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PHOTOCATALYTIC ACTIVITY OF Co_3O_4 - ZnO - ZrO_2 TERNARY NANOPARTICLES FOR THE DEGRADATION OF METHYLENE BLUE DYE

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ABSTRACT

Nano Co_3O_4 - ZnO - ZrO_2 mixed oxides were synthesized by using cobalt chloride, zinc sulphate and zirconium oxychloride and sodium hydroxide. The photocatalytic activity of Co_3O_4 - ZnO - ZrO_2 NPs was studied for degradation of methylene blue (MB) under sunlight. The photocatalytic activity is influenced by pH of dye solution, photocatalyst particle size, photocatalyst dosage and dye concentration. The rate of MB degradation is almost 2.09 fold superior in the presence of sunlight than in the absence of sunlight. The degradation efficiency of MB is significantly increased from 64.89% to 73.00% with increasing pH from 4 to 9. 0.1M Co_3O_4 - ZnO - ZrO_2 NPs with smaller particle size (28.11nm) exhibits superior photocatalytic activity as compared to other NPs (0.2M – 0.5M) with larger particle size (31.88 – 52.36nm size). The dye degradation increases with increasing catalyst quantity. As increasing the dye concentration from 1.0 to 2.5 x 10^{-5} M, the rate of degradation decreases.

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

I. INTRODUCTION

The industrial discharges from fabric industries are wealthy in residual dye stuff. Several residual dyes are non-biodegradable due to their complex molecular structures which make them more stable and tough to degrade biologically by the action of micro-organism. They cause water pollution and also create a serious hazard to the environment. Thus, elimination of this dye from water bodies is important.

Semiconductor materials which promote chemical reactions in the presence of light without being consumed are identified as photocatalysts. To be a superior photocatalyst the semiconductor material should be photostable and photoactive.

The size of a photocatalyst is a significant factor affecting the effectiveness of the photocatalytic degradation process. Especially, their efficiency is increased when the size is changed from bulk to nanoparticle size. Most

of the current research thus aim synthesizing nanoparticle size semiconductor photocatalysts and increasing their photocatalytic behavior.

In this work, we report the photocatalytic activity of Co_3O_4 - ZnO - ZrO_2 NPs for the degradation of methylene blue (MB) dye. The effect of pH of dye solution, photocatalyst particle size, photocatalyst dosage and dye concentration on the photocatalytic activity of Co_3O_4 - ZnO - ZrO_2 NPs was studied.

II. EXPERIMENTAL METHODOLOGY

2.1. Chemicals used

Cobalt chloride, zinc sulphate, zirconium oxychloride and sodium hydroxide.

2.2. Synthesis of Co_3O_4 - ZnO - ZrO_2 nanoparticles

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 $ZnSO_4$. $7H_2O$ 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 - ZnO - ZrO_2 NPs [1].

2.3. Evaluation of photo degradation

For degradation studies, 10 mg of Co_3O_4 - ZnO - 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 - ZnO - ZrO_2 NPs) and 100mL of 1 x 10^{-5} M MB dye solution under sunlight at 90min. The pH of the solution was maintained by adding required quantities 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 used. The L-H model is well established for heterogeneous photocatalysis at low dye concentration, and the equation can be expressed as follows [2]:

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

here 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 yield 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 [3]:

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% of degradation = $[(C_0-C)/C_0]$ x100

C_0 = initial concentration of the dye

C = concentration of the dye at a chosen time

The observed rate constants (k) at 90 min for the photocatalytic degradation of MB using different pH value of 4 and 9 are 0.01056 and 0.01329min^{-1} respectively. Kinetics of degradation of MB using 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 given in fig 1(d).

As shown in fig 1(e), the degradation efficiency of MB is considerably increased from 64.89% to 73.00 % with increase of pH from 4 to 9.

At 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 dye molecules on the photocatalyst surface as a result of electrostatic interaction, which results in a high degradation of MB under basic environment [4].

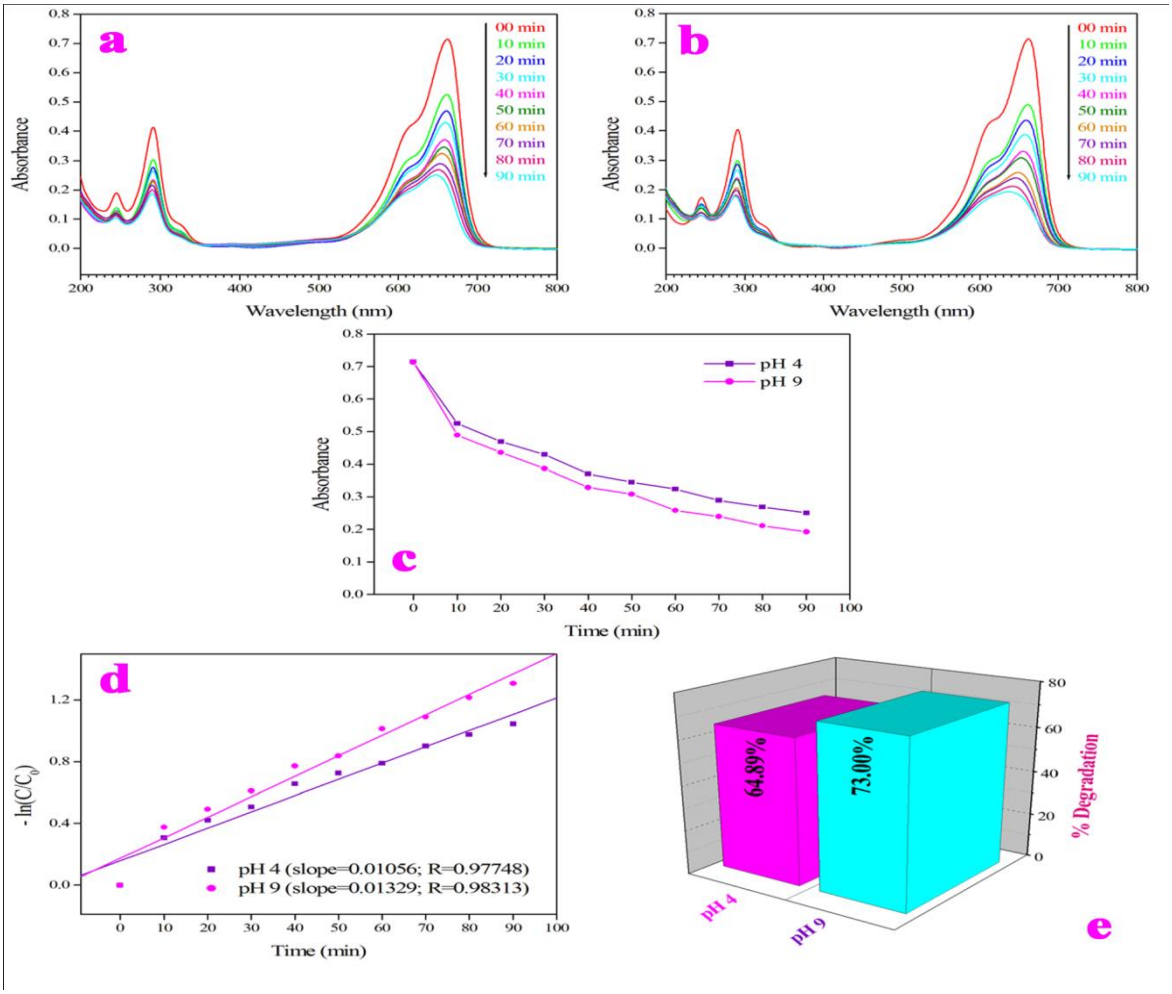

Figure 1. UV–Vis spectra of MB as a function of time in the presence of 0.1M Co_3O_4 - ZnO - ZrO_2 NPs (a) pH 4 (b) pH 9 (c) plot of absorbance versus time (d) plot of $-\ln(C/C_0)$ versus time and (e) % degradation

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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 - ZnO - ZrO_2 NPs) dosage at 10 mg per 100 mL and pH 9.

In the absence of sunlight, the intensity of absorption band of MB dye at 662 nm is decreased slowly, after 90 min 47.04 % of dye is detached without any shift in the λmax. The absorbance of MB dye is decreased from 0.71415 to 0.37821 au. In the presence of sunlight, the absorbance is decreased quickly with a blue shift in λmax, and no new absorption band is detected. The absorbance is decreased rapidly from 0.71382 to 0.19273 au corresponding to 73.00 % of elimination 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 0.00636 and 0.01329min^{-1} in the absence and presence of sunlight, respectively. The rate of MB degradation is roughly 2.09 fold higher in the presence of sunlight. This indicates the strong impact of sunlight on this reaction.

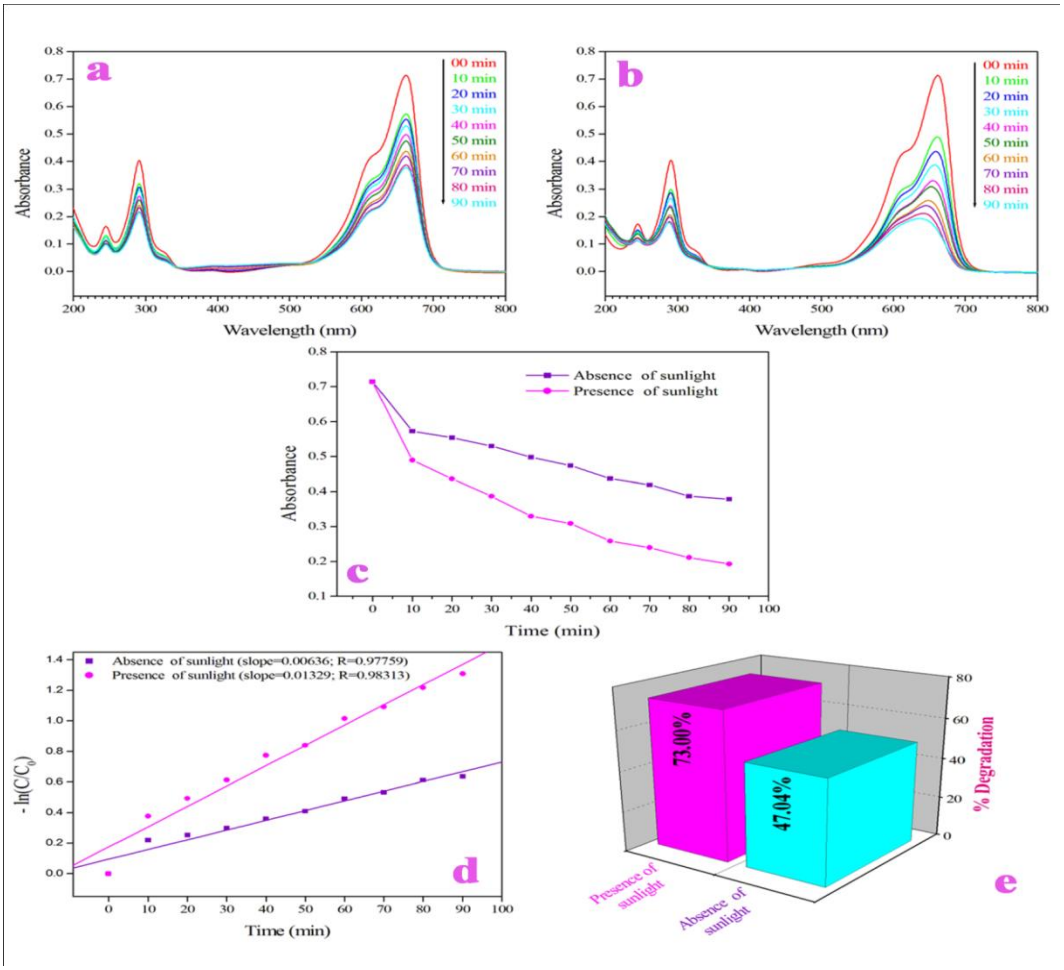

Figure 2. UV–Vis spectra of MB as a function of time in the presence of 0.1M Co_3O_4 - ZnO - ZrO_2 NPs (a) absence of sunlight (b) presence of sunlight (c) plot of absorbance versus time (d) plot of $-\ln(C/C_0)$ versus time and (e) % degradation

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3.3. Effect of particle size of photocatalyst

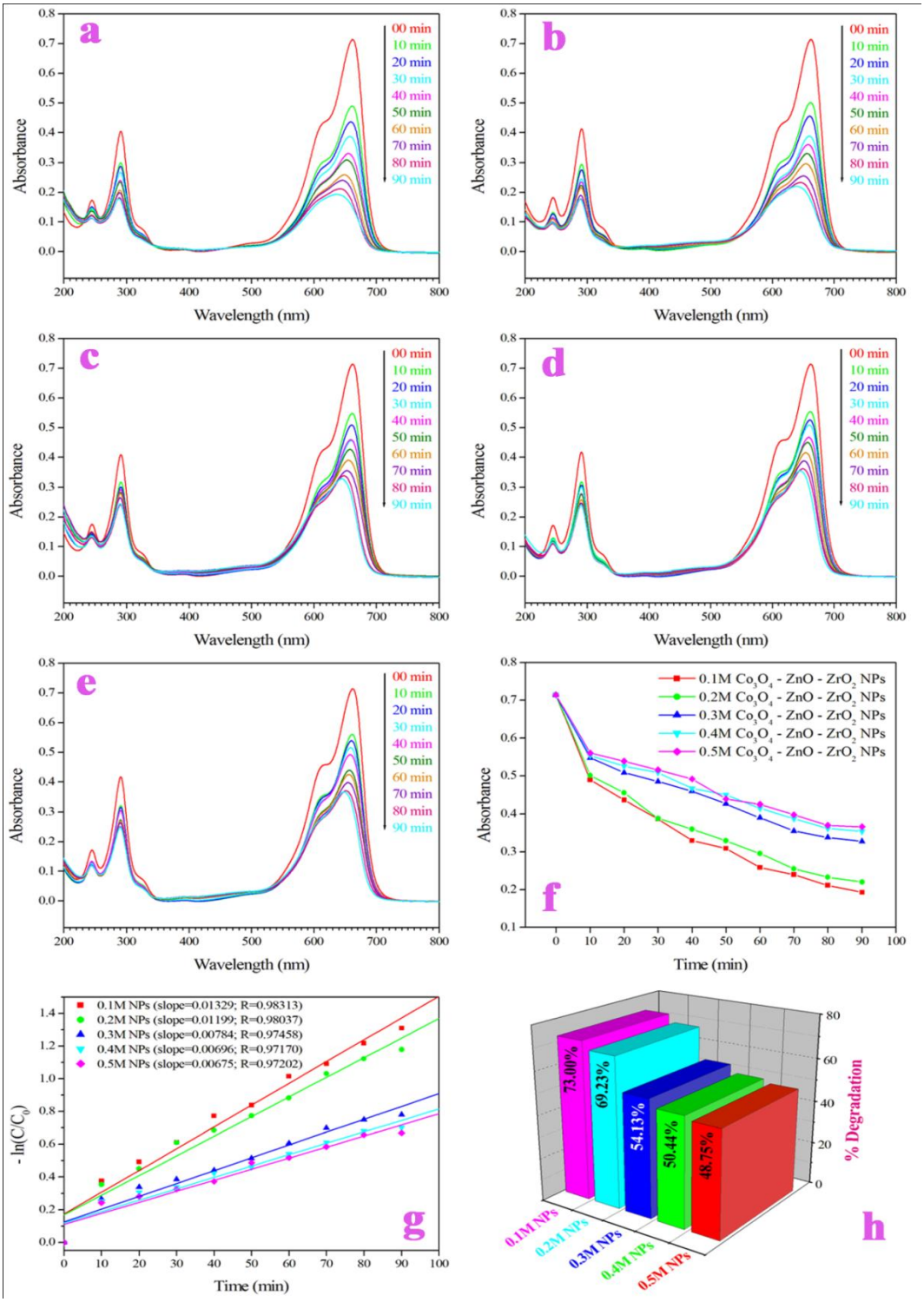

Figure 3. UV–Vis spectra of MB as a function of time in the presence of Co_3O_4 - ZnO - ZrO_2 NPs (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M (e) 0.5M (f) plot of absorbance versus time (g) plot of -ln(C/C_0) versus time and (h) % degradation

The effect of the particle size of the five samples (0.1, 0.2, 0.3, 0.4 & 0.5M Co_3O_4 - ZnO - 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 - ZnO - ZrO_2 NPs exhibit the reaction rate constant of 0.01329, 0.01199, 0.00784, 0.00696 and 0.00675min^{-1} respectively. The results reveal that the photocatalytic activity of 0.1M Co_3O_4 - ZnO - ZrO_2 NPs is much higher than those of the other four samples, which indicates its superior photocatalytic activity.

After irradiation for 90min, about 73.00, 69.23, 54.13, 50.44 and 48.75% of MB is degraded in the presence of 0.1, 0.2, 0.3, 0.4 & 0.5M Co_3O_4 - ZnO - ZrO_2 NPs respectively. Therefore, it can be concluded that 0.1M Co_3O_4 - ZnO - ZrO_2 NPs with smaller particle size (28.11nm) exhibits stronger photocatalytic activity as compared to other NPs with larger particle size (31.88 – 52.36nm size). This can be interpreted as smaller particles have large surface area than that of larger particles, hence they adsorb more dye and lead to stronger interaction between MB and photocatalyst [5].

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 - ZnO - ZrO_2 NPs) and 100mL of dye solution under sunlight for 90min at pH 9.

The plot of $-\ln(C/C_0)$ as a function of time at various concentrations of MB at 10mg photocatalyst loaded 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 0.01329, 0.01287, 0.01172 and 0.01056min^{-1} under sunlight at 90 minutes respectively. The percentage of degradation for 1.0, 1.5, 2.0 and 2.5 x 10^{-5} M concentration of MB are 73.00, 71.57, 68.16 and 64.71% respectively. While increasing the dye concentration from 1.0 to 2.5 x 10^{-5} M, the degradation rate decreases.

Two factors are responsible for the decrease in percentage degradation efficiency with an increase in the initial dye concentration: First, when 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 [6].

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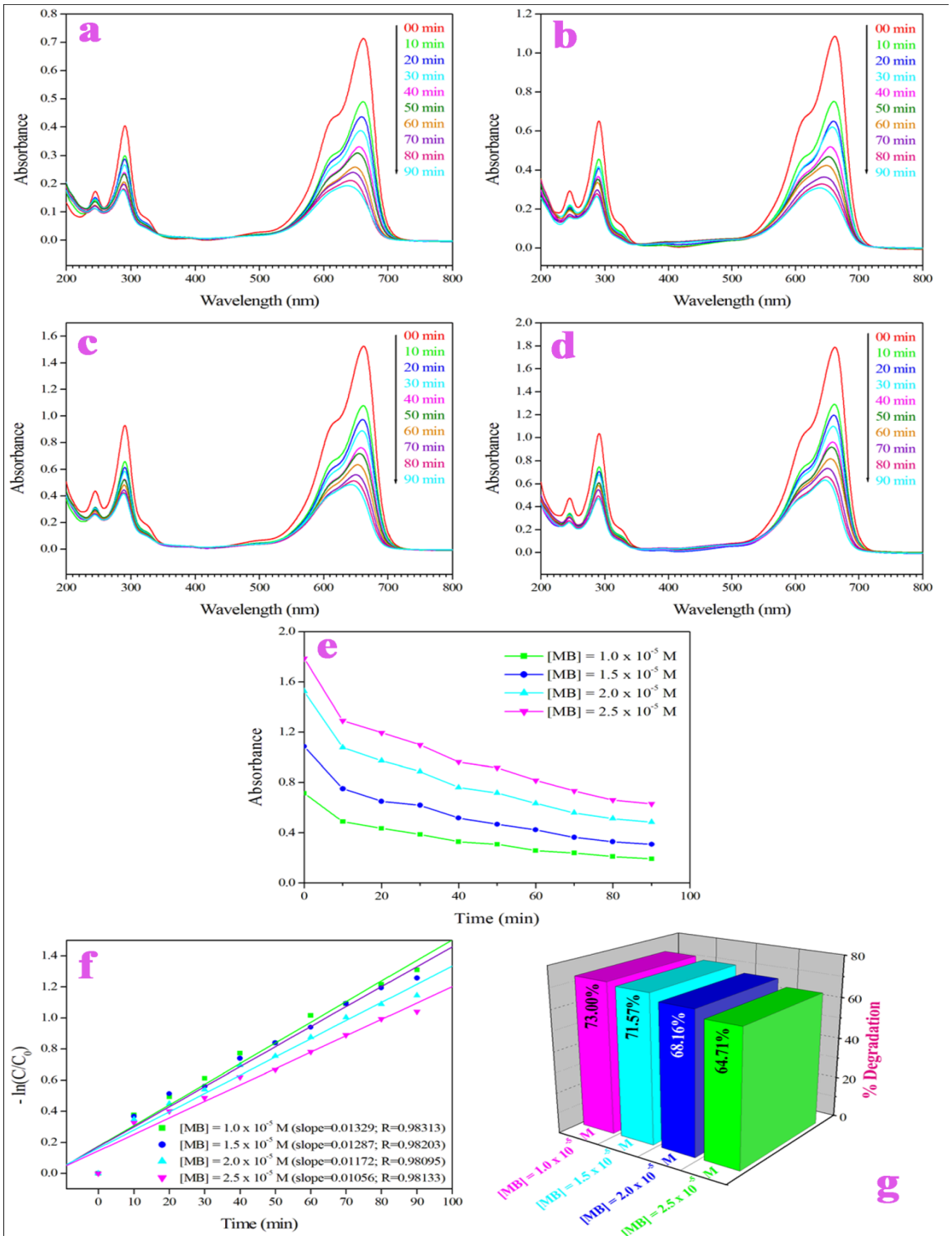

Figure 4. UV–Vis spectra of MB as a function of time in the presence of Co_3O_4 - ZnO - ZrO_2 NPs (a) [MB] = 1.0 x 10^{-5} M (b) [MB] = 1.5 x 10^{-5} M (c) [MB] = 2.0 x 10^{-5} M (d) [MB] = 2.5 x 10^{-5} M (e) plot of absorbance versus time (f) plot of -ln(C/C_0) versus time and (g) % degradation

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3.5. Effect of photocatalyst amount

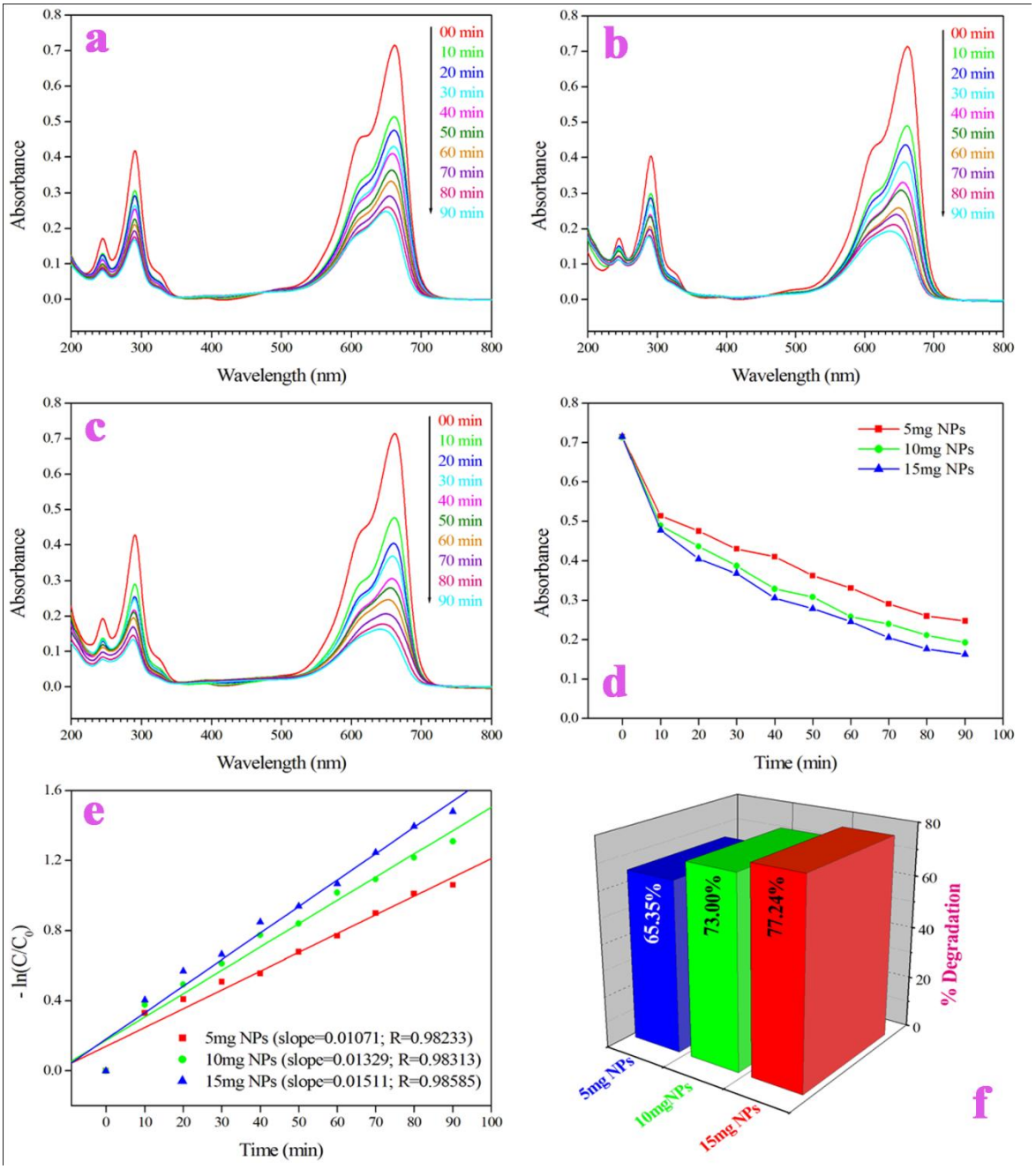

Figure 5. UV–Vis spectra of MB as a function of time in the presence of 0.1M Co_3O_4 - ZnO - ZrO_2 NPs (a) 5mg photocatalyst (b) 10mg photocatalyst (c) 15mg photocatalyst (d) plot of absorbance versus time (e) plot of -ln(C/C_0) versus time and (f) % degradation

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The effect of photocatalyst dosage on the photodegradation efficiency of MB was observed by taking different amounts of 0.1M Co_3O_4 - ZnO - ZrO_2 NPs (5, 10 & 15mg) into 100mL of 1 x 10^{-5} M dye solution in the presence 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 0.01071, 0.01329 and 0.01511min^{-1} under sunlight, respectively. Percentage degradation of MB using 5, 10 and 15mg photocatalyst are 65.35, 73.00 and 77.24% respectively.

The dye degradation 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 leading to an increase in the number of hydroxyl radicals(˙OH) which are responsible for the actual degradation of dye solution [6].

3.6. Mechanism of Photocatalytic activity

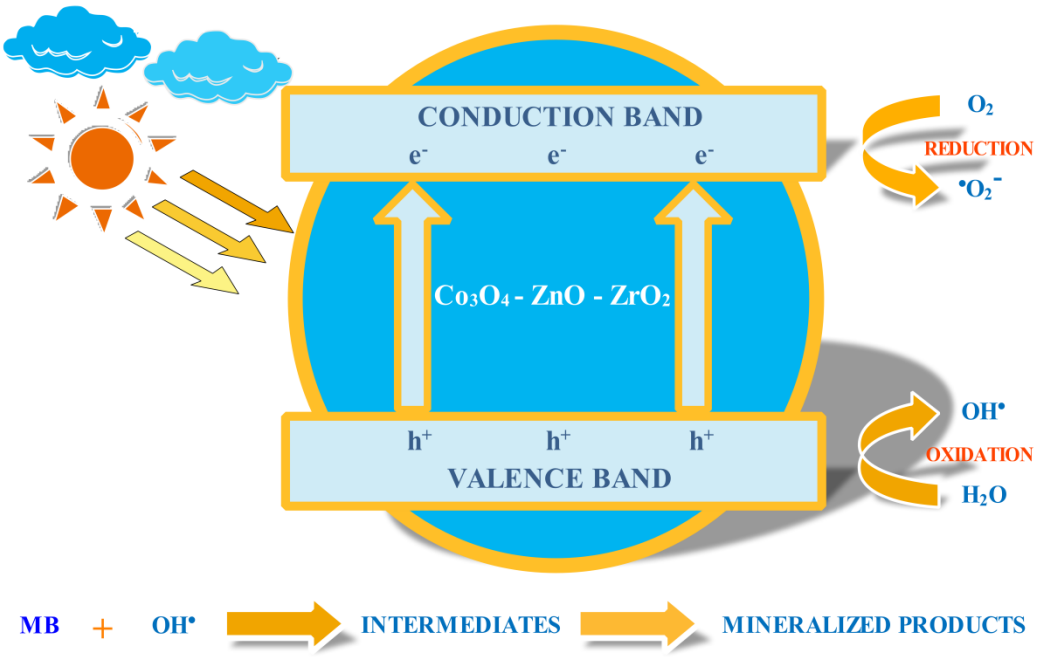

Figure 6. Mechanism for the photocatalytic degradation of MB by Co_3O_4 - ZnO - ZrO_2 NPs

IV. CONCLUSIONS

Photocatalytic activity of Co_3O_4 - ZnO - ZrO_2 NPs was studied by degradation of MB for 90min under sunlight. The photocatalytic degradation is superior for 0.1M Co_3O_4 - ZnO - ZrO_2 NPs compared to other samples and the photocatalytic degradation of MB in the presence of sunlight is observed to follow pseudo-first-order kinetics. The photocatalytic degradation depends on the pH of dye solution, photocatalyst particle size, photocatalyst dosage and dye concentration. Finally, Co_3O_4 - ZnO - ZrO_2 NPs are prospective candidates to be used as photocatalyst using sun light for the degradation of dyes to nontoxic products.

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