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Green Synthesis of Recyclable $BaPbFe_2O_6$ Nanoparticles for Photocatalytic Removal of Organic Dye Pollutant

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ABSTRACT

This study focuses on the synthesis of $BaPbFe_2O_6$ and modifying its photocatalytic activity by precipitation method on brilliant green (BG) dye. According to the characterization data, the UV-Vis absorption spectrum shows several peaks with an optical band gap of 5.45 eV. FESEM images showed irregular shapes of $BaPbFe_2O_6$ and EDX confirmed the presence of, Ba, Pb, Fe and O elements. The average particle size measured with maximum diffraction peak using Scherrer's equation was 12.31nm. XPS represents the different oxidation states of the elements. FTIR images show the presence of oxide film on the surface with a band gap of 500-600 cm^{-1} given as the characteristic stretched band of Pb-O. Maximum degradation is shown on the above optimum condition and complete degradation was held in 20 min on optimum conditions. The degradation rate of $BaPbFe_2O_6$ is 86.89% of $4*10^{-5}$ M for BG dye by exposing to sunlight for 20 minutes. Degradation of BG dye occurs due to the formation of hydroxyl radicals (.OH) on exposure to sunlight following pseudo first order kinetics. Therefore, $BaPbFe_2O_6$ synthesized in this paper can be used for the degradation of other exogenous organisms and for the treatment of wastewater and environmental polluted samples.

Keywords: Dye degradation, Waste water treatment, Brilliant green dye, Photo-degradation, Heterogeneous photo-catalysis, Hazardous material.

INTRODUCTION

Human activities are the cause of pollution. Due to the excessive release of industrial wastes to the environment, water, soil and land are polluted. In order to overcome this problem, special attention should be paid to our natural resources. waste water is contaminated with many contaminants that are difficult to remove using conventional water treatment methods.[1] The biggest challenge of the textile industry today is to create fabrics with long-lasting colors that do not fade in different weather conditions.

It is estimated that textile production is responsible for about 20% of the world's water pollution. Most of these fabrics are made from synthetic fibers and the current goal is to create new

dyes that can bind materials well. Brilliant green is an arylmethane dye that is difficult to remove because these molecules are stable and do not break easily. It also has many other medicinal uses, so avoiding it is inevitable. It is also used as an antiseptic for the injured area after surgery and as an anti-inflammatory and antiseptic if diluted with alcohol.

Many microscopic flora and fauna can be lost from the presence of a small amount of green color. Exposure to it in humans can cause digestive problems, stomach upset, eye irritation, and in some severe cases, blindness[2].

Few inorganic semiconductor nanomaterials for the photocatalytic degradation of organic pollutants in wastewater are promising catalyst as they are non-toxic, inexpensive, photostable, morphologically diverse and reusable[3]. In recent years various nanomaterials have been used as photo-catalysts in photo-catalytic degradation. The performance of some photocatalytic oxides such as Fe(III) doped PbO_2[4], Fe_3O_4[5], strontium doped BaO[6] became more attractive due to narrow band gap.

Due to their chemical stability, current wastewater treatment technologies cannot remove dyes from industrial wastewater. However, degradation by advanced oxidation process (AOP) using metal oxide semiconductors has proven beneficial due to its high efficiency, efficient degradation, non-toxicity and ease[7].

The AOPs involves the production of many reactive chemicals such as hydroxyl radicals, superoxide, hydrogen peroxide and molecular oxygen (O_2), and almost all organic pollutants can be processed into non-toxic CO_2 and H_2O using light catalyst. During dye degradation using $BaPbFe_2O_6$, the dye is usually irradiated with $BaPbFe_2O_6$ nanoparticles under UV light.

The aim of this investigation is to assess the efficacy of $BaPbFe_2O_6$ nanoparticles, specifically to evaluate degradation of brilliant green dye at high rate by varying some conditions as pH, concentration UV light intensity etc.

MATERIALS AND METHODS

Nitrate salts of Barium, Lead nitrate and Iron nitrate are used of analytical grade (merck), NaOH is used for precipitation purpose. EDTA is used for scavenger test. Brilliant green dye is used in present investigation of degradation of dye.

Synthesis of Nano-Sized $BaPbFe_2O_6$ Photocatalyst

The co-precipitation method was used to synthesize the $BaPbFe_2O_6$ nano particles. For this, 5N sodium hydroxide solution was added to a mixture of 0.1 M [$Ba(NO_3)_2$], 0.1M [$Pb(NO_3)_2$], 0.1M [$Fe(NO_3)_3$] solution and stirred at room temperature for 2 hours. The solution was then kept standstill for 8 h to obtain the precipitate. It was then washed by distilled water multiple times and dehumidified in oven at 80°C. It was calcined at 500°C for 5 h to obtain $BaPbFe_2O_6$ nano-particles. A brown colored fine powder of semiconductor with yield 96.40% was obtained. The nano-particles were then stored in desiccators in the dark for further characterization.

Characterization

UV–Vis spectra show maximum absorbance at 199.2nm with an optical bandgap of ≈5.45 eV, respectively. The absorption coefficient (α) is calculated using[8]:

$\alpha = 2.303A/t$

Where,

A = absorbent; t = sample thickness

The EDX spectrum of $BaPbFe_2O_6$ NPs, has strong band for Ba, Pb, Fe, and O bands with elemental weight percent of 4.83, 5.24, 12.91and 77.02, respectively, confirming the synthesis of $BaPbFe_2O_6$ NPs.

XPS spectrum of composite nanomaterial synthesized shows two peaks of Pb $4f_{7/2}$ 136.7 and 138 eV; 711.87eV and 724.7eV that can be attributed to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, 780.1 and 795.72 corresponding to Ba $3d_{5/2}$ and $3d_{5/2}$ and a broad peak at 531.23 eV to 533.27eV are attributed to oxygen vacancies[9].

The XRD analysis results of $BaPbFe_2O_6$ NPs and diffraction peaks are located at 24.03°, 34.38°, 40.93°, 42.21°, 44.21° corresponding to (101), (110), (111), (113) and (103) planes respectively (10, 11). The average size of pure $BaPbFe_2O_6$ nanoparticle is detected to be 12.31 nm. The FTIR band of $BaPbFe_2O_6$ exhibits low intensity at 692.55 cm^{-1} and high intensity peak at 856.06 cm^{-1} this indicates the presence of BaO[12,13]

and a strong band below 700 cm^{-1} is attributed to Fe-O stretching. Fe-O stretching mode of Fe_2O_3[14] appears at 532 cm^{-1} and 500–600 cm^{-1} is attributed to the stretching band of Pb-O[15].

Thermal analysis (TGA) of nanomaterials was carried out at a heating count of 15°C/min, and major weight loss of nanomaterial occurred in the range of 350°C to about 600°C this indicates loss of OH.

The Photoluminescence (PL) intensity reduction is evident, and the broad PL emission peak is located at 471.7, 627.5 and 548.2 nm, resulting from direct excitation of $BaPbFe_2O_6$ at the 263.2 nm region[16].

The decrease in PL intensity is shown in Fig. 4. The decrease in PL intensity can be attributed to the stabilization of charge carriers[17]. As shown, direct excitation of $BaPbFe_2O_6$ at 263.2nm results in PL emissions with peaks at 471.7, 627.5 and 548.2 nm.

Table 1: Percentage elements by EDS

Element	Weight %	Atomic %
O K	33.28	77.02
Fe K	19.47	12.91
Ba L	17.93	4.83
Pb M	29.32	5.24
Total	100.00	

HR-TEM analysis

High-resolution transmission electron microscopy (HRTEM) is a type of imaging mode of the TEM that allows the imaging of the crystal structure at atomic scale[18]. It can be seen from the image that sample has irregular particles formed by the agglomeration of small spherical/cylindrical particles. Nanoparticles have high unsaturated surface energy and therefore have a strong tendency to aggregate.

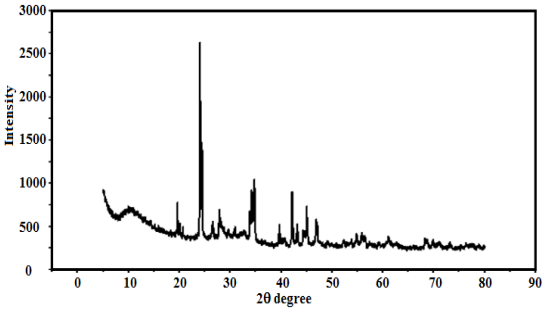

Fig. 1. XRD patterns of Photocatalyst

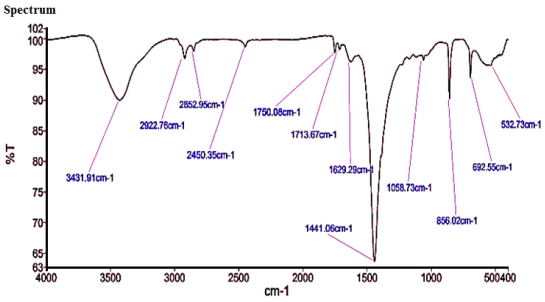

Fig. 2. FTIR spectra of photocatalyst

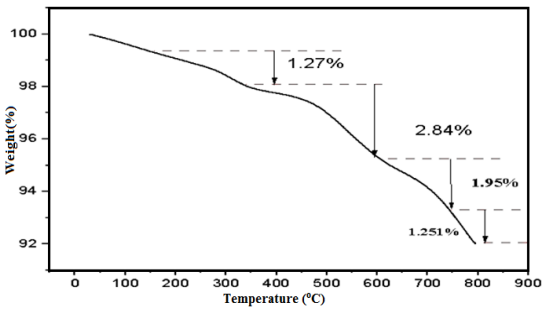

Fig. 3. TGA spectra of photocatalyst

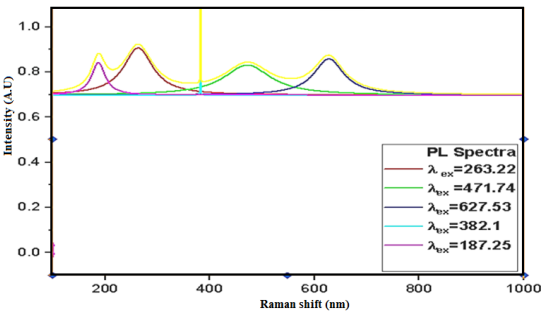

Fig. 4. Photoluminescence spectrum

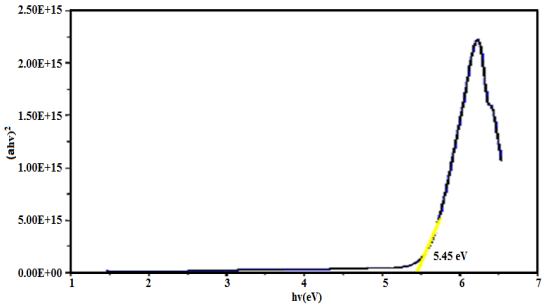

Fig. 5. UV-Vis-NIR absorbance Spectra of photocatalyst

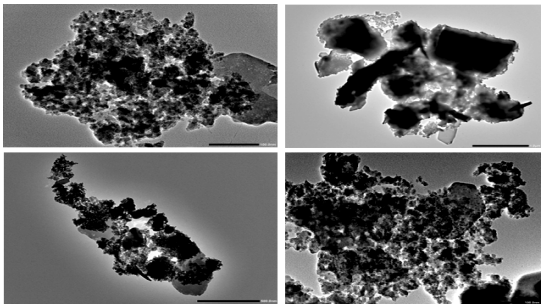

Fig. 6. HRTEM images of photocatalyst

Photocatalytic activity of $BaPbFe_2O_6$ Nanoparticles

The green hue of brilliant green dye degradation over the synthesized $BaPbFe_2O_6$ under UV irradiation was used to assess the photocatalytic activity of $BaPbFe_2O_6$. The graph of percentage degradation versus time under sunlight is shown in Fig. 7. The findings showed that after 20 min in the presence of both $BaPbFe_2O_6$ and light, the percentage of dye degradation had reached 86.89%. The findings point to strong correlations, which support pseudo-first order kinetics for the process.

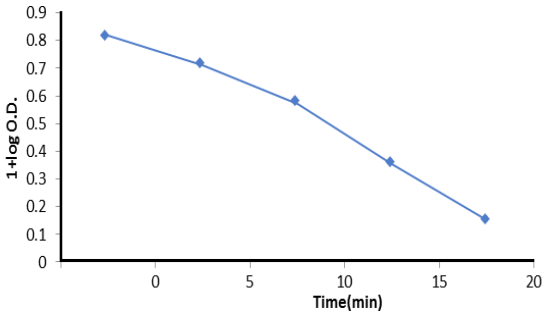

Fig. 7. Photo Catalytic activity of $BaPbFe_2O_6$ for degradation of BG dye

Effect of pH

The effect of pH on the rate of dye degradation was examined in pH range 6.4-9.5 for $BaPbFe_2O_6$, keeping all other parameters the same. The graph of % degradation against time at various pH values under solar radiation is displayed in Fig. 8. It was discovered that the rate of reaction rises as pH rises and that, once it reaches its maximum value at pH 9.5, it decreases with additional pH increase.

The increase in reaction rate up to pH 9.5 may be due to the increase in –OH ions formed as pH increases. The –OH ions react with the h^+ (hole) to form more OH radicals that interact with and disrupt color molecules. Increasing the pH causes the constant value of the catalyst activity to decrease, the catalyst to deteriorate and the color to become almost neutral because of the absorption of –OH ions on the catalyst surface.[19]

Effect of dye concentration

The degradation rate was shown to be affected by changes in brilliant green dye concentration 0.4×10^{-5} to 1.6×10^{-5} M while maintaining the same values for all other parameters. Fig. 9 represents the graph of % degradation versus time in different dye concentration with sunlight exposure. As the dye concentration increases, the reaction rate decreases as the number of dye molecules increases, and therefore the collision between the dye molecules and OH radicals decreases. Therefore, rate of reaction decreases.[20]

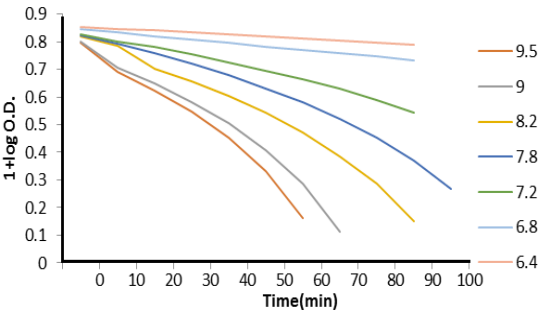

Fig. 8. Photo-degradation of BG dye on $BaPbFe_2O_6$ on different pH

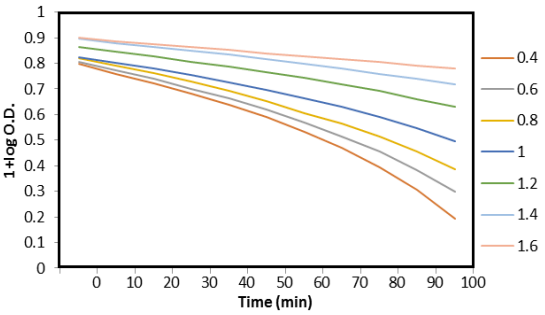

Fig. 9. Photo degradation of BG dye on $BaPbFe_2O_6$ on different Concentrations of Dye (in 10^{-5} M)

Effect of amount of catalyst

Other parameters remaining the same, various amount of catalyst changes the rate of dye discoloration in the range of 0.04 g to 0.16 g. It is clear from aforementioned statistics that the degradation rate rises with the amount of catalyst as the catalyst concentration ranges from 0.04 g to 0.120 g. The rate of reaction decreases with further increase in the catalyst concentration. This is due to the fact that catalyst surface area increases as the amount of catalyst increases. However, when the amount of catalyst is increased above a limit, the catalyst entirely occupies bottom of the reaction vessel, now only the thickness of the catalyst layer is increased and not the exposed surface area of the catalyst[21]. Fig. 10 shows the effect of change in catalyst dosage on the rate of dye degradation versus sun exposure time.

Effect of light intensity

All else being constant, the effect of change of light intensity on the rate of color degradation was also examined for

$BaPbFe_2O_6$. Fig. 11 shows plot of percentage degradation compared to sunlight exposure time at different light intensities. The statistics show that the reaction rate of degradtion increases as the irradiation intensity increases, with the highest rate of degradation is observed at 1850 W m^{-2} for catalyst. This can be elucidated by the fact that when the irradiation intensity increases, the number of photons/quanta hitting per unit area of catalyst also increases, and this results in higher rate of dye molecule degradation[22]. Additionally, the use of higher light is avoided as the use of additional light may cause some thermal side reactions.

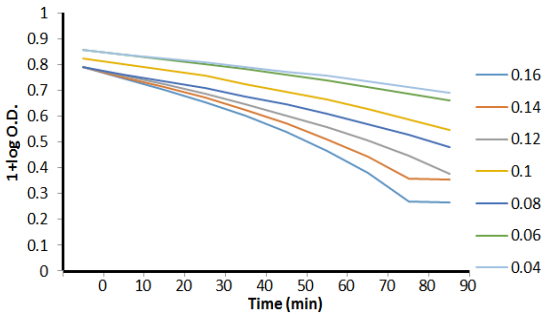

Fig. 10. Photodegradation of BG dye on $BaPbFe_2O_6$ on different photocatalyst Dosage (in gm)

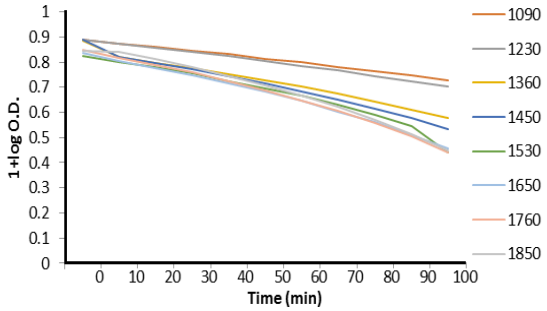

Fig. 11. Photodegradation of BG dye on $BaPbFe_2O_6$ on different Intensities of Light (in W/m²)

Mechanism

On the basis of the experimental observations a tentative mechanism has been proposed for the degradation of brilliant green dye by heterogeneous photocatalyst[23].

$$\text{Photocatalyst} + hv \longrightarrow \text{photocatalyst}\ (e^-, h^+)$$

$$H_2O_2 + 2h^+ \longrightarrow O_2 + 2h^+$$

$$OH^- + h^+ \longrightarrow {}^{\cdot}OH$$

$$H_2O + h^+ \longrightarrow H^+ + {}^{\cdot}OH$$

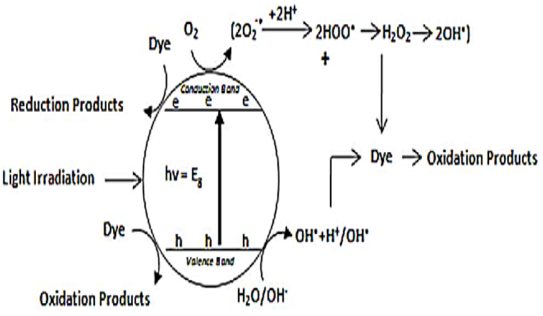

Fig. 12. Mechanism of Photocatalytic Dye Degradation

Effect of Scavenger on the Photocatalytic Degradation Efficiency of the BG Dye

The photocatalytic dye degradation efficiency of all products depends on the separation competence of electron-hole pairs (e^-–h^+), leading to the formation of active species like superoxide and hydroxyl radicals ($\bullet O_2^-$ and $\bullet OH^-$)[24]. The EDTA has been used as a scavenger for hydroxyl radicals. Degradation of BG dyes with the nanomaterial $BaPbFe_2O_6$ in the presence of 5 mL of 1N EDTA. After 45 minutes, degradation was complete and only 4.85% dyes was distorted.

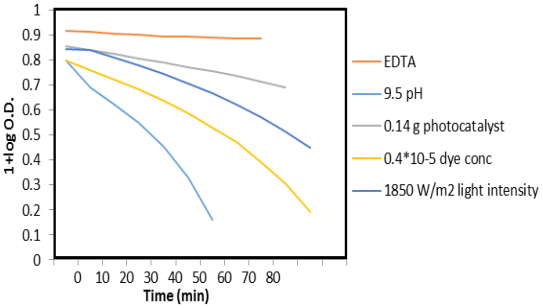

Fig. 13. Effect of Scavenger on Dye Degradation

CONCLUSION

It is concluded that the nano-particles $BaPbFe_2O_6$ were produced using co-precipitation method. The structure and morphology of nano-particles were examined using XRD, FE-SEM, EDS, XPS, HR-TEM and UV-Vis-NIR analysis. The average grain size of these particles is 12.31 nm, and there are regular particles formed by small spherical/cylindrical particles. It was found that the prepared photocatalyst was effective in the photo degradation of BG dyes in an aqueous environment. When light intensity is high the photo degradation rate increases as pH increases up to an optimal level, at a low initial concentration of dye. During heterogeneous photocatalytic process, OH radicals

react with dye molecules and break down them into smaller particles such as H_2O, CO_2, NO_3^- ions etc.

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Conflict of interest

The author declare that we have no conflict of interest.

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