

Photocatalytic Activity of Co_3O_4 - CuO - ZrO_2 Ternary Nanoparticles

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Abstract:-- Nano Co_3O_4 - CuO - ZrO_2 mixed oxides were synthesized by wet chemical method by mixing of equimolar solutions of cobalt chloride, copper sulphate and zirconium oxychloride in aqueous sodium hydroxide and refluxed at elevated temperature. The photocatalytic activity of Co_3O_4 - CuO - ZrO_2 NPs was evaluated for degradation of methylene blue (MB) under sunlight. The photocatalytic activity is affected by pH of dye solution, photocatalyst particle size, photocatalyst dosage and dye concentration. The rate of MB degradation is almost 2.49 fold higher in the presence of sunlight than in the absence of sunlight. The degradation efficiency of MB is considerably increased from 78.38% to 88.18% with increasing pH from 4 to 9. 0.1M Co_3O_4 - CuO - ZrO_2 NPs with smaller particle size (12.93nm) exhibits stronger photocatalytic activity as compared to other NPs (0.2M - 0.5M) with larger particle size (13.29 - 23.83nm size). The dye degradation increases with increasing catalyst dosage, which is characteristic of heterogeneous photocatalysis. While increasing the dye concentration from 1.0 to 2.5×10^{-5} M the rate of degradation decreases.

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

1. INTRODUCTION

The efficient removal of organic dyestuffs in polluted water has been always a challenging issue in the field of environmental remediation and pollution control. Among various physical and chemical approaches, photocatalysis has received extensive attention for removal of organic dyestuffs [1, 2].

Nanoparticles (NPs) are expected to have a better catalytic performance than general metal oxides materials, which provides a suitable way for developing highly active metal oxide photocatalysts and makes the application of general oxides more practical. Recently, earth-abundant metal oxides (Co_3O_4 , CuO and ZrO_2 etc.) are found to be active catalyst for photodegradation and can be a cheaper alternative to noble metal catalysts [1].

Therefore, the research spotlight has turned towards inexpensive metal oxides such as Co_3O_4 , CuO and ZrO_2 . In this work, wet chemical method was applied to synthesize Co_3O_4 - CuO - ZrO_2 NPs. The effectiveness of Co_3O_4 - CuO - ZrO_2 NPs was studied for the photocatalytic degradation of methylene blue using sunlight.

2. EXPERIMENTAL DETAILS

2.1. Materials

The precursors $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and the precipitant (NaOH) were purchased from Aldrich. All solutions were prepared using deionized water.

2.2. Synthesis of Co_3O_4 - CuO - ZrO_2 NPs

We have synthesized Co_3O_4 - CuO - ZrO_2 NPs using the similar procedure as published in our previous paper [1]

About 25mL of 0.1M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the aqueous solution of 75mL of 1.0M NaOH solution and stirred well. To this mixture 25mL of 0.1M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 25mL of 0.1M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ 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 synthesize different (0.2M - 0.5M) Co_3O_4 - CuO - ZrO_2 NPs.

2.3. Evaluation of photo degradation

For degradation studies, 10 mg of Co_3O_4 - CuO - ZrO_2 NPs was added to 100mL of 1×10^{-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 ($\lambda_{\text{max}} = 662\text{nm}$) using UV-Vis spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Photocatalytic Activity of Co_3O_4 - CuO - ZrO_2 NPs

To study the applicability of Co_3O_4 - CuO - ZrO_2 NPs in the degradation of dyes, methylene blue (MB) dye is taken as a model dye and the degradation studies were carried out under sunlight.

3.1.1. Effect of pH of dye solution

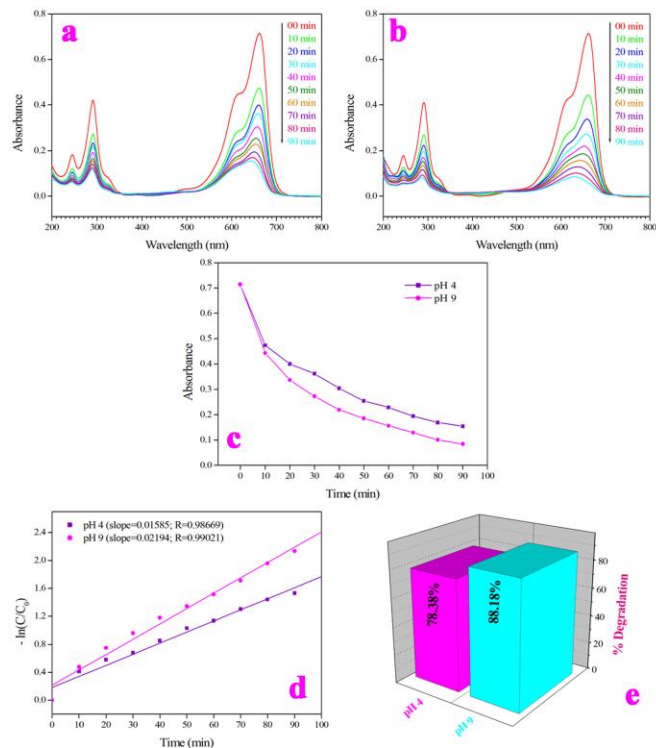


Figure 1. UV-Vis spectra of MB as a function of time in the presence of 0.1M Co₃O₄- CuO - ZrO₂ NPs (a) pH 4 (b) pH 9 (c) plot of absorbance versus time (d) plot of -ln(C/C₀) versus time and (e) % degradation

The effect of pH on the degradation of MB dye was studied at pH 4 and 9 using 10mg of photocatalyst (0.1M Co₃O₄ - CuO - ZrO₂ NPs) and 100mL of 1 x 10⁻⁵ M MB dye solution under sunlight for 90min. The pH of the solution was maintained by adding necessary amount of 0.1M H₂SO₄ 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 known for heterogeneous photocatalysis at low dye concentration, and the equation can be expressed as follows [2]:

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

here C₀, 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/C₀)

Vs time (t) will provide a slope of k with the linear correlation coefficient value (R) by lineal fitting of the experimental data.

The observed rate constants (k) at 90 min for the photocatalytic degradation of MB using pH value of 4 and 9 are 0.01585 and 0.02194min⁻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 apparent from the observed linear plots of -ln(C/C₀) as a function of time at different pH given in figure 1(d). The degradation efficiency of MB is considerably increased from 78.38% to 88.18% with increasing 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].

3.1.2. Effect of light

The effect of light on degradation of MB (1.0 x 10⁻⁵ M) was studied by keeping the photocatalyst (0.1M Co₃O₄ - CuO - ZrO₂ NPs) dosage at 10 mg per 100 mL and pH 9.

In the absence of sunlight, the intensity of characteristic absorption band of dye at 662 nm is decreased slowly, after 90 min 56.82 % of dye is detached without any shift in the λ_{max}. The absorbance of dye is decreased from 0.71428 to 0.30843 au. In the presence of sunlight, the absorbance is decreased quickly with a blue shift

in λ_{max}, and no new absorption band is observed. The absorbance is decreased quickly from 0.71453 to 0.08446 au corresponding to 88.18 % of removal of dye after 90 min of sunlight illumination. The plot of -ln(C/C₀) versus time is a straight line in the above two cases and the slope is equal to the rate of MB degradation, which is 0.00881 and 0.02194min⁻¹ in the absence and presence of sunlight, respectively. The rate of MB degradation is almost 2.49 fold higher in the presence of sunlight. It indicates the strong impact of sunlight on this reaction.

3.1.3. 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 Co₃O₄ - CuO - ZrO₂ NPs) on the dye degradation was evaluated by tracing the absorbance of MB at pH 9.

It is observed that 0.1M Co₃O₄ - CuO - ZrO₂ NPs with smaller particle size (12.93nm) exhibits stronger photocatalytic activity as compared to other NPs with larger particle size (13.29 – 23.83nm size) . This can be explained 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].

3.1.4. Effect of initial dye concentration

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

Two factors are responsible for the decrease in percentage degradation efficiency with an increase in the initial dye concentration: First, as the initial concentration of MB is increased, the amount of generated hydroxyl radicals do not correspondingly increase due to the same dosage of photocatalyst, which results in a relatively smaller $\cdot\text{OH}$ concentration. Second, an increase in the light absorbed by the dye molecules leads to a decrease in the number of photons that reach the catalyst surface [5].

3.1.5. Effect of photocatalyst amount

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

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 causing an increase in the number of $\cdot\text{OH}$ radicals which can take part in actual degradation of dye solution [6].

3.1.6. Mechanism for the photocatalytic degradation of MB

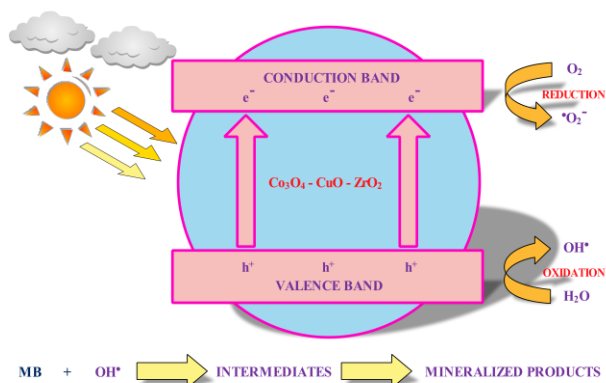


Figure 2 Mechanism for the photocatalytic degradation of MB by Co_3O_4 - CuO - ZrO_2 NPs

In the presence of sunlight, the semiconductor photocatalyst generates electron/hole pairs. These

electron/hole pairs are capable of initiating a series of chemical reactions that eventually mineralize the MB dye. When Co_3O_4 - CuO - ZrO_2 NPs absorbs a photon of energy equal to or greater than its band gap width, an electron (e^-) may be promoted from the valence band to the conduction band leaving behind an electron vacancy or hole (h^+) in the valence band [6].

The positive hole oxidizes the water adsorbed on the surface of the photocatalyst to produce hydroxyl radicals ($\cdot\text{OH}$) whereas the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst to produce superoxide radical anions ($\cdot\text{O}_2^-$). The presence of oxygen prevents the electron-hole pair recombination [7]. In the degradation of dye, the hydroxyl radical which is generated from the oxidation of adsorbed water where it is adsorbed as OH^- is the primary oxidant.

The blueshift in λ_{max} (662nm) suggests the formation of N-demethylated intermediates in degradation pathway. The bands at 245 and 290 nm decrease significantly and no new bands appear. This implies that a full oxidative decomposition of the chromophore ring structure (phenothiazine) has occurred [8]. After the completion of reaction, mineralized products like CO_2 , H_2O are formed [3]. Thus, N-demethylation and oxidative decomposition take place during MB degradation.

In the presence of sunlight, the decolorizing of MB by the Co_3O_4 - CuO - ZrO_2 NPs is mainly attributed to the photocatalytic degradation rather than the simple adsorption. In the absence of sunlight the decolorizing of MB is due to adsorption.

4. CONCLUSIONS

Nano Co_3O_4 - CuO - ZrO_2 mixed oxides were synthesized successfully by wet chemical method. Photocatalytic activity of Co_3O_4 - CuO - ZrO_2 NPs was examined by degradation of MB for 90min under sunlight. The photocatalytic degradation is higher for 0.1M Co_3O_4 - CuO - 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. It is found that the photocatalytic degradation depends on the pH of dye solution, photocatalyst particle size, photocatalyst dosage and dye concentration. Finally, Co_3O_4 - CuO - ZrO_2 NPs are potential candidates to be used as photocatalysts using solar energy for the degradation of dyes to harmless products.

REFERENCES

- [1] S. A. David and C. Vedhi, "Synthesis and Characterization of Co₃O₄ - CuO - ZrO₂ Ternary Nanoparticles," International Journal of ChemTech Research, vol. 10, pp. 905 – 912, 2017.
- [2] L. Hou, L. Yang, J. Li, J. Tan and C. Yuan, "Efficient Sunlight-Induced Methylene Blue Removal over One-Dimensional Mesoporous Monoclinic BiVO₄ Nanorods," Hindawi Publishing Corporation: Journal of Analytical Methods in Chemistry, vol. 345247, pp 9, 2012.
- [3] N. Soltani, E. Saion, M. Z. Hussein, M. Erfani, A. Abedini, G. Bahmanrokh, M. Navasery and P. Vaziri, "Visible Light-Induced Degradation of Methylene Blue in the Presence of Photocatalytic ZnS and CdS Nanoparticles," International Journal of Molecular Sciences, vol 13, pp. 12242 - 12258, 2012.
- [4] M. H. Elhussien, and Y. M. Isa, "Langmuir, Freundlich Adsorption Isotherms and Kinetics for the Removal of Methylene Blue Dye from Aqueous Solution using Activated Carbon Derived from Pods of Acacia nilotica var astringens (Sunt tree) by Chemical Activation with ZnCl₂," Chemical and Process Engineering Research, vol. 38, pp. 25, 2015.
- [5] R. M. Mohamed, I. A. Mkhallid, E. S. Baeissa, and M. A. Al-Rayyani, "Photocatalytic Degradation of Methylene Blue by Fe/ZnO/SiO₂ Nanoparticles under Visible light," Hindawi Publishing Corporation; Journal of Nanotechnology, vol. 329082, pp. 5, 2012.
- [6] Z. M. Abou-Gamra and M. A. Ahmed, "Synthesis of mesoporous TiO₂-curcumin nanoparticles for photocatalytic degradation of methylene blue dye," Journal of Photochemistry and photobiology B: Biology, vol. 160, pp. 134-141, 2016.
- [7] R. M. Tripathi, A. S. Bhadwal, R. K. Gupta, P. Singh, A. Shrivastav and B. R. Shrivastav, "ZnO nanoflowers: Novel biogenic synthesis and enhanced photocatalytic activity," Journal of Photochemistry and Photobiology B: Biology, vol. 141, pp. 288- 295, 2014.
- [8] T. Zhang, T. Oyama, A. Aoshima, H. Hidaka, J. Zhao and N. Serpone, "Photooxidative N-demethylation of methylene blue in aqueous TiO₂ dispersions under UV irradiation," Journal of Photochemistry and Photobiology A: Chemistry, vol.140, pp 163–172, 2001.