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SYNTHESIS OF NANO Co_3O_4 - MnO_2 - ZrO_2 MIXED OXIDES FOR VISIBLE-LIGHT PHOTOCATALYTIC ACTIVITY

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ABSTRACT

Nano Co_3O_4 - MnO_2 - ZrO_2 mixed metal oxides were synthesized by wet chemical method. The photocatalytic property of Co_3O_4 - MnO_2 - ZrO_2 NPs was studied for degradation of methylene blue (MB) under sunlight. The photocatalytic property is affected by pH of dye solution, photocatalyst dosage, dye concentration and photocatalyst particle size. The speed of MB degradation is almost 2.15 fold better in the existence of sunlight than in the nonappearance of sunlight. The degradation effectiveness of MB is appreciably increased from 61.66% to 68.24% with increasing pH from 4 to 9. 0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs with smaller particle size (32.87nm) exhibits higher photocatalytic activity as compared to other NPs (0.2M – 0.5M) with larger particle size (38.52 – 59.13nm size). The dye degradation increases with increasing catalyst amount. The rate of degradation decreases with increasing in the dye concentration from 1.0 to 2.5 x 10^{-5} M.

Keywords: Co_3O_4 - MnO_2 - ZrO_2 NPs, Methylene blue, Photodegradation, Photocatalyst.

I. INTRODUCTION

Methylene blue (MB) is a cationic dye and observed as important threat to human and biota due to its mutagenic and carcinogenic properties. Methylene blue dye has been extensively used in coloring wools, paper, as dying cottons and biological stains.

Numerous treatment methods have been used for removing dyes from polluted water such as electrochemical degradation, sonochemical degradation, adsorption/precipitation processes, ultra-filtration, integrated chemical–biological degradation, photocatalytic degradation.

Photocatalytic degrdation of organic dyes in the environment can be done by semiconductor materials. Among the various semiconductor materials, Co_3O_4, MnO_2, ZrO_2 are mainly used as photocatalyst due to their high activity, low cost and eco - friendly properties.

In this work, we report a photodegradation study of methylene blue dye in aqueous solution using a Co_3O_4 - MnO_2 - ZrO_2 NPs prepared via wet chemical method by cobalt chloride, manganese sulphate and zirconium oxychloride and sodium hydroxide. Based on the experimental results, the mechanisms of photocatalytic degradation of MB dye was proposed.

II.EXPERIMENTAL METHODOLOGY

2.1. Chemicals used

$CoCl_2$. $6H_2O$, $ZnSO_4$. $7H_2O$, $ZrOCl_2$. $8H_2O$, $MnSO_4$. H_2O, $CuSO_4$. $5H_2O$ and NaOH.

2.2. Synthesis of Co_3O_4 - MnO_2 - ZrO_2 NPs

About 25mL of 0.1M $CoCl_2$. $6H_2O$ was added to the aqueous solution of 75mL of 1.0M NaOH solution and stirred well. To this mixture 25mL of 0.1M $MnSO_4$. H_2O and 25mL of 0.1M $ZrOCl_2$. $8H_2O$ were added. The resulting mixture was stirred well and refluxed at an elevated temperature for 3 hours. The product was filtered, washed with water and dried. Similar procedure was carried out to prepare different concentrations of (0.2M - 0.5M) Co_3O_4 - MnO_2 - ZrO_2 NPs.

2.3. Evaluation of photo degradation

For degradation studies, 10 mg of Co_3O_4 - MnO_2 - ZrO_2 NPs was added to 100mL of 1 x 10^{-5}M methylene blue trihydrate (Sigma-Aldrich) in a beaker and exposed to bright sunlight with constant stirring using magnetic stirrer. The samples were withdrawn at regular time intervals (10min) and the dye solutions were separated from the NPs by centrifugation. The absorbance of the supernatant was subsequently measured at maximum wavelengths of dye (λ_{max} = 662nm) using UV–Vis spectrophotometer.

III.RESULTS AND DISCUSSION

3.1. Effect of pH of dye solution

The effect of pH on the degradation of MB dye was studied at pH 4 and 9 using 10mg of photocatalyst (0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs) and 100mL of 1 x 10^{-5} M MB dye solution kept under sunlight for 90min. The pH was maintained by adding necessary amount of 0.1M H_2SO_4 to maintain acidic nature & 0.1M NaOH to maintain basic nature.

To study the reaction kinetics of the MB degradation, the Langmuir- Hinshelwood model was applied. The L-H model is well established for heterogeneous photocatalysis at low dye concentration, and the equation can be expressed as follows [1]:

$$- \ln(C/C_0) = kt$$

where C_0, C, k and t are concentrations of dye in solution at time 0, concentrations of dye in solution at time t, rate constant and reaction time respectively. A plot of $-\ln(C/C_0)$ Vs time (t) will provide a slope of k with the linear correlation coefficient value (R) by linear fitting of the experimental results.

The % of photocatalytic degradation can be determined by the following equation [2]:

$$\% \text{ of degradation} = [(C_0-C)/C_0] \times 100$$

C_0 = initial concentration of the dye

C = concentration of the dye at a selected time

The observed rate constants (k) at 90 min for the photocatalytic degradation of MB using pH value of 4 and 9 are 0.00964 and 0.01171min^{-1} respectively. Kinetics of degradation of MB at pH 4 and 9 under sunlight fit well to the pseudo first-order reaction kinetic model. This is obvious from the observed linear plots of $-\ln(C/C_0)$ as a function of time at different pH as given in fig 1(d).

As shown in fig 1(e), the degradation efficiency of MB is notably increased from 61.66% to 68.24% with increase in pH from 4 to 9.

At a high pH, the surface of photocatalyst is negatively charged, but at a low pH it becomes positively charged. Since MB is a cationic dye, high pH favors the adsorption of MB molecule on the photocatalyst surface as a result of electrostatic interaction, which results in a high degradation of MB under basic environment [3].

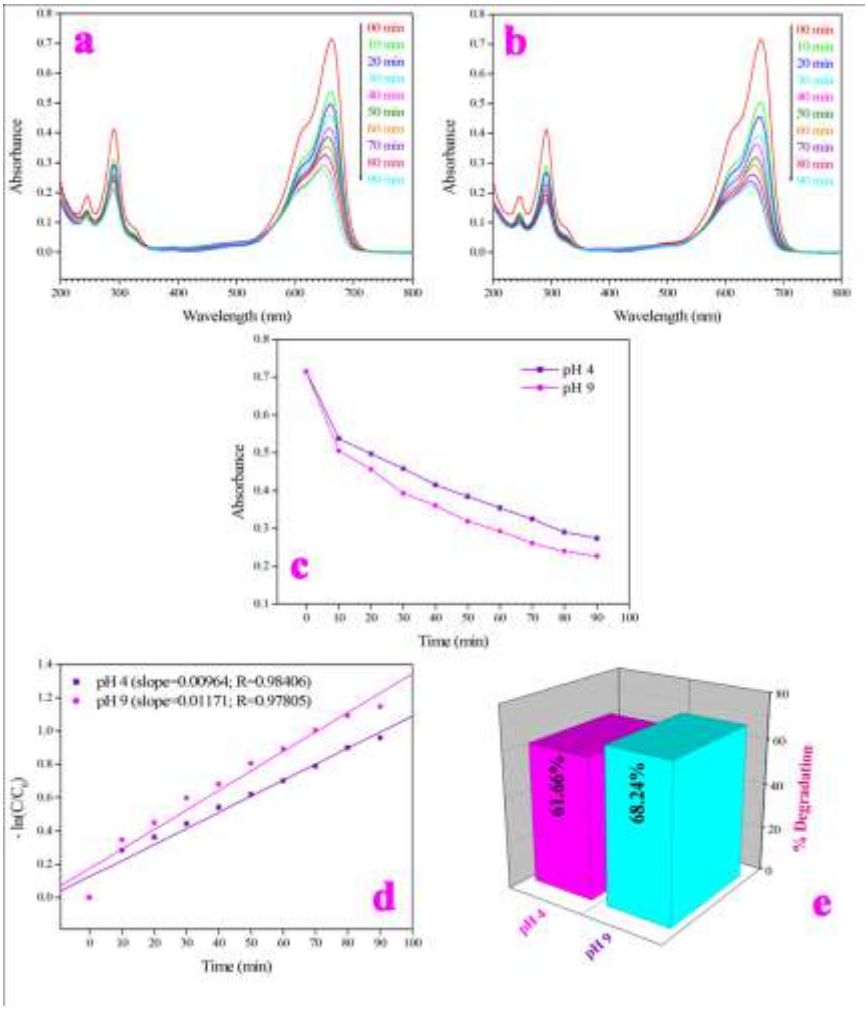

Figure 1. UV–Vis spectra of MB as a function of time in the presence of 0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs (a) pH 4 (b) pH 9 (c) plot of absorbance versus time (d) plot of $-\ln(C/C_0)$ versus time and (e) % degradation

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3.2. Effect of light

The effect of light on degradation of MB (1.0×10^{-5} M) was studied by keeping the photocatalyst (0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs) dosage at 10 mg per 100 mL and pH 9.

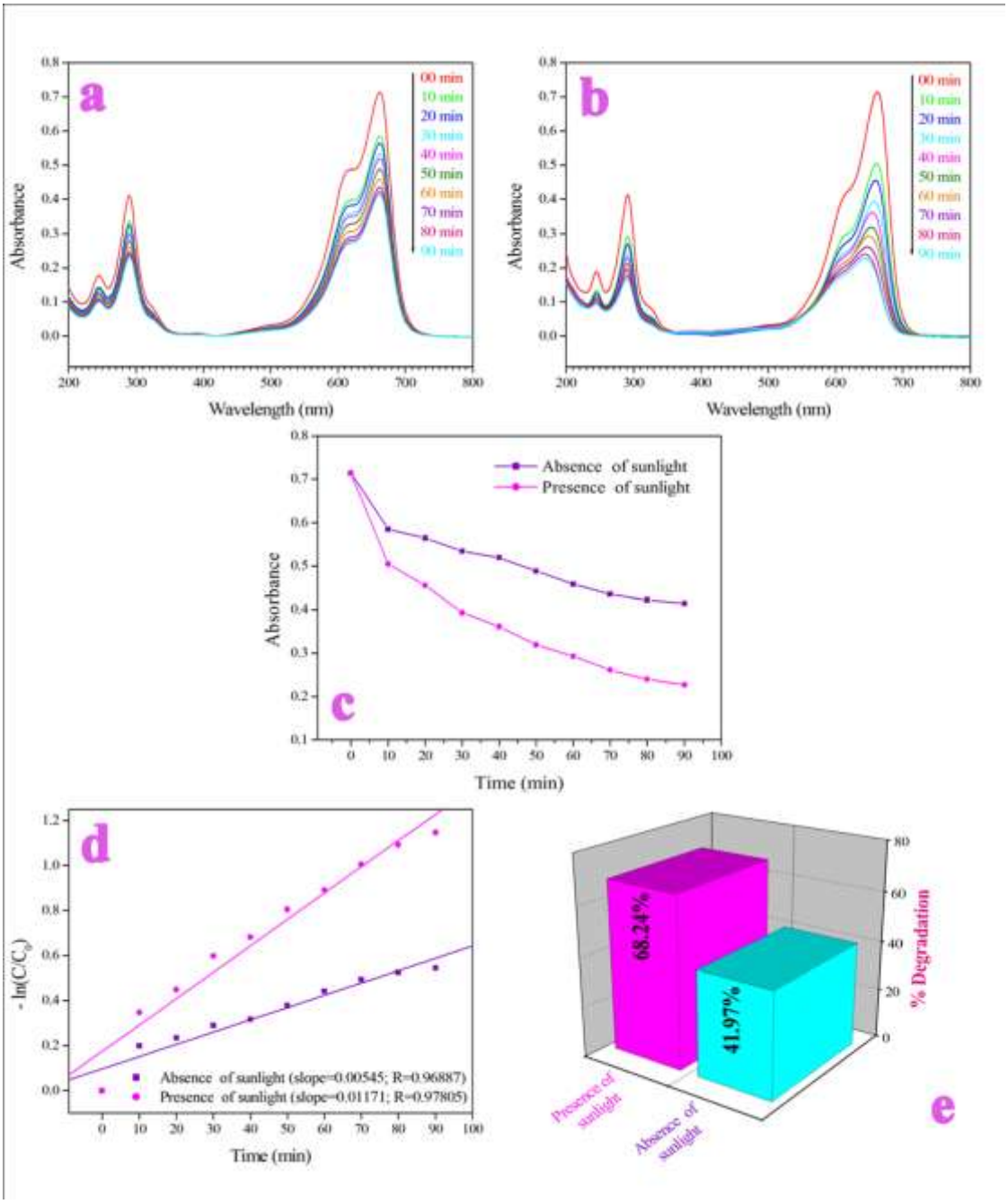

Figure 2. UV–Vis spectra of MB as a function of time in the presence of 0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs (a) absence of sunlight (b) presence of sunlight (c) plot of absorbance versus time (d) plot of -ln(C/C_0) versus time and (e) % degradation

In the absence of sunlight, the intensity of absorption band of dye at 662 nm is decreased slowly, after 90 min 41.97 % of dye is removed without any shift in the λ_{max}. The absorbance of dye is decreased from 0.71398 to 0.41432 au. In the presence of sunlight, the absorbance is decreased quickly with a blue shift in λ_{max}, and no new absorption band is detected. The absorbance is decreased rapidly from 0.71458 to 0.22695au corresponding to 68.24% of removal of dye after 90 min of sunlight illumination. The plot of $-\ln(C/C_0)$ versus time (fig 2d) is a straight line in the above two cases and the slope is equal to the rate of MB degradation, which is 0.00545 and 0.01171min^{-1} in the absence and presence of sunlight, respectively. The rate of MB degradation is roughly 2.15 fold higher in the presence of sunlight. It indicates the strong impact of sunlight on this reaction.

3.3. Effect of particle size of photocatalyst

The effect of the particle size of the five samples (0.1, 0.2, 0.3, 0.4 & 0.5M Co_3O_4 - MnO_2 - ZrO_2 NPs) on the dye degradation was assessed by tracing the absorbance of MB at pH 9.

It is illustrated in fig 3 that the 0.1, 0.2, 0.3, 0.4 & 0.5M Co_3O_4 - MnO_2 - ZrO_2 NPs exhibit the reaction rate constant of 0.01171, 0.00983, 0.00771, 0.00630 and 0.00540min^{-1} respectively. The results display that the photocatalytic activity of 0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs is much higher than those of other four samples, indicating its superior photocatalytic activity.

After irradiation for 90min, about 68.24, 62.59, 53.48, 47.57 and 41.98% of MB is degraded in the presence of 0.1, 0.2, 0.3, 0.4 & 0.5M Co_3O_4 - MnO_2 - ZrO_2 NPs respectively. Therefore, it can be concluded that 0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs with smaller particle size (32.87nm) exhibits stronger photocatalytic activity as compared to other NPs with larger particle size (38.52 – 59.13nmsize). This can be interpreted as smaller particle have large surface area than that of larger particle, hence adsorbs more dye and leads to stronger interaction between MB and photocatalyst [4].

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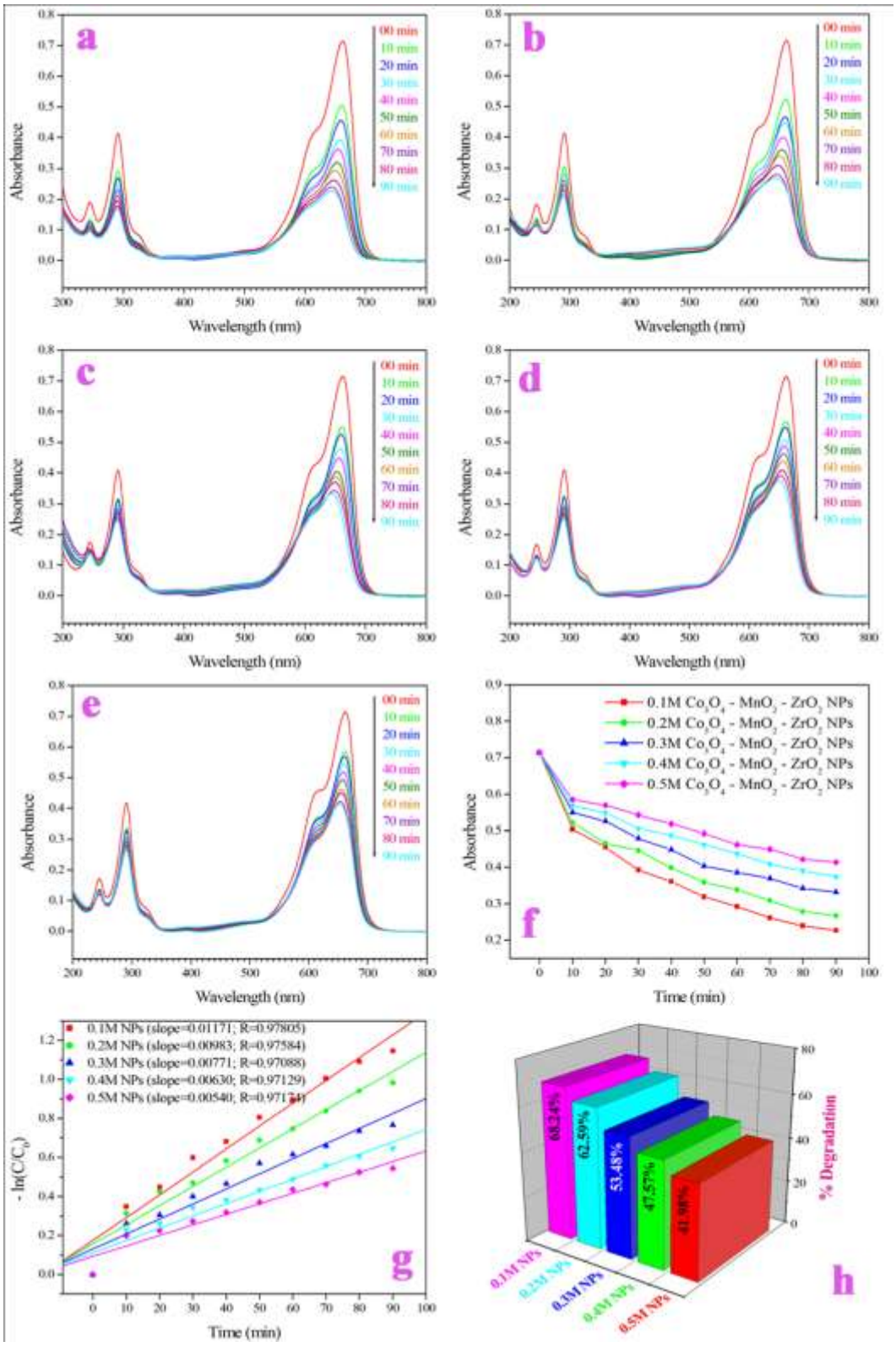

Figure 3. UV–Vis spectra of MB as a function of time in the presence of Co_3O_4 - MnO_2 - ZrO_2 NPs (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M (e) 0.5M (f) plot of absorbance versus time (g) plot of -ln(C/C_0) versus time and (h) % degradation

3.4. Effect of dye concentration

The effect of initial dye concentration was investigated by varying the initial concentration from 1.0 to 2.5 x 10^{-5} M using 10mg of photocatalyst (0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs) and 100mL of dye solution under sunlight for 90min at pH 9.

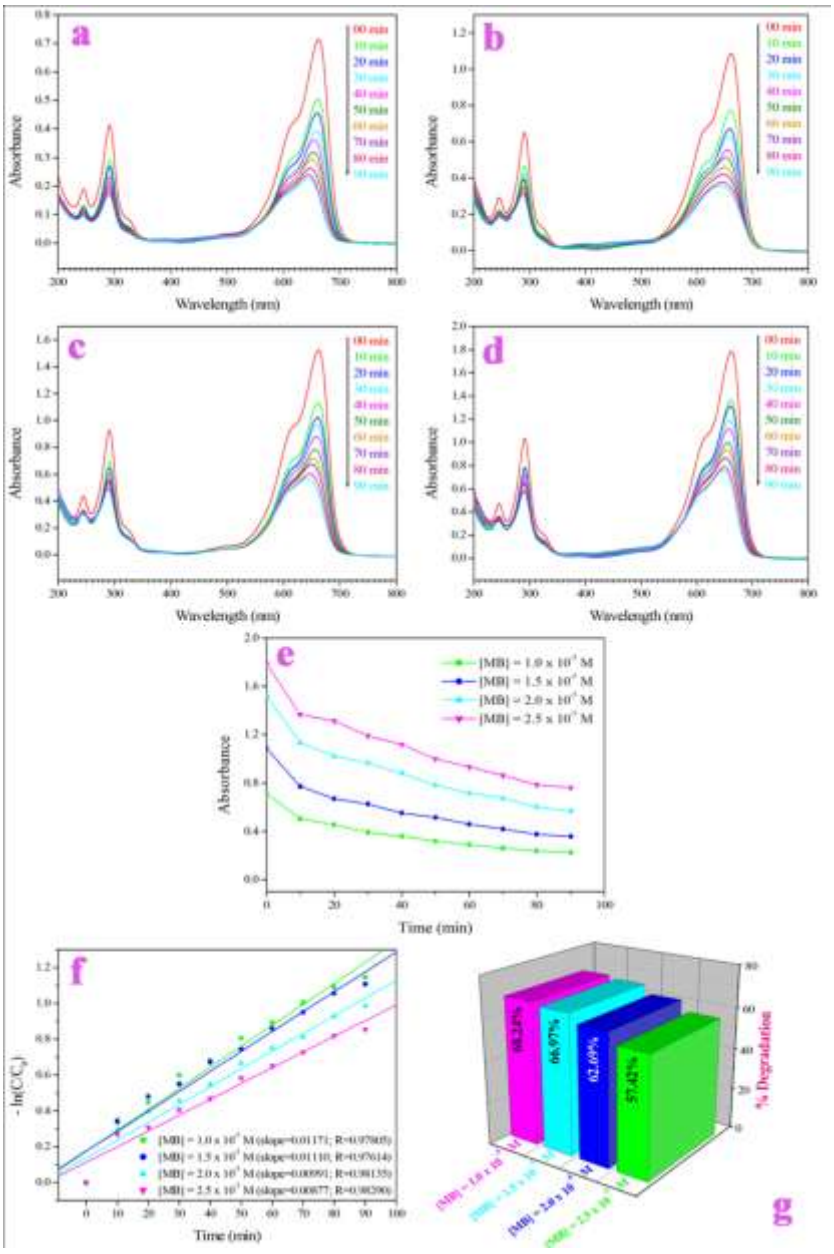

Figure 4. UV–Vis spectra of MB as a function of time in the presence of Co_3O_4 - MnO_2 - ZrO_2 NPs (a) [MB] = 1.0 x 10^{-5} M (b) [MB] = 1.5 x 10^{-5} M (c) [MB] = 2.0 x 10^{-5} M (d) [MB] = 2.5 x 10^{-5} M (e) plot of absorbance versus time (f) plot of -ln(C/C_0) versus time and (g) % degradation

Plot of -ln(C/C_0) vs time at various concentration of MB at 10mg photocatalyst load is given in fig 4. The rate constants for the photocatalytic degradation of MB solution using MB concentration of 1.0, 1.5, 2.0 and 2.5 x 10^{-5} M are 0.01171, 0.01110, 0.00991 and 0.00877min^{-1} under sunlight at 90 minutes respectively. Percentage degradation of MB using MB concentration of 1.0, 1.5, 2.0 and 2.5 x 10^{-5} M are 68.24, 66.97, 62.69 and 57.42% respectively. While increasing the MB dye concentration from 1.0 to 2.5 x 10^{-5} M, the degradation rate decreases.

Two factors are responsible for the decline in percentage degradation efficiency with an increase in the initial dye concentration: First, as the initial concentration of MB is increased, the quantity of generated hydroxyl radicals do not appropriately increase due to the same dosage of photocatalyst, which results in a comparatively smaller $^{\bullet}OH$ concentration. Second, an increase in the light absorbed by the dye molecules leads to a decrease in the number of photons that arrive at the photocatalyst surface [5].

3.5. Effect of photocatalyst amount

The effect of photocatalyst dosage on the photodegradation efficiency of MB was observed by taking different amounts of 0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs (5, 10 & 15mg) into 100mL of 1 x 10^{-5} M dye solution under sunlight for 90min at pH 9.

Kinetics of degradation of MB using different amounts of photocatalyst under sunlight follows pseudo first order kinetics. This is obvious from the observed linear plots of -ln(C/C_0) versus time given in fig 5 (e). The rate constant (k) for degradation of MB using 5, 10 and 15mg photocatalyst are 0.01014, 0.01171 and 0.01359min^{-1} under sunlight, respectively. Percentage degradation of MB using 5, 10 and 15mg photocatalyst are 62.83, 68.24 and 73.27% respectively.

The dye degradation efficiency increases with increasing catalyst dosage, which is characteristic of heterogeneous photocatalysis. The increase in catalyst amount actually increases the number of active sites on the photocatalyst surface thus leads to an increase in the number of hydroxyl radicals ($^{\bullet}OH$) which are responsible for the actual degradation of dye solution [5].

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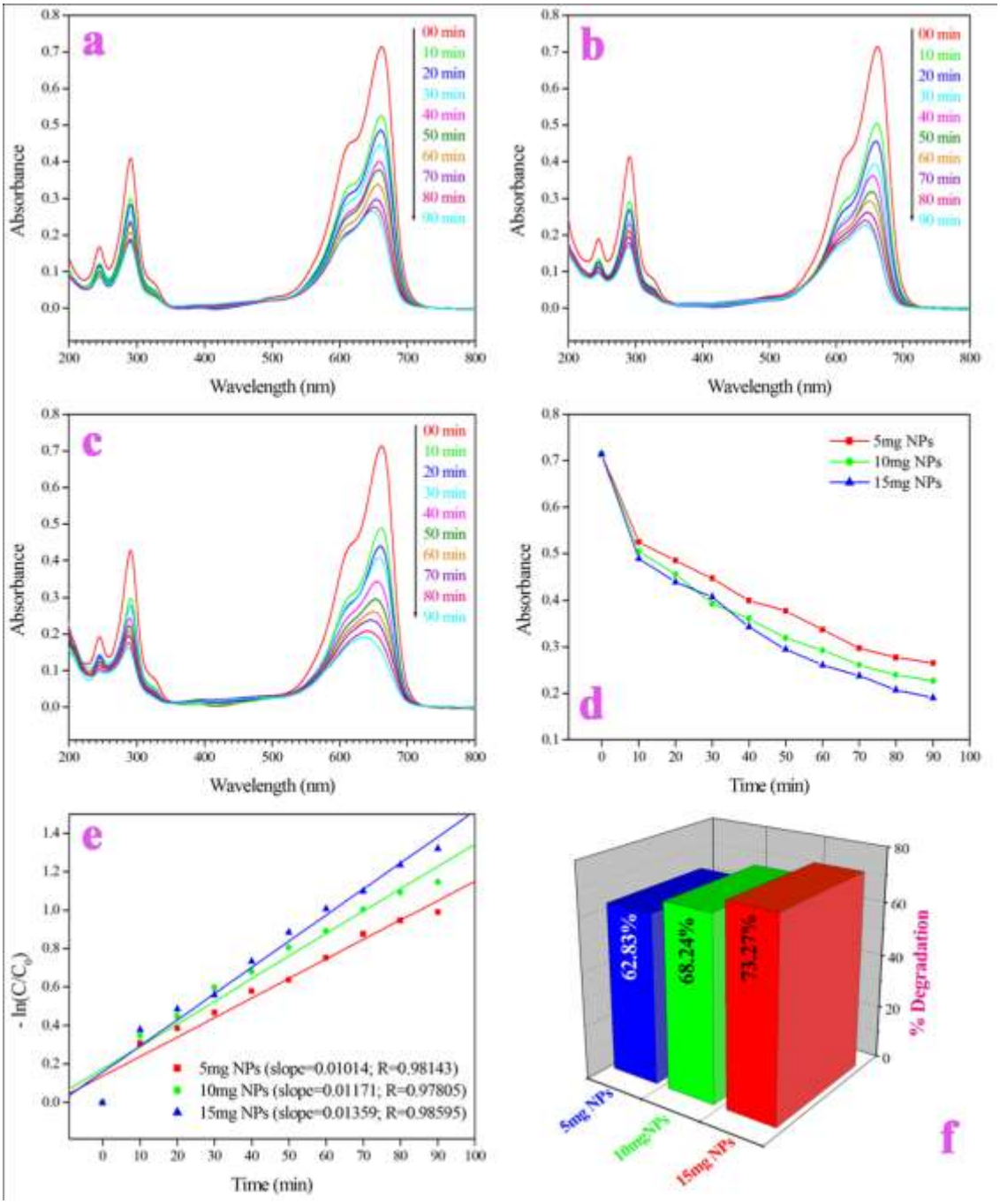

Figure 5. UV–Vis spectra of MB as a function of time in the presence of 0.1M Co_3O_4 - MnO_2 - ZrO_2 NPs (a) 5mg photocatalyst (b) 10mg photocatalyst (c) 15mg photocatalyst (d) plot of absorbance versus time (e) plot of -ln(C/C_0) versus time and (f) % degradation

3.6. Mechanism of Photocatalytic activity

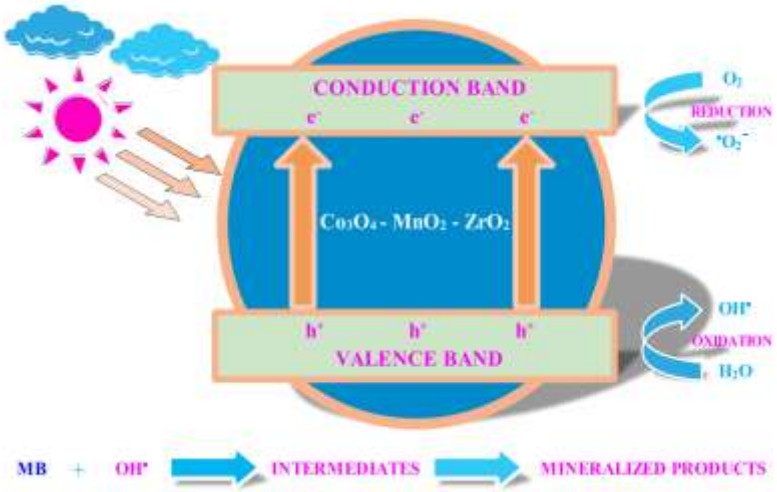

Figure 6. Mechanism for the photocatalytic degradation of MB by Co_3O_4 - MnO_2 - ZrO_2 NPs

IV.CONCLUSIONS

Co_3O_4 - MnO_2 - ZrO_2 NPs have been successfully synthesized by wet chemical method. Photocatalytic action of Co_3O_4 - MnO_2 - ZrO_2 NPs was investigated by degradation of methylene blue dye for 90min under sunlight. The photocatalytic degradation was affected by the pH of dye solution, photocatalyst particle size, photocatalyst dosage and dye concentration. Finally, It was found that the Co_3O_4 - MnO_2 - ZrO_2 NPs showed moderate photocatalytic activity in MB dye system.

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