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Enhanced Photocatalytic Degradation of Thymol Blue and Rhodamine B Using Calcinated $ZnFe_2O_4$

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Article Details

Keywords: SEM,EDX, Thymol Blue, Rhodamine, Co Precipitation

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ABSTRACT

Water pollution cause by synthetic dyes released from industrial effluents remains a significant environmental challenge .among various remediation strategies ,photo catalytic degradation has emerged as an effective and environmentally friendly technique due to its cost efficiency and minimal generation of toxic byproduct. In this study a zinc ferrite based nanophotocatalyst was synthesized via a co- precipitation method followed by calcinations and employed for the visible –light driven degradation of two model dyes Thymol blue (TB) and Rhodamine B (RB).the prepared ZnFe2O4 nanoparticles were characterized using SEM, EDX analysis.the point of zero charge (PZC)of the catalyst was also determined. Various opretional parameter including PH, contact time, initial dye concentration, catalyst doseage and temperature were optimized to evaluate their effect on photocatalytic efficiency. The degradation kinetics followed a pseudo-second order model with high correlation coefficient (R>0.99) indicating multiple cycles and performed effectively in real water samples. These result confirm that ZnFe2O4 is a promising reusable photo catalyst for the sustainable treatment of dye contaminated wastewater .

INTRODUCTION

Water is an essential resource that plays a vital role in sustaining al forms of life on earth. Despite covering approximately 70% the plant surface only about 1% of water ia available as clean and accessible and urbanization water resources are being increasingly contaminated by a wide range of pollutant including dyes, pharmaceuticals , pesticides and other hazardous chemicals.among these pollutant synthetic dyes are particularly concering due to their complex aromatic structure which confer high chemical resistance to biodegradation these dyes are extensive used in varius industries such as textile ,leather,cosmetics plastics and food processing .it is estimated that over 0.7 million tons of dyes are produced annually with a significant proportion being released into water bodies as untreated effluents . . [1]. Without it, life would not be possible; it is essential to sustaining life. However, a number of pollution sources have surfaced in recent years as a result of new toxins such as contemporary mixes, pesticides, herbicides, pharmaceuticals, and bug sprays. [2]. Dye is used by many industries, and dyes are extremely poisonous, destructive, and dangerous, especially for humans, because the dye is colored, and the color of the dye is not only very toxic but deteriorates the color of water Traditionally, people used natural or synthetic dyes to color cloth, wool, hides, pelts, skin, and other materials, mostly with plants and animals. [4]. These dyes are used to decrease sunlight penetration, which lowers the rate of photosynthesis. Therefore, lowering the use of dyes is an important issue. Living things' survival is at danger because many of these pigments are exceedingly toxic and deadly. [6, 7]. Each year, different sectors utilize about 0.7 million tons of dyes, the most of which are discharged into water bodies, creating major health dangers to people, animals, and aquatic life in particular. [8]. Therefore, the best and most practical way to remove color dyes and contaminants from water and textile materials must be found. Numerous techniques, such as photo degradation, have been studied to remediate wastewater that contains dyes.[9], reverse osmosis [10], adsorption, biosorption, electrochemical oxidation [11], coagulation, and ozonation, etc. are currently used [[12]. These techniques are also expensive, inefficient, and time-consuming because they just move contamination from one phase to another and are not destructive.

These sources consequently produce a variety of contaminants. [13]in this study we synthesized calcinated $ZnFe_2O_4$ nanoparticles via a co-precipitation method and investigated their photo catalytic activity for the degradation of two model dyes Thymol Blue and Rhodamine B under visible light . comprehensive characterization of the catalyst was performed

using SEM and EDX techniques. The effect of critical operational parameter such as including PH, contact time, initial dye concentration, catalyst dosage and temperature were optimized to evaluate their effect on photo catalytic efficiency were systematically studied. Furthermore kinetic modeling , reusability testing and real sample analysis were conducted to evaluate the practical applicability and robustness of the ZnFe2O4 photo catalyst.

EXPERIMENTAL SECTION

CHEMICALS AND REAGENTS

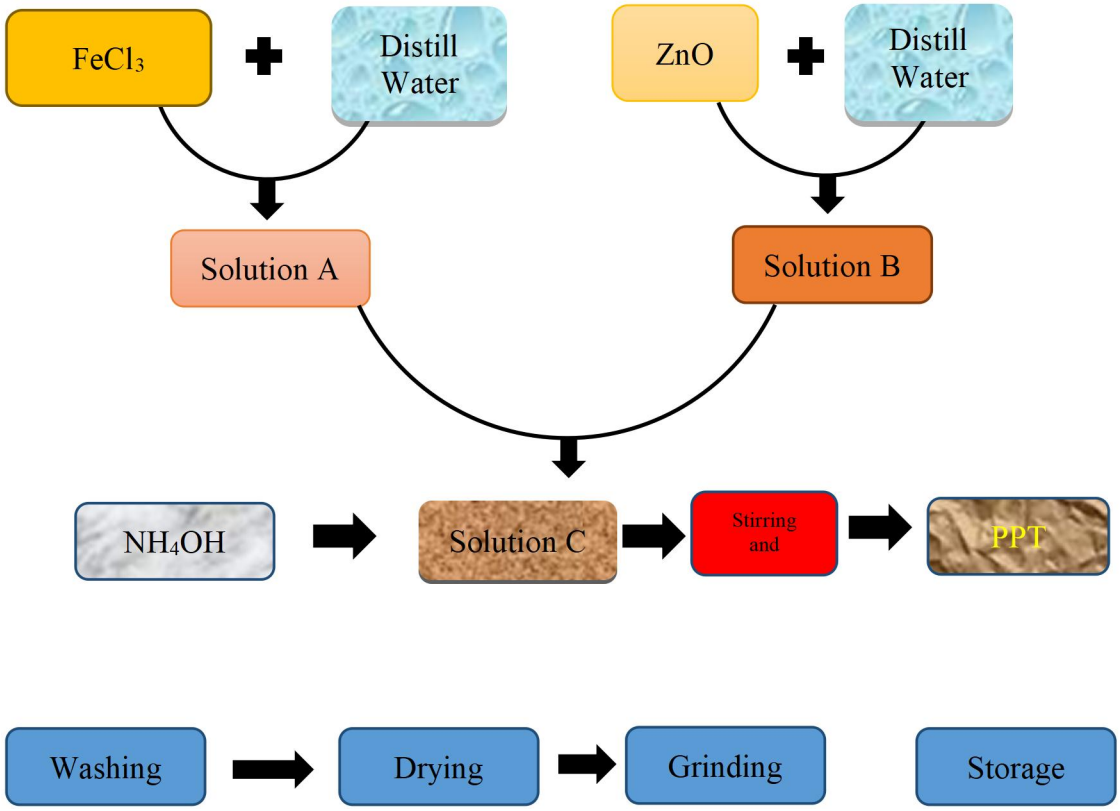
Zinc oxide (ZnO ,99%) ,Iron(III) chloride FeCl3.6H2O were purchased from Sigma Aldrich (Germany) Ethanol,, acetic acid ,ammonium hydroxide(NH4OH), ammonium chloride (NH4Cl) and sodium acetate were obtained from merck(Germany). ThymolBlue, and Rhodamine B dyes were used as model pollutants distilled water.

INSTRUMENTS

The degradation studies in this research project were conducted using a single beam UV/visible spectrometer (manufactured by Biotechnology Medical Services, K. Canada Inc.), which was operated at the λmax of both Thymol Blue and Rhodamine B dyes. The determination of the λmax was performed using a double beam UV / visible spectrometer (model AE-S90-2D, manufactured by A & E Lab). For the adjustment and measurement of the pH level of the solutions, as well as buffer preparation, a pH meter (manufactured by HANNA instruments Romania) was utilized. Additionally, the laboratory equipment used in the research project included a furnace (model LMFC-16, manufactured in China), oven (model FCE043L, manufactured by Electrolux), analytical balance (model PA214, manufactured by OHAUS corporation, USA), centrifuge (model 800d, manufactured in Hunan, China), visible light source, and magnetic stirrer (model 79-1, manufactured by Jiangsu Jinyi instrument Technology Co.Ltd).

SYNTHESIS OF $ZNFE_2O_4$ NANOPHOTOCATALYST

$ZnFe_2O_4$ nanoparticles were synthesized via chemical co-precepitation A0.1M aqueous solution of FeCl3 was prepared by dissolving the appropriate mass in 100ml distilled water .separatly a 0.05 M suspension of ZnO was prepared. The FeCl3 solution was added dropwise to the ZnO suspension under constant stirring. Subsequently 0.1M NH4OH was added until the PH reached 12 and the solution was maintained at 70c for 2-3 hours leading to the formation of brown precipitation. The precipitate was washed with ethanol and distilled water until free of impurities .it was then dried at 70C ground into fine powder and stored in airtight container for further use.



CHARACTERIZATION OF PHOTOCATALYST

The morphology and structure of the ZnFe2O4 nanoparticles were stuided using SEM and EDX the optical properties and dye absorption maxima were determined using UV-Vis spectroscopy .stock dye solution (1000ppm) were prepared and diluted to desired concentration. TB and RB exhibeted lemda max at 590nm and 550nm respictively.

POINT OF ZERO CHARGE ;(PZC)

To determine the PZC of the catalyst 25ml of 0.2M NaNO3 was placed in nine 100ml flask the PH of each was adjusted between 3 and 12 using 0.1M HCl or 0.1M NaOH. Then 0.1g of ZnFe2O4 was added to each flask for 24hours .the final PH was measured and plotted against initial PH to identify the PZC.

PHOTOCATALYTIC DEGRADATION EXPERIMENTS

All photocatalytic experiments were conducted under visible light at room temprature unless otherwise specified.in each experiment known concentration was mixed with ZnFe2O4 and stirred under light samples were withdrwan at intervals, centrifuged to remove suspended

particles and analyzed using UV-Vis spectrophotometry.

OPTIMIZED PARAMETER

The photocatalytic degradation of Thymol Blue TB and Rhodamine B RB was optimized by studying various factors. The PH was varied from 2 to 10 contact time from 5 to 40 minutes and dye concentration from 10 to 50 ppm TB and 10 to 30 ppm RB . catalyst dosage ranged from 0.01 to 0.5g and temprature were adjusted between 30C and 100C .

RESULT AND DISCUSSION

SCANNIG ELECTRON MICROSCOPE (SEM)

SEM images of ZnFe2O4 nanoparticles reveal irregular flake like structure forming small cluster with particles size ranging from 10 to 100nm figure c,d suggest as well developed surface morphology with icreased surface area . because of Fe_3O_4.Therefore, ZnFeO-NPC is considered a powerful photocatalyst for organic pollutants' photodegradation.

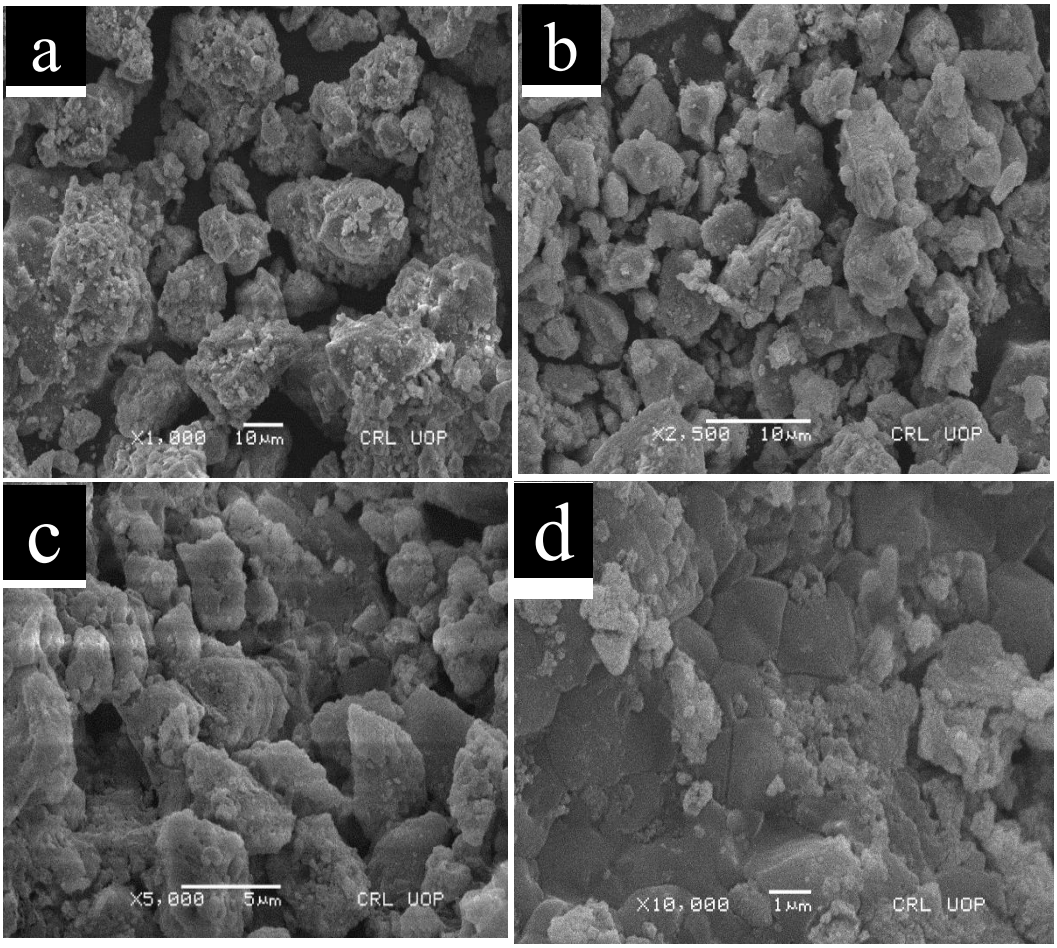


FIGURE 8. SEM IMAGES ZNFEO-NPC

ENERGY DISPERSIVE X-RAY ANALYSIS(EDX)

The graph and table of weight and atomic percentage of energy diffraction x-ray analysis of ZnFeO-NPCis shown in Figure 9, there were prominent peaks of zinc and iron in ZnFeO-NPC on the EDX spectrumindicated that the photocatalyst was successfully synthesized. EDX spectrum also showspeaks for oxygen, chlorine and sodium as residue present.

POINT OF ZERO CHARGE (PZC)

The point of zero charge of the catalyst was determined to be PH 7.3 below this PH the surface of the catalyt is positive charged the surface become negatively charged.since TB and RB are cationic dyes higher degradation efficiency is achived at PH values the PZC due to enhanced electrostatic attraction.

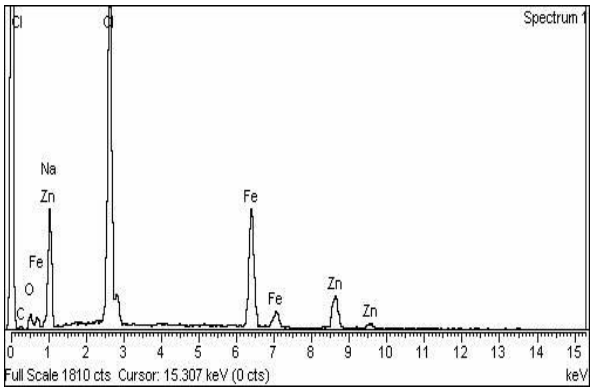


FIGURE 9. EDX OF ZNFEO-NPC

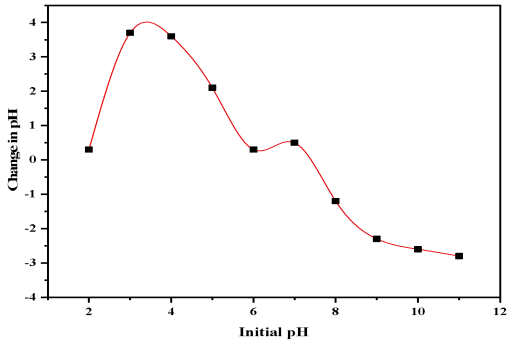


FIGURE 10. DETERMINATION OF PZC FOR ZNFEO-NPC

PARAMETER CONDITIONS

The optimal condition for photocatalytic degradation using ZnFe2O4 were determined as follow PH 8 for Thymol Blue and PH 4 for Rhodamine B and 30 minutes contact time for 97% degradation 10ppm dye concentration 0.1g catalyst dosage and temperature dependent behavior TB degradation increased with temperature while RB degradation decreased .

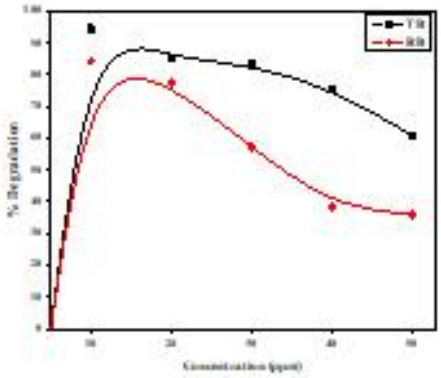


FIGURE 15. EFFECTS OF DYES CONCENTRATION

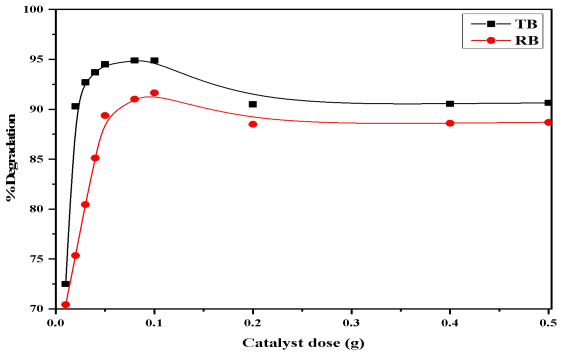


FIG 16. EFFECT OF PHOTOCATALYST DOSE

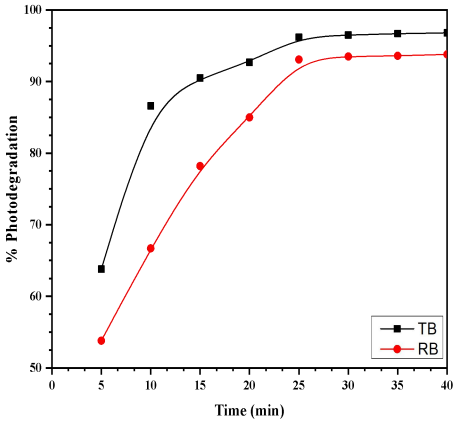


FIGURE 14. EFFECT OF CONTACT TIME

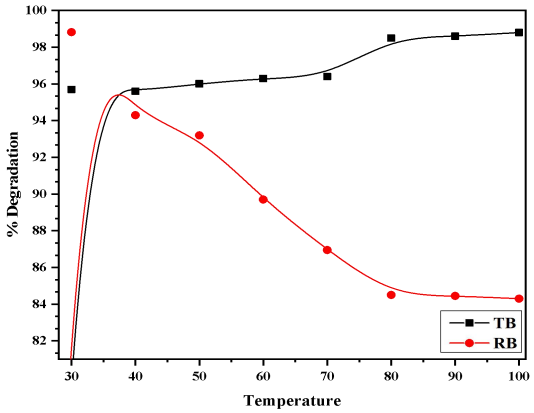


FIGURE 17. TEMPERATURE EFFECT.

KINETIC STUDIES

PSEUDO-FIRST ORDER MODEL

Kinetic data fitted to the pseudo –first order model revraled rate constant of -0.086min-1(TB) and -0.1.49min^{-1} (RB) with correltion coefficient R^2 of 0.9249 and 0.9545 however the model showed liited accuracy in predicting actual degradation rates.

PSEUDO- SECOND ORDER MODEL

The pseudo –second order kinetic model provided a better fit for the data rate constant (k_2) were higher and R_2 values were unity 0.9928 for TB ,0.9976 for RB confirming that the degradation followed pseudo- second order kinetic .

EFFECT OF INTERFERING IONS

The presence of common cation (Na^+,K^+, Ca^{2+}, Mg^{2+}) infulnced degration effiency ca and K had

more significant inhibitory effect due to their larger ionic radii and higher charge densities which likely competed with by molecules for active site on the catalyst surface.

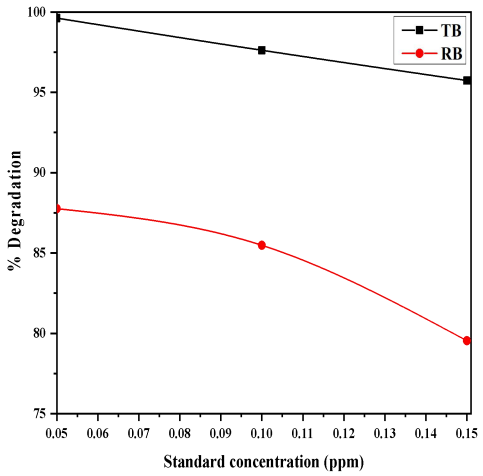
REUSABILITY OF ZNFEO-NPC

The experimental findings revealed that the photocatalyst was capable of being utilized for up to three cycles, suggesting that the ZnFeO-NPC has the potential for TB and RB dyes complete photodegradation.

APPLICATION

REAL WATER SAMPLE

ZnFe2O4 was tested on river and industrials water samples spiked with TB and RB dyes at different oncentration .high degradation efficiency up to 99.9% was achived even in the presence of natural water matrices indicating strong real-world applicability.



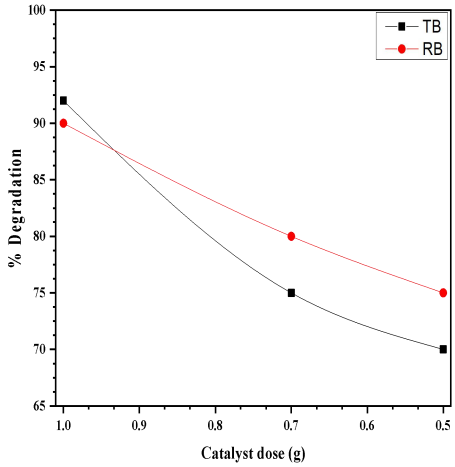


FIGURE 24. % DEGRADATION OF TB AND RB IN SAMPLES OF INDUSTRIAL WATER

FIGURE 25. CATALYST REUSABILITY FOR TB AND RB DEGRADATION

CONCLUSION

The increasing contamination of water bodies by synthetic dyes such as Thymol Blue (TB) and Rhodamine B (RB) present a serious threat to environmental and public health. In this study ZnFe2O4 nanoparticles were successfully synthesized via a simple co-precipitation method followed by calcinations and their photo catalytic potential under visible light was systematically investigated. The catalyst demonstrated excellent degradation efficiency for both TB and RB dyes under optimized condition, with maximum degradation observed at PH 8 and 4 respectively .kinetics studies revealed that the photo degradation process followed a pseudo

second order model confirming strong adsorption and surface mediated degradation dynamics. The ZnFe2O4 catalyst exhibited robust stability high reusability over multiple cycles and strong performance even in real wastewater samples ,highlighting its practical applicability .overall these findings suggest that calcined ZnFe2O4 nanoparticles are an efficient ,low cost and environmentally friendly photo catalyst suitable for the treatment of dye- laden industrials wastewater.

AUTHOR CONTRIBUTION

A.bashir conceptualization investigation formal analysis data curation ,writing ,figures, original draft and review and editing R.kabir methodology ,investigation .

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