodegradation of Methyl Orange

From Table 2 and Fig. 2(a), it is seen that the highest degradation of methyl orange solution was observed for the ZnO of 1.4g/100mL for 2mg/100ml dye solution during 60 minutes of irradiation [32].

4.4 Effect of Initial Concentration of Dye Solution

After optimizing the catalyst concentration of ZnO suspension (1.4g/100ml), the photocatalytic degradation methyl orange solution was carried out by varying initial concentration of dye from 6mg/100mL to 10mg/100mL in order to assess the appropriate concentration required for maximum degradation [33-35]. Fig. 3 shows change of absorption of the degraded solution with time using initial concentration of MO, 6mg/100ml.Change of absorption of the 7 mg, 8 mg degraded the solution is gradually decreased, 6 mg degraded solution is scattered and 9 mg, 10 mg shows linearity with increasing time [36].

Fig. 3 shows % of degradation of MO solution with time using different initial concentration. % of degradation of the 6mg, 7 mg, 8 mg degraded solution are scattered and 9 mg, 10 mg shows linearity with increasing time.

4.4.1 Determination of optimum concentration of methyl orange for photodegradation

Results obtained from Table 3 and Fig. 3 indicates that the highest degradation of methyl orange solution was observed for the ZnO of 7mg/100mL during 60 minutes of irradiation. Fig. 3 shows the effect of the initial concentration of MO on the percentage of degradation during 60 minutes of irradiation [37].

4.5 Effect of Initial pH of the Solution

The pH of the aqueous solution is one of the important environmental parameters significantly influencing the physicochemical properties of semiconductors, including the surface charge on the ZnO particle [38]. Experiments were carried out at various pH values ranging from 2 to 7 for constant dye concentration (2mg/100ml) and catalyst concentration (1.4g/100ml).

4.5.1 Determination of optimum pH for photo-degradation of methyl orange in presence of ZnO suspension

Results obtained from Table 4 and Fig. 4(a) indicates that the highest degradation of methyl orange solution is 64.458 which were obtained at pH 7. Fig. 4(a) shows % of degradation is increased from pH=2, pH=3 and decreased from pH=4, pH=5, pH=6 and finally increased at pH 7. So we say that if we increase or decrease pH % percentage of degradation is scattered and pH=7 is selected for the optimum pH.

References	Water
Volume of solution irradiated	100 ml
Wavelength of MO solution	463 nm
Initial pH of medium	6.4
Temperature	30°C
[MO]	2mg/100ml

Table 1. Effect of concentration ZnO suspension on photodegradation

(A) Amount of ZnO = 0.2 g			
No.	Time of photolysis (Mins.)	Absorbance	% of degradation
1	0	2.550	0.000
2	5	2.450	3.922
3	10	2.364	3.510
4	20	2.351	0.549
5	30	2.303	2.042
6	40	2.291	0.521
7	50	2.288	0.130
8	60	2.128	6.993

No.	Time of photolysis (Mins.)	Absorbance	% of Degradation
1	0	2.019	0.000
2	5	2.004	0.743
3	10	1.957	2.345
4	20	1.940	0.868
5	30	1.696	12.577
6	40	1.680	0.943
7	50	1.628	3.095
8	60	1.606	1.351

(B) Amount of ZnO = 0.4 g

(C) Amount of ZnO = 0.6 g

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	5	3.310	0
2	10	2.092	36.797
3	20	2.068	1.147
4	30	1.995	3.529
5	40	1.952	2.155
6	50	1.928	1.229
7	60	1.903	1.296
8	60	1.879	1.261

(D) Amount of ZnO = 0.8 g

No.	Time of photolysis	Absorbance	% of degradation
1	0	2.133	0
2	5	2.068	45.586
3	10	1.977	3.047
4	20	1.965	4.400
5	30	1.911	0.606
6	40	1.890	2.748
7	50	1.851	1.098
8	60	1.920	2.099

(E) Amount of ZnO = 1.0 g

No.	Time of photolysis (Mins.)	Absorbance	% of degradation
1	0	3.414	0
2	5	1.908	44.112
3	10	1.846	3.249
4	20	1.783	3.412
5	30	1.748	1.962
6	40	1.699	2.803
7	50	1.655	2.589
8	60	1.608	2.839

(F) Amount of ZnO = 1.2 g

No.	Time of photolysis (Mins.)	Absorbance	% of degradation
1	0	1.853	0
2	5	1.581	14.679
3	10	1.554	1.708
4	20	1.538	1.029
5	30	1.536	0.130
6	40	1.513	1.497
7	50	1.475	2.511
8	60	1.463	0.813

No.	Time of photolysis (Mins.)	Absorbance	% of degradation
1	0	3.332	0
2	5	1.577	52.671
3	10	1.461	7.356
4	20	1.448	0.889
5	30	1.384	4.419
6	40	1.376	0.578
7	50	1.342	2.470
8	60	1.304	2.831

(G) Amount of ZnO = 1.4 g

(H) Amount of ZnO = 1.6 g

No.	Time of Photolysis (Mins.)	Absorbance	% of Degradation
1	0	3.006	0
2	5	1.967	34.564
3	10	1.888	4.016
4	20	1.872	0.847
5	30	1.703	9.028
6	40	1.701	0.117
7	50	1.655	2.704
8	60	1.631	1.450

(I) Amount of ZnO = 1.8 g

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	0	3.483	0
2	5	2.833	18.662
3	10	2.632	7.094
4	20	2.630	0.076
5	30	2.629	0.038
6	40	2.617	0.456
7	50	2.605	0.458
8	60	2.505	3.839

(J) Amount of ZnO = 2.0 g

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	0	3.160	0
2	5	2.510	20.569
3	10	2.204	12.191
4	20	2.154	2.269
5	30	2.133	0.975
6	40	2.128	0.234
7	50	2.091	1.739

Table 2. Data of % of degradation of the solution with time using different amount of ZnO suspension

References	=	Water
Volume of solution irradiated	=	100mL
wave length of RR solution	=	463 nm
Initial pH of medium	=	6.4
Temperature	=	30°C
[MO]	=	2 mg/100 mL

Exp. no.	Amount of ZnO/g	% of degradation
1	0.2	6.993
2	0.4	12.577
3	0.6	36.797
4	0.8	45.586
5	1.0	44.112
6	1.2	14.679
7	1.4	52.671
8	1.6	34'564
9	1.8	18.662
10	2.0	20.569



Fig. 1. The percentage of degradation of the solution with time using at different amount of ZnO suspension



Amount of $ZnO \rightarrow (mg/100 \text{ ml})$

Fig. 2(a). Effect of concentration of suspention on % degradation during 60 Minutes of irradiation



Fig. 2(b). % of degradation of MO solution with time using different initial concentration

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Table 3.	Effect of the initial	concentration	or methyl	orange on	photodegradation

References	=	Water
Volume of solution irradiated	=	100 mL
wave length of MO solution	=	463 nm
Initial pH of medium	=	6.4
Temperature	=	30°C
Amount of ZnO	=	1.4 g

(A) Methyl orange = 6 mg/100 mL

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	0	3.976	0
2	5	3.793	4.603
3	10	3.780	0.342
4	20	3.748	0.847
5	30	3.722	0.694
6	40	3.705	0.457
7	50	3.520	4.993
8	60	3.396	3.523

Table 4. Data of % of degradation of MO solution with time using different initial concentration

No. of experiment	[MO] mg/100mL	% of degradation
1	6	4.993
2	7	16.312
3	8	12.990
4	9	0.200
5	10	0.075



Fig. 3. Effect of initial concentration of MO on % percentage of degradation during 60 minutes of irradiation

 Table 5. Effect of the different pH on the photodegradation of MO in presence of ZnO suspension

References	Water
Volume of solution irradiated	100 mL
wave length of MO solution	463 nm
Temperature	30°C
Amount of ZnO	1.4 g
[MO]	2 mg/ 100 mL

(A) pH = 2

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	0	0.375	0.000
2	5	0.362	3.467
3	10	0.342	5.525
4	20	0.271	20.760
5	30	0.251	7.380
6	40	0.229	8.765
7	50	0.206	10.044
8	60	0 162	21 359

(B) pH = 3

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	0	0.213	0.000
2	5	0.174	18.309
3	10	0.144	17.241
4	20	0.117	18.750
5	30	0.087	25.641
6	40	0.055	36.781
7	50	0.043	21.818
8	60	0.027	37.209

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	0	2.703	0
2	5	2.102	22.234
3	10	1.874	10.847
4	20	1.713	8.591
5	30	1.533	10.507
6	40	1.384	9.719
7	50	1.278	7.659
8	60	1.208	5.477

(C) pH = 4

(D) pH = 5

No.	Time of photolysis (mins)	Absorbance	% of degradation	-
1	0	2.365	0	
2	5	1.872	20.846	
3	10	1.811	3.258	
4	20	1.653	8.724	
5	30	1.541	6.775	
6	40	1.343	12.849	
7	50	1.285	4.319	
8	60	1.212	5.680	

(E) pH = 6

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	0	1.717	0.000
2	5	1. 608	6.348
3	10	1.522	5.348
4	20	1.395	8.344
5	30	1.340	3.942
6	40	1.319	1.567
7	50	1.188	9.931
8	60	1 089	8 333

(F) pH = 7

No.	Time of photolysis (mins)	Absorbance	% of degradation
1	0	1.057	0.000
2	5	0.785	25.733
3	10	0.279	64.458
4	20	0.171	38.709
5	30	0.108	36.842
6	40	0.070	35.185
7	50	0.066	5.714
8	60	0.043	34.848

Table 6. Data of % degradation of MO for different pH of the solution

Exp. no.	рН	% of degradation
1	2	21.359
2	3	37.209
3	4	22.234
4	5	20.846
5	6	9.931
6	7	64.458



Fig. 4(a). Change of absorption of the degraded solution with time using different pH of the solution



Fig. 4(b). % of degradation of the Mo solution with time using different pH of the solution



Fig. 5. Effect of pH on percent degradation of MO during 60 minutes of irradiation

5. CONCLUSIONS

Dyes in the effluents discharged from textile dyeing factories, pharmaceuticals, chemicals and leather industries are important environmental pollutants. It pollutes water and damages aquatic system. The photocatalytic oxidation which causes complete destruction of the pollutants is a promising method for degradation these pollutants. To destroy these pollutants from the aqueous solution photo-degradation using a suitable catalyst may be used. Photocatalytic degradation of a non-biodegradable azo dye, such as methyl orange is frequently used in textile and leather industries.

It is observed that by irradiating with a light source for 4 hours, about 97.46% of MO was degraded in 1.4g/100ml of ZnO suspension containing 7mg/100mL in the table and Fig. 3 of the MO dye. The pH of the suspension plays an important role in photo-degradation. The photodegradation of MO dye was found to be scattered with decreasing pH due to easy adsorption of the MO⁻ on positively charged ZnO suspension. In the alkali medium, the degradation was not satisfactory due to the fact that adsorption of anionic dye on negatively charged is unlikely. Hence suitable acidic condition could be used for photo-degradation of anionic dye. The optimum catalyst concentration was found to be 1.4g/100ml.The optimum experimental condition 2mg/100 ml) of MO can be degraded up to 67.94% with 60 minutes of irradiation.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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