Photocatalytic Degradation of Aqueous Dyes by ZnO/Fe_2O_3/PEG Based Nanocomposites

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ABSTRACT

Purpose: *Dyes are organic compounds, which alter the quality of the water. The present study aims to develop new photocatalytic materials for the oxidation of dyes in the water.*

Methodology: *Mixed nanocomposite material of ZnO /ferric oxide /Polyethylene glycol was synthesized by the solution phase method. The synthesized nanocomposites were characterized by SEM and particle size analyzer to evaluate the surface morphology and particle size determination.*

Analysis/Results: *Aqueous dye solutions of Eriochrome Black T, Methylene Blue, and food color yellow were prepared and investigated for the synthesized nanocomposite material for the photocatalytic action. The present nanocomposite shows superior photocatalytic activity on Eriochrome Black T with photocatalytic activity of 81.6% oxidation of dyes and moderate activity to Food colour Yellow and Methylene Blue.*

Originality/Value: *In the present study new nanocomposite materials were prepared and evaluated for photocatalytic activity, the action of nanocomposite on Eriochrome Black T dye solution, results in promising activity for the colour removal. The synthesized nanocomposite may be useful for the large quantity of color removal in contaminated water.*

Type of Paper: *Experimental.*

Keywords: Nanocomposites; ZnO; Photocatalysis; SEM; Eriochrome Black T, Polyethylene Glycol.

1. INTRODUCTION :

Rising consumer demands and living standards have intensified pollution levels [1]. Water bodies are now contaminated with a range of pollutants, including chemicals, trace elements, industrial effluents, spills, pesticide residues, sludge, and hazardous waste, all contributing to soil and water pollution [2]. Water contamination occurs when foreign materials such as chemicals, microorganisms, or pollutants contaminate a water source, making it unsafe for human consumption or use. Contaminated water can lead to serious health issues, from gastrointestinal problems to long-term illnesses. Common sources of water contamination include agricultural runoff, industrial discharge, improper waste disposal, and aging infrastructure [3]. Water treatment processes are used to eliminate contaminants and ensure water safety. The presence of dyes in water bodies poses a significant challenge, but it can be mitigated through photo-catalytic processes utilizing various photo catalysts [4]. Wastewater, laden with significant environmental pollutants, has become a crucial focus of research. Nanoparticles, known for their high reactivity, expansive surface area, functional versatility, and treatment efficacy, are increasingly used in wastewater treatment and purification [5-7]. Among various treatment techniques, adsorption stands out as a cost-effective, highly efficient, and powerful method for water purification

[8-11]. A diverse range of nanomaterials and nanocomposites possess unique properties, with certain semiconducting nanomaterials demonstrating exceptional photocatalytic capabilities under both UV and visible light. Dyes, which pose significant health risks, are being targeted for degradation and removal from water using various approaches, including conventional and biological methods [12]. Semiconductor materials such as Fe_2O_3, TiO_2, WO_3, and Cu_2O are particularly responsive to UV and visible light, making them effective photocatalysts in applications like environmental pollution reduction, wastewater treatment, and hydrogen production through water splitting [13]. Among the semiconducting metal oxides investigated, such as TiO_2, ZnO, CeO_2, $BiVO_4$, $Bi_{12}TiO_{20}$, and WO_3, TiO_2 has garnered particular attention due to its exceptional properties [14-15].
Additionally, residual dyes from industries such as textiles, pharmaceuticals, and dye intermediates are classified as non-biodegradable organic pollutants that contaminate natural water sources and wastewater systems [16-18]. Currently, photocatalysis is a highly effective method for degrading a wide range of organic pollutants in wastewater [19-21]. Research on the photodegradation of aqueous methyl orange using $MnTiO_3$ powder across different initial pH levels has shown that this catalyst holds significant potential for applications in heterogeneous catalysis and environmental decontamination [22]. In the recent days ZnO and TiO_2 received greater attention because of their excellent photo catalytic activity [23]. The synthesis of metal oxide nano particles have higher efficiency and low cost material for the functionalized materials and exhibits good hydrophobic and magnetic properties also [24]. However, nanostructured materials have been employed as efficient photocatalysts or as hybrids, combined or doped with other substances, to aid in the degradation of various organic pollutants. Hence, in the present study we development of advanced materials like our ZnO/Fe_2O_3/PEG based nanocomposites as a photocatalytic degradation of aqueous dyes.

2. REVIEW OF LITERATURE :

Removal of the colour, which is generated from the textile and dye industries can be carried out by using nutraceutical spent, which is the waste material. In the literature different bio-adsorbents have been identified and evaluated for their colour removal by the adsorption study.
Various previous studies are prior to single dyes and some of the adsorptions are reversible. A number of agricultural waste materials are being studied for the removal of different dyes from aqueous solutions which includes coir pith [24], orange peel [25], banana peel [26], rice husk [27], straw [28], banana stalk waste [29], durian (Durio zibethinus Murray) peel [30], *Tabebuiarosea* Peel [31] as natural adsorbent. Due to the other applications of these nutraceutical spent, such as bio-material, organic manure production and longer duration for the adsorption process, it has limitation to apply large amount of the waste material. It is found better to adopt photocatalysis mechanism compare to the adsorption for the decolorization. The various Zinc and Titanium based photo catalysts have been recorded for the photocatalytic activity. Nano composites such as Fe_3O_4/NiO was investigated for the removal of Rhodamine B dye [32], TiO_2/Fe_2O_3/polyvinyl alcohol [33], ZnO/Fe_2O_3/polyvinyl alcohol [34], ZnO-Fe_2O_3/PVA [35] *etc*., these nanocomposites are working on the principle of photocatalytic oxidation of the dyes, In the literature available material show slightly high band gap energy, they found to be lesser photo catalytic activity. In the present study, planned to incorporate polyethylene glycol as the organic matrix, to hold Zinc oxide and impurity dopant as ferric oxide. This aims to increase the photocatlytic action of the nanocomposite material by absorbing visible radiation.

3. OBJECTIVES OF THE PAPER :

On the basis of literature Review and research gap the following objectives are framed for the present work.
(1) Synthesis of new metal nanocomposite material with organic polymer matrix.
(2) Characterization of synthesized nano composite by SEM and particle analyzer.
(3) To carry out batch experiments to evaluate photocatalytic activity.

4. MATERIALS AND METHODS :

4.1 Chemicals and Materials:

All reagents utilized amid the project work were of analytical grade and all arrangements were carried out utilizing distilled water. Eriochrome Blak-T, Methylene Blue were procured from SD fine India Pvt Limited, $FeCl_3.6H_2O$, ZnO, PEG (poly Ethylene glycol), NaOH were procured from Rankem.

4.2 Methods:

4.2.1 Preparation of ZnO nanocomposite :

2.027g of $FeCl_3.6H_2O$ dissolve in 50ml of water and 2.0g of ZnO added to the above solution and 2.5g of PEG added to the above solution stirred for 30 min. During stirring add 3g of NaOH solution which is already dissolved in 50ml H_2O continue stirring until the precipitate obtained and the obtained precipitate is filtered. Wash with water dried residue collected and heated 20°C in hot air oven for 2hr, after drying, put in a mixer grinder until they got to be fine powder. The powder was sieved to ensure uniform particle size for consistent use. Finally, the ZnO/Fe_2O_3 nanocomposite powder was stored in an airtight container to preserve it for future use without requiring additional treatment.

4.2.2 Preparation of dye solution:

A series of aqueous solutions containing Eriochrome Black-T, food color, and methyl blue dyes at different concentrations were prepared by diluting stock solutions. The study involved exploring various parameters such as contact time and initial concentration of the solution. Each experiment utilized 0.5mg of composites, allowing for a systematic investigation into the degradation process under different conditions.

4.2.3 Preparation of ZnO nanocomposites:

Batch techniques were utilized to study the adsorption of Eriochrome black T, food colour yellow and methylene blue dyes using ZnO nanocomposite powder firstly 50ppm solution of dye was prepared by adding 0.05g of each dye to the 500ml of distilled water. Then 0.5g of ZnO nanocomposite was added to each 50 ml dye solution of Eriochrome black T, food colour Yellow and methylene blue and it is observed at different time intervals. And we have observed the nanocomposites absorbing the colour of the solutions at different time intervals by using colorimetry.

4.2.4 Study of Contact Time:

The aqueous dye solutions with 50 ppm concentration is taken for study of contact time. During the photocatalytic study, sample with nanocomposite serves as test solution and without nano composite, only dye solution serves as control.

The wavelength in which maximum (λ_{max}) absorption occurs to each dye was determined by recording absorption to the various wavelength and absorption of the dye solution at regular time interval was measured at regular time interval.

5. RESULTS AND DISCUSSION :

5.1 Morphology Analysis:

The properties of nano-heterostructures are influenced not only by their size but also significantly by their morphology, which can be crucial for optimizing their properties and performance in specific conditions. This section explores how adjusting the morphology of ZnO/Fe_2O_3 nanostructures impacts their optical and photocatalytic characteristics. High-resolution scanning electron microscopy (HR-SEM) images of the synthesized nanoparticles are presented in Figure 1. From the images it may be noted that, the high-quality image confirms the presence of ZnO and Fe_2O_3 phases within the composite and polymer act as the binding material between the metals, shows uniform distribution of the particle. Particle size distribution shows that particle size slightly above the 1000nm, with needle shape nono Zinc is dispersed in the phase.

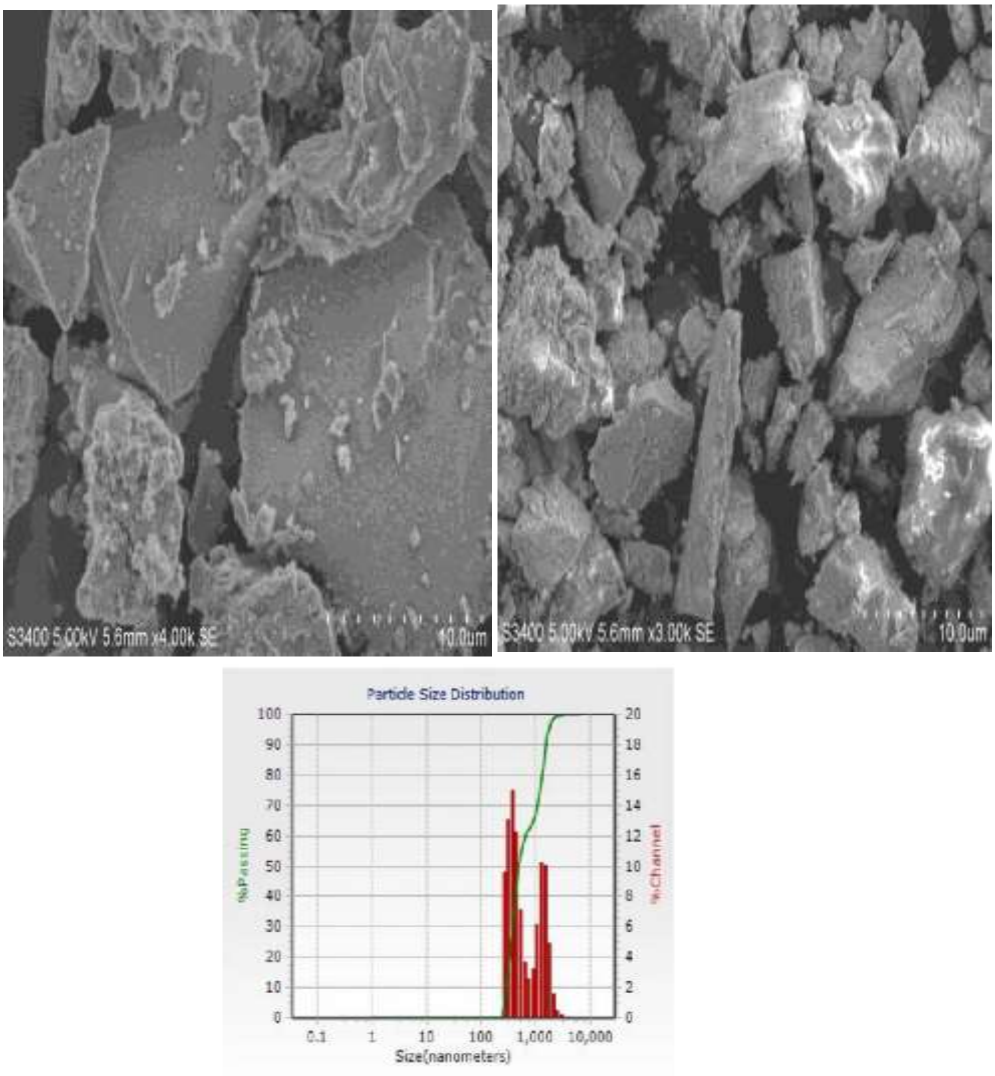

Fig. 1: SEM image of synthesized ZnO/Fe_2O_3 nanocomposite.

5.2 Photocatalytic action:

The photo catalytic activity of the synthesized ZnO/polyethylene glycol/Fe_2O_3 nano composite material was investigated on aqueous dye degradation through batch experiments. Table 1 shows data of the color removal with different time interval among the Food colour Yellow, Eriochrome Black-T and methylene blue dye solution. The recorded data shows that the photocatalytic activity of ZnO on Eriochrome Back-T dye solution is superior compare to the others. Table 1 shows that, color degradation of food color yellow was found to be 33.34 percent over the time of 720 minutes. The synthesized nano composite is moderately active on photo catalytic oxidation of food colour yellow dye.

Table 1: Percentage removal of Food colour Yellow dye in contact time

Time (Min)	Percentage Removal of Dyes		
	Food colour Yellow	Eriochrome Black-T	Methylene blue
20	17.86	12.5	6.4
80	19.45	22.6	10.76
140	21.4	32.6	15.8
260	22.8	42.6	18.8

320	24.8	46.12	22.4
720	33.34	81.6	28.23

Photo catalytic action of ZnO/polyethylene glycol/Fe_2O_3 nano composite was studied on Eriochrome Black-T dye solution in aqueous batch experiments, Table 1 shows that percentage removal of Eriochrome Black-T dye solution on the action of photocatalyst. The amount of dye removal data shows that at the 81.6 percent removal at the time interval of 720 minutes. The synthesized nano composite is excellent photocatalytic material for removal of Eriochrome Black-T.
Results of photo catalytic action of ZnO/polyethylene glycol/Fe_2O_3 nano composite on Methylene blue, shows that percentage removal of Methylene blue dye solution is 28.33 percent, Photocatalytic action of nano composite is moderately low.
The comparative photocatalytic action of three dyes such as, food colour yellow, Eriochrome Black T, Methylene blue is shown in the figure 2. The result clearly indicates that the efficient photocatalytic action of the ZnO/polyethylene glycol/Fe_2O_3 nano composite on Eriochrome Black T dye, as contact time increases, the photocatalytic oxidation of the dyes in aqueous solution also increases. In the graph, percentage removal of the dyes versus contact time by photo catalytic oxidation shows that moderate action of nanocomposite on Food color yellow and Methylene blue. This variation of the activity of synthesized nanocomposite is depends upon the structure of dyes and available weaker bond in their molecular structure.

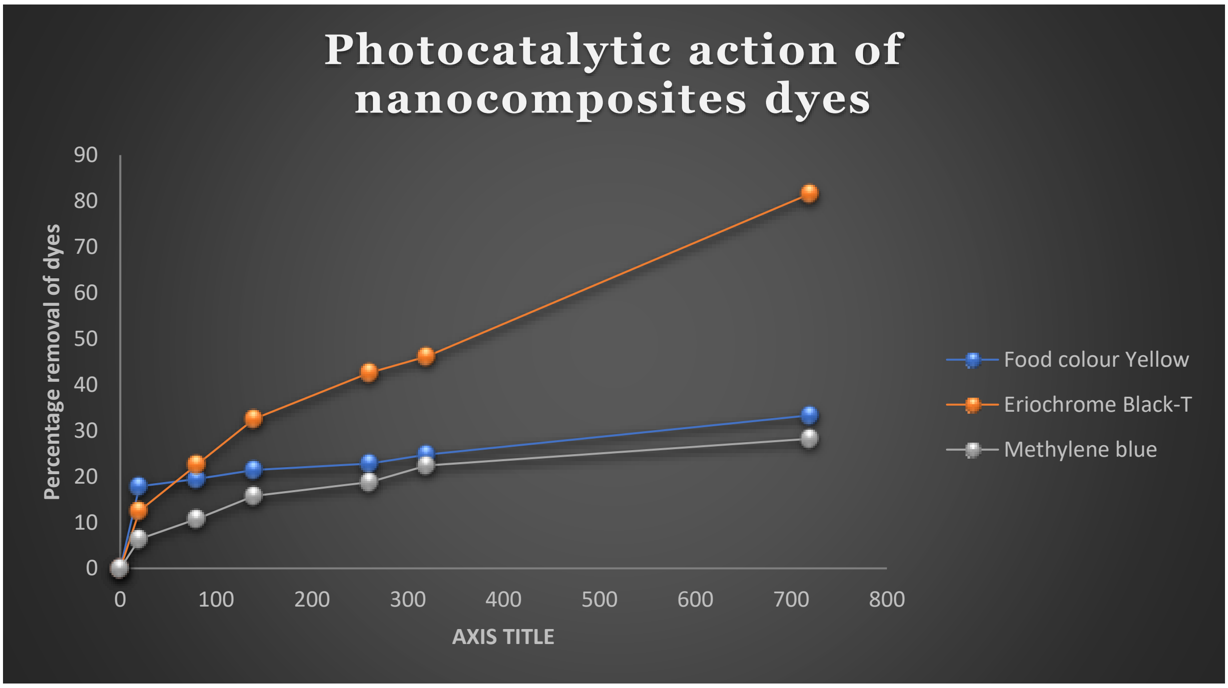

Fig 2: Percentage removal of dyes with contact time

6. CONCLUSION :

In this present study mixed nano composites of TiO_2 /ferric oxide /starch was synthesized by the solution phase method. The synthesized nano composites was characterized by SEM EDEX and particle size is confirmed. Aqueous solution of dyes solution of dyes are prepared at 50 ppm. Batch experiments are carried out for the study of photocatalytic oxidation of dyes. The present nanocomposite shows superior photocatalytic activity on Eriochrome Black T with photocatalytic activity of 81.6 % oxidation of dyes. The synthesized nanocomposites are moderately act as photocatalytic for the oxidation for the Food color yellow and methylene Blue dues in aqueous dyes.

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