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Original Research Article

Photocatalytic degradation of aqueous dyes by TiO_2/Fe_2O_3/Starch nanocomposites

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ABSTRACT
In this study, mixed nano composites of TiO_2 /ferric oxide /starch was synthesized by the solution phase method. The synthesized nano composite was characterized by SEM and particle size analyser. SEM Shows that TiO_2 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 below the 100nm, with needle rod shaped nono titanium is dispersed in the phase. 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 synthesized nanocomposite shows superior photocatalytic activity on food colour yellow with photocatalytic activity of 49.2 % oxidation of dyes. The synthesized nanocomposites are moderately act as photocatalytic for the oxidation for the Eriochrome Black T and methylene Blue dues in aqueous dyes.

1. Introduction

Substance that absorbs energy from a light source, generating catalytic activity without being consumed in the process is known as photocatalyst [1]. These substances, often semiconductors, are activated by photon absorption and can significantly accelerate chemical reactions. Semiconductors with superior optical and physiochemical properties are ideal candidates for photocatalysis. These materials have valence and conduction bands separated by a band-gap [2]. When photons with energy equal to or greater than the band-gap are absorbed by the semiconductor surface, electrons are excited from the valence band to the conduction band, creating holes in the valence band. These holes facilitate the oxidation of organic compounds by generating hydroxyl radicals, while the excited electrons promote reduction and oxidation reactions through the formation of superoxide radicals [3]. Due to their potential in solar energy conversion and environmental purification, semiconducting oxide photocatalysts have garnered significant attention in recent years [4]. Photocatalysts are used for degrading organic pollutants in wastewater, air purification, and antibacterial activities [5].

Compared to other methods, photocatalysis is rapidly advancing due to its efficiency and low cost. Among the most commonly used photocatalysts are TiO_2 and ZnO, which are integral to addressing energy and environmental challenges [6].

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 [7]. In the recent days ZnO and TiO_2 received greater attention because of their excellent photo catalytic activity [8-9]. 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 [10]. The photocatalytic activity of TiO_2 is significantly influenced by properties such as crystalline phase, crystalline size, and specific surface area, with surface area being a crucial factor. TiO_2 photocatalysts with large surface areas exhibit high photocatalytic activity. Additionally, their small size causes them to agglomerate into larger particles, reducing surface energy and catalytic performance. To address these issues, various methods such as dye sensitization, doping, coupling, and capping of TiO_2 have been extensively studied [11]. TiO_2/PVA/Fe_2O_3 nanocomposites is evaluated for the efficient removal of dyes from aqueous solution [12]. 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. TiO_2 nanocomposites has high chemical stability, inexpensive and non-toxic [13]. TiO_2 /PVA nanocomposites was evaluated for electrical properties [14] and has applications as anti-reflection coatings in solar cells [15]. Thin film of polyvinyl nanocomposite was decreased from 3.94 eV to 3.04eV when significant TiO_2 was doped [16].

2. Experimental section

2.1 Chemicals and materials

Eriochrome black T, food colour, methylene blue, $FeCl_3.6H_2O$, TiO_2, starch, NaOH all are laboratory reagents procured from SD fine chemicals and Loba Chemi.

2.2 Methods

2.2.1 Preparation of TiO_2/ferric oxide/ starch nanocomposites

2.027g of $FeCl_3.6H_2O$ dissolve in 50ml of water and 2.0 g of TiO_2 (solid) added to the above solution and 2.5 g of starch is added to the reaction mixture, stirred for 30 min. During stirring added 3 g of NaOH solution which is already dissolved in 50 ml water, continue for stirring until the precipitate obtained and the obtained precipitate is filtered. Wash with water dried residue collected and heated 100°C in autoclave for 2 hr, after drying, put in a mixer grinder until they got to be fine powder. The powder was sieved so that all the particles to be utilized are of uniform size. Finally the TiO_2 nanocomposite powder was stockpiled in air tight container so they can be utilized in the future without any further treatment.

2.2.2 Dye solution

A series of aqueous solutions containing Eriochrome black T, food colour yellow and methyl blue dyes at 50 ppm 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 0.5 mg of composites, allowing for a systematic investigation into the degradation process under different conditions.

2.2.3 Batch experiments

Batch techniques were utilized to study the photocatalytic study of Eriochrome black T, food colour and methylene blue dyes using TiO_2 nanocomposite. 50 ppm solution of dye was prepared by adding 0.05 g of each dye to the 500 ml of distilled water. Then 0.5 g of TiO_2 nanocomposite was added to each 50 ml dye solution of Eriochrome black T, food colour 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 spectrophotometer.

3. Results and discussion

3.1 Batch experiment

The aqueous dye solution of 50 ppm concentration was prepared and during the photocatalytic study both sample with nanocomposite serves as test solution and without nano composite, only dye solution serve as control.

The wavelength in which maximum (λ_{max}) absorption occurs to each dye was determined. To the 50 ml aqueous dye solution 0.5 g of TiO_2 nanocomposite was added to each beaker. The absorbance of the dye solution was recorded at different time intervals in colorimetry. The initial sample for which the nanocomposite is not added was also observed to compare it with other solutions and to study the percentage removal of the dye and concentration of dye after each time interval. This study revels that a very good photocatalytic activity was observed TiO_2 on food yellow dye solution and dyes are oxidized, results in decrease of dye concentration.

Amount of the colour removal of aqueous dyes solution is tabulated in the Table 1, Table 2, and Table 3. Table 1 shows that colour degradation of food colour yellow was found to be 49% over the time of 320 min. The synthesized nanocomposite is efficient for the photo catalytic oxidation of dye.

Photo catalytic action of TiO_2/starch/Fe_2O_3 nanocomposite was studied on Eriochrome Black-T, Table 2 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 16.5% removal at the time interval of 320 min. The moderate photocatalytic oxidation took place.

Photo catalytic action of TiO_2/starch/Fe_2O_3 nano composite was studied on methylene blue. Table 3 shows that percentage removal of methylene blue dye solution on the action of photocatalyst. The amount of dye removal data shows that at the 22.48% removal at the time interval of 320 min. The moderate photocatalytic oxidation took place.

Table 1: Percentage removal of food colour dye in contact time

Time (in min)	Absorbance	Concentration (in ppm)	Percentage removal of dye
0	0.63	50	0
80	0.49	38.8	22.24
160	0.45	35.70	28.60
240	0.34	26.97	46.06
320	0.32	25.38	49.24

Table 2: Percentage removal of Eriochrome Black-T dye in contact time

Time (in min)	Absorbance	Concentration (in ppm)	Percentage removal of dye
0	1.94	50	0
80	1.86	47.93	4.14
160	1.68	43.29	13.42
240	1.66	42.77	14.46
320	1.62	41.73	16.54

Table 3: Percentage removal of methylene blue dye solution

Time (in min)	Absorbance	Concentration (in ppm)	Percentage removal of dye
0	1.47	50	0
80	1.36	46.25	7.5
160	1.29	43.86	12.28
240	1.22	41.48	17.04
320	1.14	38.76	22.48

The comparative photocatalytic action of three dyes such as, food colour yellow, Eriochrome Black T, Methylene blue is shown in the Figure 1. The result clearly indicates that the efficient photocatalytic action of the TiO_2/starch/Fe_2O_3 nano composite on food colour yellow, 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 Eriochrome Black-T 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.

The present study, synthesized the nanocomposite material from TiO_2, Ferrous sulphate and starch by the solution phase method. Synthesized composite exhibited moderate activity on food colour yellow, Eriochrome Black T, Methylene blue aqueous dye solution. In literature many Titanium based nano composite materials were synthesized and utilized for the various study, here we reported for the dye degradation, if studies continued it may emerge as one of the excellent nanocomposite material.

3.2 Scanning Electron Microscope (SEM) image analysis

The nano heterostructure depend not only on their size but also on their morphology. In certain circumstance, the morphology plays a crucial role in tuning the properties and activities. This section investigates tuning the morphology of TiO_2 /ferric oxide /starch nanostructures and its effect on the optical and photocatalytic properties. High-resolution Scanned electron microscopy (HR-SEM) of synthesized nanoparticles was shown in Figure 5 from the images it may be noted that, the high-quality image confirm the presence of TiO_2 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 below the 100 nm, with needle rod shaped nono titanium is dispersed in the phase.

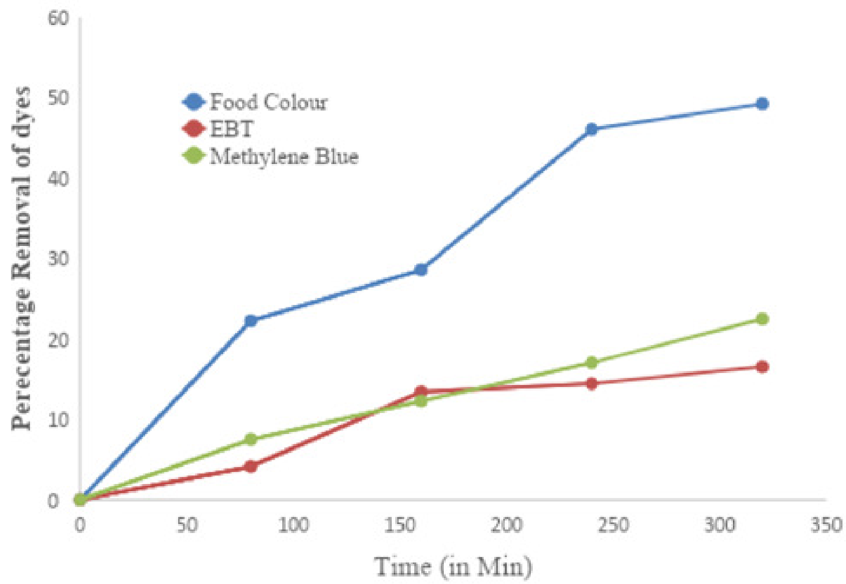

Figure 1: Percentage removal of dyes with contact time

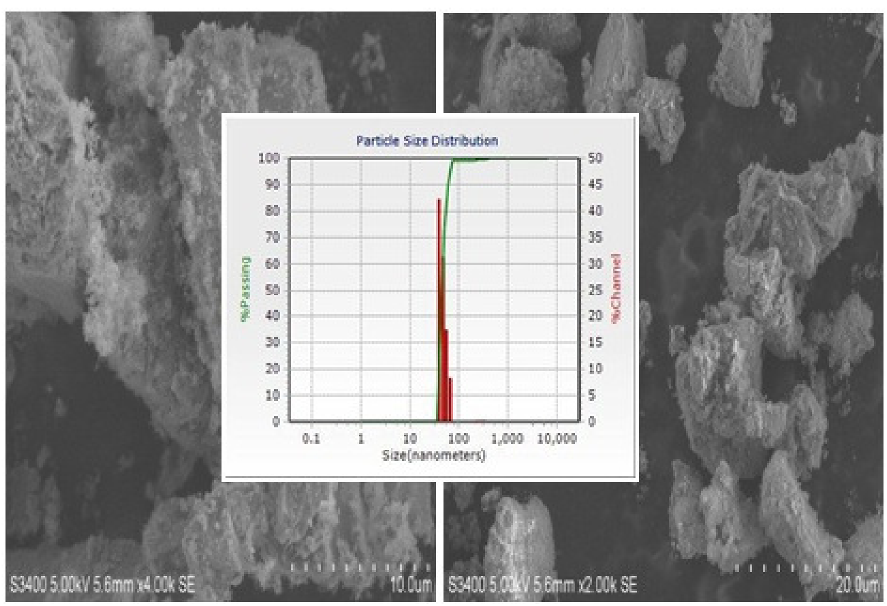

Figure 2: SEM image of the synthesized nano composite

4. Conclusions

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 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 food colour yellow with photocatalytic activity of 49.2 % oxidation of dyes. The synthesized nanocomposites are moderately act as photocatalytic for the oxidation for the Eriochrome Black T and methylene blue dues in aqueous dyes.

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